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

Growth and Devices Technology of Group III-Nitrides

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Thin Film
Room 105A - Session TF-MoM
ALD Precursors and Surface Reactions

Moderators: Robert Grubbs, Micron Technology, Erwin Kessels, Eindhoven University of Technology, Netherlands

8:20am **TF-MoM1 New Heteroleptic Precursors Enabling Industrial Scale ALD of Next Generation Metal Oxides and Metal Films***, **Nicolas Blasco**,* Air Liquide, France **INVITED**

Thermal and Plasma Enhanced Atomic Layer Deposition (ALD & PEALD) have been major enablers to access new film systems in complex 3D architectures such as sub-14nm logics, sub 20nm DRAM architectures as well as new memory concepts. For example, new oxides film systems could be deposited in a conformal way. Similarly, Ni, Co, Ru metal (PE)ALD drew tremendous attention, with recent efforts towards selective deposition. Chemical functionalization requirements of ALD precursors have been more and more challenging, requiring creative approaches to overcome limitations of previous processes.

Leading groups in 2005-2006 opened the path to the use of "combinatorial" heteroleptic chemicals as ALD precursors. This approach consists in multi-functionalizing the molecule by combining the advantages of several ligand systems, and therefore empirically tailoring its physical and chemical properties (for instance melting point, volatility, thermal stability) - a traditional example being Air Liquide's ZyALD™ precursor, $ZrCp(NMe_2)_3$. This concept has been extended to multiple ligands and elements. Beyond expected outcome (e.g. physical properties tuning), surprising effects have been observed such as synthesis yield improvement, deposited film crystallinity/stability impact, or even selective deposition.

In this work, achievements using this methodology with new ligand systems and elements will be presented. Specific emphasis will be put on necessary requirements for an industrially viable new precursor, and benchmark with standard molecules.

First, a new set of rare-earth/lanthanide (La, Lu, Sc, Y) precursors will be presented and characterized by various techniques, from a physical & chemical point of view (TGA, DSC, VP), and from deposition behavior point of view (growth rate, film composition). Those novel precursors, for instance combining amidinate ($-(R^1NC(R^2)NR^3)$ and alkylcyclopentadienyl (C_5R_5) ligands, present unique properties which enable access to new material systems via ALD, not only ternary oxides in semiconductor field but also in other areas such as hydrophobic surfaces. This concept will be illustrated with new elements and for example new viable high yield liquid Scandium and lanthanum Oxide precursors will be introduced.

Second, recent improvements in Co, Ni metal ALD/PEALD processes will be presented, especially with the introduction of alkylsilyl ligands for Co precursors chemistry and allyl/amidinate ligands for Ni precursors chemistry. Applicability of those new precursors for advanced logics metal PEALD/ALD/CVD and their comparison with standard molecules (like dicobalt haxacarbonyl tert-butylacetylene - CCTBA) will be presented.

9:20am **TF-MoM4 Time-resolved IR Spectroscopy during ALD of La_2O_3/Al_2O_3 Nanolaminates***, **Brent Sperling**, J.E. Maslar, B. Kalanyan,* National Institute of Standards and Technology (NIST)

Atomic layer deposition (ALD) of La_2O_3-containing films is of interest for high-k dielectric layers in semiconductor manufacturing. Characterization of as-deposited films is made difficult by the tendency of La_2O_3 to form lanthanum carbonates and hydroxides upon exposure to the atmosphere. Previous *in situ* studies have shown evidence for the formation of carbonates during the actual deposition process using an amidinate and water. *Ex situ* studies have found unusual growth behavior that is typically attributed to lanthanum hydroxide formation during deposition. One of the strategies often employed for establishing typical ALD-type growth in La_2O_3-containing films is the incorporation of a second oxide. Although known to be effective, the reasons why are not known. Here, we use time-resolved IR spectroscopy to study surface reactions during La_2O_3/Al_2O_3 nanolaminate formation. A laminar flow reactor using $La(^iPrCp)_3$, TMA, and H_2O as precursors is used. We show that, contrary to previous speculation, non-ideal growth is not due to hydroxide formation. The benefits of incorporating the second oxide is unrelated to suppressing lanthanum hydroxide; alternate explanations must be considered.

9:40am **TF-MoM5 Incomplete Elimination of Precursor Ligands during Atomic Layer Deposition of Metal Oxides***, **Adrie Mackus**,* Eindhoven University of Technology, Netherlands*; C. MacIsaac,* Stanford University*; V. Vandalon, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands*; S.F. Bent,* Stanford University **INVITED**

Atomic layer deposition (ALD) has become an important technique for the deposition of ultrathin and conformal films for a wide variety of applications in nanoelectronics and photovoltaics. Although the reactions mechanisms of several metal oxide ALD processes have been investigated in detail, there are still some open questions regarding the understanding of their growth characteristics. ALD typically relies on two fundamental surface reactions: (*i*) the adsorption of a precursor molecule at specific surface groups (e.g. hydroxyl groups) in the first half-reaction, (*ii*) the elimination of the precursor ligands (while new functional surface groups are formed) in the second half-reactions. In this presentation, it will be shown that the elimination of precursor ligands is often not complete, which has broad implications for the growth characteristics of binary and ternary metal oxide ALD processes.

Experimental evidence for the presence of persisting ligands after the H_2O half-reaction at low temperatures (< 200 ºC) will be presented for the binary ALD processes of Al_2O_3 from TMA, SnO_2 from TDMASn, and ZnO from DEZ. The data for Al_2O_3 was measured using broadband sum-frequency generation (BB-SFG) spectroscopy,[1] while the SnO_2 and ZnO processes were studied using Fourier transform infrared (FTIR) spectroscopy. The incomplete removal of precursor ligands will be explained based on previously reported density functional theory (DFT) studies on cooperative effects during the H_2O half-reaction.[2] In addition, we found that the elimination of precursor ligands is even less effective when ZnO ALD is carried out after SnO_2 ALD, which likely causes the nucleation delay that has been observed for ZnO during the growth of the ternary material zinc-tin-oxide (ZTO).[3,4]

The consequences of the persisting ligands on the growth rate and temperature dependence of the binary ALD processes will be described. Moreover, it will be discussed that the incomplete removal of precursor ligands is expected to play an important role during many other ternary ALD processes, which can explain some of the deviating growth characteristics that have been reported.

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

2. M. Shirazi and S.D. Elliott, *Nanoscale***7**, 6311 (2015)

3. M.N. Mullings *et al.*, *Thin Solid Films***556**, 186 (2014)

4. C. Hägglund *et al.*, *J. Vac. Sci. Technol. A* **34**, 021516 (2016)

10:40am **TF-MoM8 Surface Chemistry of Pt and Al2O3 ALD Studied with Vibrational Sum-Frequency Generation***, **Vincent Vandalon**, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands

The surface chemistry during atomic layer deposition (ALD) of Al_2O_3 and Pt were investigated with vibrational broadband sum-frequency generation (BB-SFG) spectroscopy. These two processes represent examples of two different material classes for ALD: For metal oxides, ALD of Al_2O_3 with $Al(CH_3)_3$ and H_2O as reactants is the prototypical ALD process. Whereas for noble metals, ALD of Pt using $MeCpPtMe_3$ and O_2 as reactants can be considered as prototypical.

Vibrational BB-SFG spectroscopy is excellently suited for in-situ studies of the surface chemistry governing ALD because of its inherent interface selectivity, submonolayer sensitivity, and short acquisition times. It is a nonlinear optical technique which uses the mixing of picosecond visible and femtosecond mid-IR pulses to probe the vibrational response of surface groups. The unique nature of BB-SFG allows the *in-situ* investigation of the surface chemistry on both reflective and transparent substrate without any modifications to the setup.

For ALD of Al_2O_3, both the $-CH_3$ and -OH surface groups ruling the growth mechanism were monitored in-situ with BB-SFG. This study resulted in several new insights into the surface chemistry of this ALD process: Persistent $-CH_3$ groups were observed after the H_2O half-cycle at low temperatures and these significantly influence the growth [Vandalon and Kessels, Appl. Phys. Lett., 2016, Vol. 108] Moreover, the reaction kinetics were studied as a function of temperature and reaction cross sections for both half-cycles were quantified. At low temperatures it was found that the reaction kinetics in the H_2O half-cycle showed a strong dependence on surface coverage. Furthermore, the initial growth of Al_2O_3 on H-terminated silicon was investigated.

ALD of Pt was studied with BB-SFG by probing the C-H stretch region around 3000 cm^{-1}. After precursor exposure, the signature of the C-H stretch mode of the $-CH_3$ groups was clearly observed. Moreover, a spectrally broad feature was observed in the BB-SFG spectra. This contribution was assigned to unsaturated C chains such as present in the Cp ring. Dosing gas phase MeCp on a Pt and SiO_2 surfaces showed a similar broad feature, supporting this assignment. After O_2 exposure both the $-CH_3$ and Cp related signals disappeared. These results suggest that after precursor adsorption both $-CH_3$ and Cp rings (or parts of it) are present at the surface and these groups are removed in the O_2 half-cycle.

11:00am **TF-MoM9 Surface Chemistry of Molybdenum Oxide Atomic Layer Deposition: Role of Precursor Chemisorption on Nucleation Delay and Initiating the ALD Process***, **Charith Nanayakkara**, A. Vega,* The University of Texas at Dallas*; G. Liu, C. Dezelah, R. Kanjolia,* SAFC Hitech*; Y.J. Chabal,* University of Texas at Dallas

Atomic layer deposition (ALD) is an attractive technique for thin film deposition due to its sequential and self-limiting surface reactions leading to conformal and controlled film growth. However, nucleation delays (incubation) can lead to non-uniform island growth, particularly for metal films, often requiring many cycles to obtain a continuous film.

Molybdenum oxide thin films are important for a number of electrical, catalytic, and optical applications. Several Mo precursor-oxidant combinations have been used. For instance, molybdenum hexacarbonyl and ozone (with ALD window between 152 and 172 ^{0}C),[1] and Bis(tert-butylimido)bis(dimethylamido) molybdenum and ozone (with an ALD window between 250 and 300 ^{0}C)[2] gave good film with higher nitrogen content at deposition temperatures less than 250 ^{0}C for the latter.[2] The use of oxygen plasma with bis(tert-butylimido)bis(dimethylamido) molybdenum has shown film growth between 50 - 350 ^{0}C with high elemental H (4 – 11%).[3]

Here, we introduce a new molybdenum precursor, $Si(CH_3)_3CpMo(CO)_2(\eta^3\text{-2-methylallyl}))$ (MOTSMA), which has a good thermal stability (>200 °C), higher volatility with increased vapor pressure (3s exposure results 0.6 Torr gas phase pressure with bubbler at 90 ^{0}C), and increased deposition rates. However, *In-situ* FTIR spectroscopy of the MOTSMA and ozone ALD process reveals that there is a ~15 cycle incubation period at 250°C on OH-terminated oxidized Si(100) surfaces. After this incubation period, i.e. once the steady state ALD process is established, the expected ligand exchange is observed, with formation of surface $Si(CH_3)_3CpMo(\eta^3\text{-2-methylallyl})$ species after the precursor exposure and their removal during the ozone pulse, resulting in $Mo(=O)_2$ surface species. Since this nucleation delay can be reduced by raising the temperature above 300°C, the initial adsorption of the precursor on OH-terminated surfaces was examined as a function of temperature. Indeed, this initial adsorption of MOTSMA on OH-terminated surfaces was found to require higher temperatures. Therefore, we used an initial 350 ^{0}C MOTSMA grafting step in order to overcome the nucleation delay but then performed the ALD process at 250 ^{0}C and 300 ^{0}C. In this manner, steady state film growths with no nucleation delay were obtained at both temperatures, with stoichiometric composition (MoO_3) as confirmed by X-ray photoelectron spectroscopy. The current study highlights the critical role of precursor grafting on eliminating the nucleation delay for ultra-thin ALD grown film deposition.

1. *J. Mat. Chem.* **2011**, *21*, 705

2. *J. Vac. Sci. & Tech. A* **2014**, *32*, 01A119

3. *J. Vac. Sci. & Tech. A* **2016**, *34*, 01A103

11:20am **TF-MoM10 *In situ* FTIR Study of the Surface Reactions during Plasma-assisted Atomic Layer Deposition of SiN_x from Silicon Amides***, **Noemi Leick**, R.A. Ovanesyan, R.J. Gasvoda, P. Walker,* Colorado School of Mines*; K.M. Kelchner, D.M. Hausmann,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

Recently, atomic layer deposition (ALD) of silicon nitride (SiN_x) films has been increasingly researched for applications with stringent conformality and processing temperature (≤ 400°C) requirements, such as conformal spacer or etch stop dielectric material in 3-D transistors and air gap interconnect technologies. The necessity for a low-temperature ALD process has shifted focus toward plasma-assisted ALD, mainly using N_2 or NH_3 plasmas. While Cl-based Si precursors have been widely used in ALD of SiN_x films due to their high reactivity, these precursors also form undesirable corrosive byproducts. Silicon amide precursors can overcome these challenges while maintaining a sufficiently high reactivity for ALD.

In this contribution, the focus will be on the growth mechanism of SiN_x films during ALD using $H_2Si(N(C_2H_5)_2)_2$ (BDEAS) and N_2 or NH_3 plasma, at substrate temperatures between 200 – 300 °C. Specifically, we have employed *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy to study the film composition, surface reactions during each half-cycle, and the surface species involved in the growth process. From these measurements, we conclude that BDEAS adsorption occurs via a ligand-exchange reaction between one of the diethylamino ligands and surface H, liberating $HN(C_2H_5)_2$ into the gas phase as the main reaction by-product. During the N_2 plasma based ALD process, the N_2 plasma removes the remaining diethylamino ligands from the surface and restores the surface sites necessary for BDEAS chemisorption during the subsequent cycle. The hydrocarbon species on the surface during the N_2 plasma step also leads to the incorporation of C_xN_y species in the SiN_x film. In contrast to the N_2 plasma-based process, NH_3 plasmas in combination with very similar amide precursors have been reported to inhibit SiN_x growth. While our results ultimately confirm these findings, our infrared measurements show that SiN_x growth can initially be achieved with a NH_3 plasma, but attenuates rapidly after the first 5 cycles. The infrared data however suggests that the NH_3 plasma leads to complete removal of the carbon-containing species leading to C-free SiN_x films. Since the composition of SiN_x films deposited by ALD using amide precursors is affected by the nitrogen source in the plasma, a 3-step ALD process involving a NH_3 plasma (to remove C-containing species) followed by a N_2 plasma (to restore surface reactive sites) can potentially optimize the film composition and growth process.

Thin Film

Room 105A - Session TF+EM-MoA

ALD for Energy Conversion and Storage

Moderators: Virginia Wheeler, U.S. Naval Research Laboratory, Angel Yanguas-Gil, Argonne National Laboratory

1:40pm **TF+EM-MoA1 Fabrication of Nano-power Generators using Thin Atomic Layer Deposited Films***, **Giovanna Scarel**, H.S. Mann, B.N. Lang,* James Madison University*; V.D. Wheeler,* Naval Research Laboratory*; B.C. Utter,* Bucknell University

Infrared power generation is emerging as a useful method to harvest infrared (IR) light and transform it into usable energy available day and night. So far, this method is implemented using bulk power generator (PG) devices, neglecting any effort to improve the materials employed as their active element. Here we initiate this effort by fabricating thin thermoelectric TiO$_2$/TiN multilayer films via atomic layer deposition (ALD) and focusing on the exploration of the effects of film resistance on the voltage produced by nano-PG devices with these films as their active elements. By changing the number and thickness of the TiO$_2$/TiN layers, we control the sheet resistance (W/□) over three orders of magnitude. We observe that the voltage produced by nano-PG devices linearly increases with the thin multilayer films resistance, especially in the k-W/□ range. On the contrary, we measure an almost constant voltage jump versus film resistance when we excite the nano-PG device through Joule heating. The observed behavior suggests that the nano-PG device works effectively when mimicking the mechanism of a capacitor, similar to the case of a bulk device. Our studies pave the way to improving the properties of nano-PG devices by improving the properties of the active materials in the form of thin films fabricated via ALD.

2:00pm **TF+EM-MoA2 Ultrafast Triggered Transient Energy Storage by Atomic Layer Deposition Into Porous Silicon for Integrated Transient Electronics***, **Anna Douglas**, N. Muralidharan, R.E. Carter, K. Share, C.L. Pint,* Vanderbilt University

We demonstrate the first on-chip silicon-integrated rechargeable transient power source based on atomic layer deposition (ALD) coating of vanadium oxide (VO$_x$) into porous silicon. A stable specific capacitance above 20 F g^{-1} is achieved until the device is triggered with alkaline solutions. Due to the rational design of the active VO$_x$ coating enabled by ALD, transience occurs through a rapid disabling step that occurs within seconds, followed by full dissolution of all active materials within 30 minutes of the initial trigger. This work demonstrates how engineered materials for energy storage can provide a basis for next-generation transient systems and highlights porous silicon as a versatile scaffold to integrate transient energy storage into transient electronics.

2:20pm **TF+EM-MoA3 Refractory Solar Selective Coatings Synthesized by Atomic Layer Deposition***, **Jeffrey Elam**, A. Mane, A. Yanguas-Gil, J.A. Libera, J.R. Avila,* Argonne National Laboratory

One of the most economically viable methods for solar power uses an array of mirrors to concentrate sunlight onto a central receiver tower. The receiver surface heats up, and this heat is used to drive turbines that generate electricity. To improve the efficiency of these "power tower" facilities, the receiver must operate at higher temperatures and this requires developing high performance coatings. These coatings must be spectrally selective in order to absorb all of the visible light while emitting as little infrared radiation as possible (low emissivity). In addition, these coatings must be refractory to endure decades of high temperature operation under ambient conditions. We are pursuing a novel strategy to develop refractory solar selective coatings using ALD. Our strategy uses thin film nanocomposites composed of conducting metallic nanoparticles in a dielectric matrix. These films are prepared by combining the ALD processes for a metal (e.g. W using Si$_2$H$_6$/WF$_6$) with that of an oxide (e.g. Al$_2$O$_3$ using TMA/H$_2$O). The resulting nanocomposites have tunable optical properties that can be adjusted to achieve a high solar selectivity. In addition, we use these ALD coatings to infiltrate inverse opal scaffolds which serve as photonic crystals to further enhance the spectral selectivity. In this presentation I will discuss our ongoing work synthesizing and characterizing these refractory solar selective coatings. In particular, I will describe in situ quartz crystal microbalance, mass spectrometry, and infrared spectroscopy measurements performed to elucidate the unusual surface chemistry for these ALD nanocomposites, and discuss the relationships between the composition and the optical/electrical properties of these films. I will also describe the results of finite difference time domain modeling to understand how the photonic scaffold modulates the spectral selectivity, and finally I will report on the high temperature performance of these coatings.

2:40pm **TF+EM-MoA4 Sequential Infiltration Synthesis of Doped Polymer Films with Tunable Electrical Properties for Efficient Triboelectric Nanogenerator Development***, **Yanhao Yu**[*], X.D. Wang,* University of Wisconsin-Madison

Triboelectric nanogenerator (TENG) is rising as a promising technology for converting mechanical energy into electricity with merits of high output, simple design and low cost. The working principle of TENG is based on the combined effect triboelectrification and electrostatic induction. According to this mechanism, controlling the charge density on the triboelectric surface is the most fundament strategy for improving the performance of TENG. Nowadays, surface modification of triboelectric polymer is the predominate approach to regulate the charge density. However, operation of TENGs requires intimate contact and sometimes friction between triboelectric materials, which inevitably induces wearing of surface. In this regard, surface modification/engineering yields little contributions toward the performance gain in long-term operation. Therefore, one essential solution is to extend the property engineering from mere surface to the bulk of material.

Atomic layer deposition (ALD) is a powerful thin film growth technique on the basis of sequential self-limiting surface reactions. When implemented to certain polymers, the large permittivity of metalorganic precursors allows deep infiltration of inorganic compounds during ALD process, leading to inorganic/organic hybrid materials. This process is known as sequential infiltration synthesis (SIS). It has been successfully used to convert block co-polymer nanopatterns into more durable inorganic patterns and to improve the polymeric lithography resistance to subsequent etching. Inspired by these developments, we expect SIS could effectively tailor the internal composition and electrical properties of polymer films, which may provide an ultimate solution for triboelectric material design in the development of high-performance TENGs. Here, we report an internal AlO$_x$ doping of several polymers *via* SIS, including polydimethylsiloxane (PDMS), polyimide (Kapton) and poly(methyl methacrylate) (PMMA).[1,2] We showed that SIS can introduce AlO$_x$ molecules ~3 µm deep into these polymers, which effectively tuned the bulk electrical property of the film. TENG devices using the modified polymer films exhibited enhanced power output; and this enhancement remained effective after the surface of polymer film was polished off for more than 2 µm. This polymer doping approach opens a new route to bulk electrical property modification of polymer films, demonstrating a promising strategy for improving the performance of functional polymer based devices, such as TENGs.

Reference

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2. Y. Yu, X. Wang. *Extreme Mech. Lett.,* doi:10.1016/j.eml.2016.02.019, 2016.

3:00pm **TF+EM-MoA5 ALD for Interfacial Engineering of Energy Conversion Devices***, **Neil P. Dasgupta**[†],* University of Michigan, Ann Arbor

INVITED

Recently, there has been a dramatic increase in research of nanoscale materials for energy conversion and storage applications due to several advantageous features such as high surface areas, short transport distances, novel optical phenomena, and tunable material properties. However, with these benefits come challenges. In particular, the ability to precisely control the properties of surfaces and heterogeneous interfaces at the nanoscale limits the performance of many of these devices, and requires novel approaches. This problem becomes increasingly important as dimensions decrease, as the surface-to-volume ratios continually increase with decreasing feature size.

One technique that has been increasingly explored for surface and interfacial engineering of nanostructured energy conversion and storage devices is Atomic Layer Deposition (ALD). This gas-phase process allows for highly conformal deposition of a wide variety of materials with sub-nm precision in material thickness and tunable chemical composition. A wide range of materials, including oxides, sulfides, and metals can be deposited by ALD. The combination of conformality and thickness control of ALD

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

[†] **Paul Holloway Award Winner**

facilitates precise tuning of the electronic, optical, thermal, and chemical properties to optimize their interfaces in energy conversion devices.

This talk will present several examples of using ALD to fabricate highly-controlled interfaces for energy conversion and storage devices. Examples include batteries [1], photovoltaics [2-3], and photoelectrochemical cells [4-5]. The key theme linking these studies is that through deterministic control of interfacial layer composition, thickness, crystallinity, and morphology, we can "program" properties such as charge transfer resistance, catalytic activity, and chemical stability. This control enables interfacial materials engineering to optimize both device efficiency and lifetime. The importance of fully understanding ALD surface chemistry will be discussed from a theoretical and experimental perspective. The talk will conclude with a perspective on future directions and challenges for widespread commercial adaption of these technologies.

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4:00pm **TF+EM-MoA8 Anchoring Down Soluble Polysulfides for Lithium and Sodium Sulfur Battery Cathodes using Atomic Layer Deposition***,* ***Rachel Carter****, A.P. Cohn, L. Oakes, N. Miralidharan, A.E. Douglas, K. Share, C.L. Pint,* Vanderbilt University

Among the most significant challenges for practical lithium or sodium sulfur batteries is polysulfide shuttling, where intermediate discharge products (M_2S_8, M_2S_6 and M_2S_4) dissolve into the electrolyte lowering active sulfur mass and fouling the metal anode. To overcome this, we demonstrate the use of atomic layer deposition (ALD) to produce thin oxide coatings on cathode materials to stabilize these soluble polysulfides and mitigate active material loss. We specifically focus on V_2O_5 (vanadium pentoxide) due to its demonstration in recent theoretical studies to exhibit strong polar interaction with soluble polysulfides that exceeds other oxide materials. With the application of the V_2O_5 binding interlayer the initial discharge capacity of the sulfur cathodes is enhance by 20%, which is a direct result of anchoring the soluble species for optimal complete discharge of the sulfur. The capacity retention of the sulfur cathode is enhanced to 87% capacity retention over 100 cycles, in comparison to less than 50% retention without ALD binding layer. The binding effect was also probed using UV-Vis analysis, since there are distinct absorption peaks for the soluble S_6^{2-} state in the electrolyte. Solutions of Li_2S_6 and Na_2S_6 we studied before and after exposure to ALD binding layers with dramatic decrease in the S_6^{2-} signature in solution observed proving the binding interactions between the polysulfides and V_2O_5 binding interlayer. Overall, our work shows how ALD is a versatile tool to atomically engineer surfaces to sustain excellent performance without compromising the gravimetric performance needed for practical battery applications.

4:20pm **TF+EM-MoA9 Hybrid Inorganic-Organic Thin Films by ALD/MLD for Emerging Energy Technologies***,* ***Maarit Karppinen****,* Aalto University, Finland **INVITED**

For hybrid inorganic-organic materials it is in principle possible to realize properties not seen for conventional materials. An elegant, yet industrially feasible way to link the inorganic and organic entities *via* strong chemical bonds to form coherent multi-layered hybrid materials is to combine the ALD (*Atomic Layer Deposition*) technique originally developed to deposit high-quality thin films of simple inorganic materials with MLD (*Molecular Layer Deposition*) cycles based on organic precursors. This enables the atomic/molecular layer-by-layer production of inorganic-organic hybrid thin films through sequential self-limiting gas-surface reactions with high precision for the film thickness and composition.

In this talk I will discuss our recent efforts towards synthesizing new functional materials by the combined ALD/MLD technique.[1] In particular, we have fabricated oxide-organic thin-film superlattices in which the periodically introduced single/thin organic layers between oxide layers are *e.g.* shown to hinder phonon transport and substantially enhance the thermoelectric properties of (Zn,Al)O[2,3] and (Ti,Nb)O_2[4] films. Other exciting application areas foreseen for the ALD/MLD hybrid thin films include the flexible and transparent Li-ion microbattery materials[5,6] and so-called metal organic framework (MOF) materials.[7]

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2. T. Tynell, I. Terasaki, H. Yamauchi & M. Karppinen, Thermoelectric characteristics of (Zn,Al)O / hydroquinone superlattices, *J. Mater. Chem. A* 1, 13619 (2013).

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4. J.-P. Niemelä, A, Giri, P.E. Hopkins & M. Karppinen, Ultra-low thermal conductivity in TiO_2:C superlattices, *J. Mater. Chem. A***3**, 11527 (2015).

5. M. Nisula, Y. Shindo, H. Koga & M. Karppinen, Atomic layer deposition of lithium phosphorous oxynitride, *Chem. Mater.***27**, 6987 (2015).

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Thin Film
Room 102B - Session TF+PS+SE-MoA

Plasma-based Deposition Techniques and Film Characterization

Moderators: Jim Fitz-Gerald, University of Virginia, Tansel Karabacak, University of Arkansas at Little Rock

1:40pm **TF+PS+SE-MoA1 Microcrystalline Silicon Thin Film Deposited by Tailored Voltage Waveform Plasmas using an $SiF_4/H_2/Ar$ Chemistry and its Application to Photovoltaics***,* ***Junkang Wang****,* LPICM, CNRS, École Polytechnique, Université Paris Saclay, France*; M. Elyaakoubi,* TFSC-Instrument, Palaiseau, France*; E.V. Johnson,* LPICM, CNRS, École Polytechnique, Université Paris Saclay, France

For the growth of hydrogenated microcrystalline silicon (μc-Si:H) thin film by low temperature plasma-enhanced chemical vapor deposition (PECVD), silicon tetrafluoride (SiF_4) has recently attracted interest as a precursor due to the resilient optoelectronic performance of the resulting material and solar cell device. However, many questions remain concerning the critical factors determining the quality of the PECVD-deposited film.

Tailored voltage waveforms (TVWs), non-sinusoidal voltage waveforms used to excite radio-frequency capacitively coupled plasma (RF-CCP) processes, has recently been shown to be effective to separately control the maximum ion bombardment energy (IBE) and the ion flux on each electrode. Due to this unique feature, TVWs have attracted considerable research interest in a very short time. When applied to the growth of μc-Si:H film by PECVD, it can provide an elegant approach for one to gain more insight into the physical principles governing film growth and the optimization of process parameters.

To advance knowledge on this subject, we present studies looking at the deposition of μc-Si:H film from SiF_4 using TVWs, particularly focusing on the material's optoelectronic properties and its resulting PIN solar cell device. We underline recently obtained results concerning critical experimental findings: (1) the significant impact of the maximum IBE to the crystalline grains sizes of the deposited films, (2) the considerable different in films' properties resulting from two types of "sawtooth" waveforms, i.e. "sawtooth-up" and "sawtooth-down", which give similar films deposition rates and the maximum IBE but opposite plasma sheath dynamics during processing. The films generated in these studies have furthermore been characterized using the steady-state photoconductivity and steady-state photocarrier grating techniques, analyzing the coplanar electronic transport properties of the material. The modulated photoconductivity method is also utilized to reveal more specific details about the materials' sub-gap density of states. These studies - along with residual gas analysis studies and Fourier transform infrared absorption results - allow us to optimize the appropriate process parameters of such film and its resulting PIN solar cell device using SiF_4 as the precursor.

2:00pm **TF+PS+SE-MoA2 Boron Carbide-Aromatic Composite Films by PECVD: A Novel Approach to Electron-hole Separation***, B. Dong, A. Oyelade,* University of North Texas*; E.M. Echeverria,* University of Nebraska-Lincoln*; Y-S. Jun, G.D. Stucky,* University of California at Santa Barbara*; P.A. Dowben,* University of Nebraska-Lincoln*; **Jeffry Kelber**,* University of North Texas

Many photovoltaic and photocatalytic systems employ band-bending at surfaces or interfaces to achieve electron-hole separation and functionality. Boron carbide-aromatic composites, formed by plasma-enhanced co-deposition of carboranes and aromatic precursors, present an alternative approach where such separation is achieved by aromatic coordination to the carborane icosahedra. Photoemission, density functional theory calculations, and variable angle spectroscopic ellipsometry demonstrate that for orthocarborane/pyridine and orthocarborane/aniline films, with controlled aromatic/orthocarborane ratios between 1:1 and 10: 1, states near the valence band maximum are aromatic in character, while states near the conduction band minimum include those of either carborane or aromatic character. Thus, excitation across the band gap results in electrons and holes on carboranes and aromatics, respectively. Further such aromatic-carborane interaction dramatically shrinks the indirect band gap from 3 eV (PECVD orthocarborane) to ~ 1.6 eV (PECVD orthocarborane/pyridine) to ~1.0 eV (PECVD orthocarborane/aniline), with little variation in such properties with aromatic/orthocarborane stoichiometry. Recent photoabsorbance measurements show that in orthocarborane/pyridine films, the indirect band gap energy is significantly less than the exciton formation energy of 2.1 eV, allowing facile exciton elimination by phonon scattering of electrons into the conduction band at room temperature. The opposite is true for the PECVD orthocarborane film, where the exciton formation energy (2.4 eV) is less than the indirect band gap, inhibiting exciton elimination by electron-hole separation. The enhanced electron-hole separation, narrowed band gap, and significantly increased carrier lifetimes (350 µsec for PECVD orthocarborane/pyridine vs 35 µsec for PECVD orthocarborane), indicate the potential for greatly enhanced charge generation, as confirmed by zero-bias neutron voltaic studies. Those results--an 850% increase in charge generation per B atom for the PECVD pyridine/orthocarborane film relative to the PECVD orthocarborane film--indicate that the enhanced electron-hole separation and band gap narrowing observed for aromatic/orthocarborane films relative to PECVD orthocarborane, have significant potential for a range of applications, including neutron detection, photovoltaics, and photocatalysis.

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2:20pm **TF+PS+SE-MoA3 Impact of Pulsing the rf Power and the Precursor Injection on the Structure and Optical Properties of TiO_2 and TiSiO Thin Films Deposited by PECVD***, **Agnes Granier**, S. Elisabeth, R. Michaud, N. Gautier, M. Richard Plouet,* IMN, University of Nantes CNRS, France*; M. Carette,* IEMN CNRS/Université Lille 1, France*; A. Goullet,* IMN, University of Nantes CNRS, France

TiO_2 thin films are good candidates for the development of passive optical components due to high optical refractive index (1.8 < n < 2.7 at 633 nm) combined with high transparency in the visible range. They are compatible with semiconductor technologies and can be synthesized at low temperature by plasma enhanced chemical vapor deposition (PECVD). PECVD is known for its ability to prepare amorphous or partially crystallized films at low temperature and to tune the film composition and optical properties. In the case of TiO_2, columnar polycrystalline anatase films can be prepared by PECVD at substrate temperature less than 150°C. Whereas these TiO2 films are very attractive for photocatalysis, their columnar structure and low optical gap (3.2 eV) appear to be drawbacks for optical applications. Adding a small amount of silicon to TiO_2 allows both obtaining amorphous films and increasing the optical gap, which is highly suitable for optical applications.

In this study, TiO_2 and Ti-Si-O films were deposited in a low pressure rf inductively coupled plasma (ICP) from titanium tetraisopropoxide (TTIP - $Ti(OC_3H_7)_4$) and hexamethyldisiloxane (HMDSO - $SiO_2(CH_3)_6$) vapors mixed with oxygen. The structure and chemical composition of the films were investigated by X-ray diffraction, photoelectron spectroscopy, Fourier transform infrared spectroscopy and Raman spectroscopy. The morphology of the thin films was characterized by scanning and transmission electron microscopies. The optical properties were investigated by UV -Visible spectroscopic ellipsometry and absorption spectroscopy. When deposited at the floating potential, the TiO_2 films deposited in the continuous mode in oxygen rich O_2/TTIP ICP plasmas were previously shown to be columnar and highly crystallized in the anatase form. As silicon is added to titanium, the films become amorphous. Their refractive index decreases and their optical gap increases [1].

Here, we investigate the effects of pulsing both the rf power and the precursor injection on the film structure and optical properties.

On the one hand, in the case of TiO_2 and Ti-O-Si films, the pulse frequency was fixed at 1 kHz and the duty cycle was varied from 100 to 10%. Pulsing the power allows to decrease the deposition temperature (down to about 50°C) while conserving the anatase structure in the case of TiO_2 films, so that anatase and amorphous high refractive index Ti-Si-O films can be deposited on polymer substrates.

On the other hand, TTIP and HMDSO flow rates have been pulsed, either to get benefit from oxygen plasma treatment following oxide deposition or to deposit TiO_2/SiO_2 stacks.

[1] D. Li et al, Plasma Processes and Polymers, 2016

2:40pm **TF+PS+SE-MoA4 Plasma CVD of Boron-Carbon Thin Films from Organoboron Precursors for Next Generation Neutron Detectors***, **Mewlude(Maiwulidan) Imam (Yimamu)**,* Linköping University, Sweden*; C. Höglund,* Linköping University and European Spallation Source ERIC, Sweden*; R. Hall-Wilton,* European Spallation Source ERIC, Sweden*; J. Jensen,* Linköping University, Sweden*; S. Schmidt,* Linköping University and European Spallation Source ERIC, Sweden*; I.G. Ivanov, J. Birch, H. Pedersen,* Linköping University, Sweden

A novel design for neutron detectors based on thin films that are rich in the ^{10}B isotope has been suggested for the European Spallation Source (ESS), in order to overcome the very limited availability of ^3He. The detector design uses $^{10}B_4C$ films deposited onto both sides of neutron transparent substrates, e.g., Al blades [1]. The use of aluminum (melting point at 660 °C) limits the deposition temperature for CVD processes and the use of chlorinated precursors due to etching of Al by HCl. Therefore, reactive organoborons are evaluated as precursors for these films using both thermal CVD [2, 3] and plasma CVD.

Plasma CVD of B_xC thin films has been studied by introducing the organoborons trimethylboron $B(CH_3)_3$ (TMB) or triethylboron $B(C_2H_5)_3$ (TEB) into a microwave-induced Ar plasma without using any intentional substrate heating. The effect of plasma power, TMB or TEB to Ar ratio and total pressure on the film composition, morphology, density, chemical structure and internal stress were investigated by means of Tof-ERDA, SEM, XRR, XPS and HRXRD, respectively. Tof-ERDA results showed that the highest B/C ratio of 2 was achieved when using TMB at high plasma power. Densification of the films was accompanied by decreasing the total pressure below 0.4 mbar, resulting in a columnar film with densities of 2.16 ± 0.01 g/cm^3. The H content in the films was high (15±5 at. %) due to the low substrate temperature (~300 ^{o}C). XPS revealed that films deposited using TMB mainly contained B-C bonds and small contribution from C-C/CH bonds, that was evidenced by the observed amorphous carbon phases in the films by Raman spectroscopy. The internal compressive stresses in the films were increased with the Ar gas flow causing film delamination, while a low flow of Ar showed good adhesion and stress level is less than 300 MPa. In addition, the plasma composition studied by optical emission spectroscopy (OES) showed that BH, CH, C_2 and H lines were the most intensive lines in the spectrum. Considering the high H content in the films, we propose that BH and CH are the most likely species to contribute to the film formation.

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[2] H. Pedersen et al. *Chem. Vap. Deposition***2012**, *18*, 221

[3] M. Imam et al. *J. Mater. Chem. C***2015**, *3*, 10898

3:00pm **TF+PS+SE-MoA5 Plasma Enhanced Atomic Layer Deposition of Superconducting Nb_xTi_yN Films***, **Mark Sowa**,* Ultratech/CNT*; Y. Yemane, J. Provine,* Stanford University*; E.W. Deguns,* Ultratech/CNT*; F. Prinz,* Stanford University

NbN, TiN, and their mixtures have been studied for their use in superconducting applications. These materials are commonly deposited via sputtering techniques, but a lack of thickness control limits this technique from applying thin, uniform films. Atomic Layer Deposition (ALD) has been widely recognized for its ability to coat substrates with uniform film thicknesses ranging from a few Ångstroms to 100's of nanometers. Plasma Enhanced ALD (PEALD) extends the capabilities of the ALD technique, improving the properties of certain films, particularly nitrides deposited at low temperatures. PEALD of NbTiN has previously demonstrated superconducting properties[1] and PEALD NbN has been previously reported with a critical temperature of 10.4K [2].

In this work, Nb_xTi_yN (0 ≤ x, y ≤ 1) has been deposited using PEALD in an Ultratech/CNT Fiji system at substrate temperatures between 100 and 300°C. Stoichiometry was controlled by adjusting the ratio of NbN:TiN cycles during the film deposition. Precursors utilized for this study were (t-butylimido) tris(diethylamido) niobium (TBTDEN) and tetrakis(dimethylamido) titanium (TDMAT). A mixture of N_2 and H_2 was used as the plasma gas for the NbN cycles while TiN was deposited with an N_2 plasma. Films were analyzed for thickness and optical properties through spectroscopic ellipsometry. Room temperature resistivity was derived from four point probe measurements. Samples were analyzed with X-ray photoelectron spectroscopy to determine stoichiometry and impurity levels. Superconductivity characteristics of the films will also be presented.

A 20nm, 300°C deposition of NbN, which had a room temperature resistivity of 282μΩ-cm, was shown to have a critical temperature of 12.4K and a critical field greater than 12 Tesla.

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[2] M. Ziegler, et al., "Superconducting niobium nitride thin films deposited by metal organic plasma-enhanced atomic layer deposition," Supercond. Sci. Technol. 26 (2013) 025008.

3:20pm **TF+PS+SE-MoA6 Mechanical Reliability of PECVD Barrier Films for Flexible Electronics**, ***Kyungjin Kim***, *A. Singh, H. Luo, T. Zhu, O. Pierron, S. Graham,* Georgia Institute of Technology

The development of PECVD and ALD barrier films have proven to be viable approaches to create barrier films for flexible electronic applications. While much research has focused on the water vapor transport properties of these films, the mechanical reliability during flexural deformation is critical to the performance and durability of these coatings. Overall, the use of the critical onset strain is limiting in trying to define the limits of performance since it ignores time-dependent processes that can occur during mechanical deformation. In this work, we investigate the time-dependent channel crack growth behavior of silicon nitride and ALD barrier films on polyethylene substrates in humid and dry air. The evaluation of the cracking process versus applied strain and load was measuring in-situ using optical and laser scanning confocal microscopy. The results show that crack growth can occur at strains that are much lower than the standard measured onset critical strains. The results of the work show that both polymer relaxation of the PET substrate as well as environmentally assisted crack growth occurs in the films, both in a time dependent manner. Tests in dry air versus tests in humid air show crack growth rates increasing from 100 nm/s to 10 um/s for an applied stress intensity factor of 1.6 MPa.m^0.5. In addition to the dramatic changes in crack growth rates with environmental conditions, larger crack densities were observed in humid environments. This suggests an easier initiation and growth of crack in humidity versus dry air. Overall, the results presented will show the strong link between environment, temperature, and the rate at which cracks grow in barrier films. Finally, the energetics of the crack growth process will be presented as a better metric than onset crack strain to evaluate the mechanical reliability of the barriers for a given application.

4:00pm **TF+PS+SE-MoA8 Origin of Stress in Sputtered CdTe and ZnS Films: Influence of Sputter Ion Mass on Mechanical and Chemical Layer Properties**, ***Ségolène Liénard***, Univ. Grenoble Alpes, LTM CNRS, 38000 Grenoble, France; *D. Sam-Giao, A. Kerlain,* Sofradir, BP 21-38113, Veurey-Voroize, France; *F. Boulard, C. Vallée,* Univ. Grenoble Alpes, France

Physical vapor depostion is a mature, well understood and established technology in integrated circuit fabrication. CdTe and ZnS binary II-VI compounds materials are commonly used in photovoltaic solar cells or infrared optics. However, sputtering deposition of these materials still suffer from a lack of comprehensive study to optimize process integration.

Our study is focused on the influence of projectile ions mass on properties of sputtered deposition CdTe and ZnS films. We compare physico-chemical, mechanical and electrical properties of CdTe and ZnS films deposited with Ar and Xe ions as sputter gas. Ar and Xe concentration in these films are characterized by Time of Flight Secondary Ions Mass Spectrometry (TOF-SIMS). Dedicated implanted reference samples are used to quantify the absolute concentration. Layers microstructures are characterized by Scanning Tunneling Electron Microscopy (STEM) and dielectric constant by capacitance-voltage measurements. We use the curvature method based on the well known Stoney concept [1] to calculate film stress while density is estimated by differential weighing.

With Ar ion deposition process (low sputter on target mass ratio), we observe Ar and cavities inside the CdTe layer. The density as well as the dielectric constant are below bulk values. A good agreement is found between the cavity density and the effective dielectric constant determined by the Bruggeman model [2-3]. on the contrary, Xe ion target sputtering (high sputter on target mass ratio) leads to denser films, without Xe inside the layers, and close to theory density and dielectric constant values. We discuss these observations in terms of backscattered ions incorporation. Moreover, the effect of thermal annealing time on stress evolution is discussed in regards of Ar or Xe incorporation and outgasing.

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[2] Aspnes D. E., Thin Solid Films 89 (1982) 249.

[3] Othman M.T., PhD "Spectroscopic Ellipsometry Analysis of Nanoporous Low Dielectric Constant films Processed via Supercritical CO2 for Next-generation Microelectronic Devices"., University of Missouri-Columbia, 2007

4:20pm **TF+PS+SE-MoA9 Synthesis and Characterisation of MoB_{2-x} and Mo-B-C Thin Films by Non-Reactive DC Magnetron Sputtering**, ***Paulius Malinovskis,*** Uppsala University, Sweden; *J.P. Palisaitis,* Linkoping University, Sweden; *P.O.A. Persson,* Linköping University, Sweden; *E.L. Lewin, U.J. Jansson,* Uppsala University, Sweden

Transition metal diborides (MeB_2) with the AlB_2-type structure have many unique properties such as high hardness, high conductivity and oxidation resistance One of the most studied diboride compounds is TiB_2 but also other transition metals like Cr, Nb and Mo can form the simple AlB_2 type structure.

Non-reactive magnetron sputtering is an excellent technique to deposit thin films of different MeB_2 phases. It is well-known that phases with rather simple crystal structures are preferably formed in magnetron sputtering where the quenching rates of the incoming atoms are high. Such metastable MeB_2 films may be chemically more reactive in a tribocontact and form a lubricating tribofilm of metal oxides and layered BO_x. Some metal oxides such as MoO_3 and boric acid (forming in humid atmosphere from BO_x) have been predicted to exhibit low friction coefficients. Consequently, it is possible that metastable MeB_2 films with the AlB_2-structure may exhibit excellent low friction properties. Another way to tailor metal diboride properties is to alloy it with third element, e.g. carbon.

In this study we have investigated the microstructure, mechanical and tribological properties of DC magnetron sputtered MoB_{2-x} and Mo-B-C thin films from Mo/B and graphite carbon target. The films were characterized with XRD, XPS, TEM, nanoindentation and tribological ball-on-disk method. All films exhibited the AlB_2-type structure with substoichiometric MeB_{2-x} grains surrounded by a tissue phase of a-B and a-BC_x. The MoB_{2-x} films were substoichiometric with respect to boron and exhibited a much higher hardness compared to bulk samples, which could be attributed to a hardening effect of the tissue phase. Friction measurements confirmed the hypothesis that a significant tribofilm formation is present on the metastable MoB_{2-x} films. However, a reduced friction coefficient could not be observed. Addition of carbon resulted in a change in the composition of the tissue phase. This caused a reduction in hardness and a reduction of the friction coefficient. General trends in the phase formation and properties of Mo-B-C films will be explained in detail and compared with other Me-B-C systems (Me= Ti, Cr, Nb).

4:40pm **TF+PS+SE-MoA10 Molybdenum Back Contacts Deposited by High Power Impulse Magnetron Sputtering**, *D.A. Loch,* ***Arutiun Ehiasarian,*** Sheffield Hallam University, UK

Molybdenum thin films used in chalcopyrite solar cells can influence the Na diffusion rates and the texture of the $Cu(InGa)Se_2$ absorber according to the microstructure and morphology. The lowest resistivity films are achieved at low working pressure and are accompanied by high residual stress and poor adhesion due to the resulting high energy of the deposited flux. High Power Impulse Magnetron Sputtering was employed to ionise the sputtered flux, achieve high adatom mobility at low energy and influence the growth of Mo back contacts. Pulse durations in the range 60 to 1000 µs, sputtering voltages between 800 and 1500 V and deposition pressures of 2×10^{-3} mbar and 4×10^{-3} mbar resulted in ten-fold variations in the flux ratios of Mo^{1+}/Mo^{0} Mo^{2+}/Mo^{1+}, Ar^{2+}/Ar^{1+} and Mo^{1+}/Ar^{1+} as determined by optical emission spectroscopy and time-resolved plasma-sampling energy-resolved mass spectroscopy. The energy of metal and gas double and single-charged ions reduced with pulse duration and increased with voltage. The microstructure of the films varied from open columnar with faceted tops to fully dense as observed by secondary electron microscopy. The reflectivity of the films improved by 20% compared to industry-standard materials. The lowest resistivity was in the range of 12 µΩ-cm as observed by four-point probe measurements of 570 nm thick films. The correlation between resistivity, microstructure, crystallographic texture, stress and deposition flux characteristics is discussed.

5:00pm **TF+PS+SE-MoA11 Plasma Characterization of Al and Cu with HIPIMS**, ***Jason Hrebik***, Kurt J. Lesker Company; *R. Bandorf, H. Gerdes, D. Spreemann,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

High power impulse magnetron sputtering (HIPIMS) is a well-known technique for tailoring the coating properties in comparison to DC. In many cases the thin films were developed in smaller scale R&D facilities and afterwards transferred to industrial scaled machines. But the source configuration, magnetic field, and overall mechanical layout differs for the larger sputtering plant, and therefore a direct upscaling of the process is quite difficult. Since often the thin film properties are correlating with the plasma properties, plasma characterization is very useful tool for determining the main important parameters for a process transfer.

This investigation is focused on the plasma characterization of Al and Cu on a small circular target (3 inch) and will give a short comparison to a rectangular target (10 inch by 15 inch). As plasma properties the ion density and the optical emission was measured. The measurements were carried out in a time resoled mode and can be correlated to target voltage and current.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 103C - Session SA+2D+AC+AS+TF-TuM

Applications of Synchrotron-based Techniques to 2D Materials (8:00-10:00 am)/Complex Functional Materials and Heterostructures (11:00 am-12:20 pm)

Moderators: Nicholas Barrett, CEA Saclay, Giacomo Ceccone, European Commission, Joint Research Centre, IHCP, Italy

8:20am **SA+2D+AC+AS+TF-TuM2 A Versatile Method for the Fabrication of 2D-electron Systems at Functional Oxide Surfaces***, T.C. Rödel,* Université Paris-Sud - SOLEIL, France*; **Patrick Le Fèvre,*** Synchrotron SOLEIL, France*; F. Fortuna, E. Frantzeskakis,* Université Paris-Sud - IN2P3, France*; F. Bertran,* Synchrotron SOLEIL, France*; T. Maroutian, P. Lecoeur,* Université Paris-Sud - CNRS, France*; B. Mersey,* Université de Caen, France*; A.F. Santander-Syro,* Université Paris-Sud - IN2P3, France

A critical challenge of modern materials science is to tailor novel states of matter suitable for future applications beyond semiconductor technology. In this prospect, 2D electron systems (2DESs), analogous to those created in semiconductors heterostructures, have been observed at the $LaAlO_3/SrTiO_3$ interface [1] and show amazing physical properties like metal-to-insulator transitions, superconductivity or magnetism. It was then demonstrated that 2DES could also be stabilized at the surface of $SrTiO_3$ [2] or other oxides [3], although it requires the use of intense UV or X-ray synchrotron radiation to desorb oxygen from the surface and dope it with electrons. This opened the way for the use of surface sensitive techniques, like Angle-Resolved PhotoEmission spectroscopy (ARPES) which provided a clear description of the microscopic electronic structure of the quantum well states. However, 2DESs at oxygen-deficient surfaces can be only manipulated and studied in ultra-high vacuum (to preserve the O-vacancies from re-oxidation) and thus, are not suited for experiments or applications at ambient conditions. Here we demonstrate a new, versatile and cost-effective method to generate passivated 2DESs on large areas of UHV-prepared functional oxide surfaces. It consists in a simple evaporation at room temperature of an aluminum film onto the oxide surface. Aluminum acts as a reducing agent and pumps oxygen from the substrate. It oxidizes into an insulating AlO_x layer, protecting an underlying homogeneous 2DES confined in the first atomic planes of the oxide substrate. 2 Å of Al are sufficient to create a saturated 2DES on differently oriented surfaces of $SrTiO_3$, anatase-TiO_2, or $BaTiO_3$, which were all studied by ARPES to determine the band structure (effective mass, orbital order and charge carrier densities) [4].

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[2] A. F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhes, R. Weht, X. G. Qiu, F. Bertran, A. Nicolaou, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthélémy, M. J. Rozenberg, Nature **469**, 189 (2011).

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[4] T. C. Rödel, F. Fortuna, S. Sengupta, E. Frantzeskakis, P. Le Fèvre, F. Bertran, B. Mercey, S. Matzen, G. Agnus, T. Maroutian, P. Lecœur, and A. F. Santander-Syro, Adv. Mater. **28**, 1976 (2016).

8:40am **SA+2D+AC+AS+TF-TuM3 Advanced Spectro-microscopy of Ion Irradiated Graphene-metal Interfaces: From Substitutional Implantation to Nanobubble Formation***, **Andrea Locatelli,** A. Sala, T.-O. Menteş,* Elettra - Sincrotrone Trieste, Italy*; G. Zamborlini,* Peter Grünberg Institute (PGI-6) Jülich*; L. Patera, C. Africh,* IOM-CNR Laboratorio TASC, Italy*; M. Imam, N. Stojić, N. Binggeli,* Abdus Salam International Centre for Theoretical Physics, Italy **INVITED**

The exploitation of graphene in the next generation electronics depends on our ability of preserving and tailoring its unique electronic and transport properties. Whereas the preservation of the free-standing characteristics of graphene demands to decouple the film from its support, their modification requires functionalization and thus chemical doping. Varied methods have been devised to implant exospecies into and under the C lattice mesh. Among them, irradiation of nitrogen ions has emerged as one of the most powerful approaches, producing enhanced physical and chemical properties rather than detrimental effects. At variance with other methods, ion irradiation enables implementation of lithographic approaches for doping graphene, a feature which is most desirable for creating arrays of devices.

The characterization of complex and laterally-heterogeneous interfaces, such as that of ion-irradiated graphene, demands advanced microscopy tools. Here, we will demonstrate the present capabilities of cathode lens spectro-microscopy. As a first example, we report a proof of principle experiment demonstrating that low energy ion irradiation through an aperture can be used to achieve local control on doping in graphene. Our study tackles the fabrication of a 2-dimensional heterojunction between *n*-doped and almost neutral single-layer graphene on Ir(111). Here, XPEEM is employed to characterize the transition region between areas with metallic and semimetal-like density of states and its thermal stability [1].

Then, we will focus on the irradiation of graphene with low energy Ar and Ne ions, reporting on the formation of nanobubbles upon annealing. The morphology and local stoichiometry of the Ar-ion irradiated interface were characterized by LEEM, XPEEM and STM, specifically addressing the thermal stability of noble gas nanobubbles. These structures display a lateral size up to tens of nanometers and height of several atomic layers. Remarkably, the Ar clusters remain trapped under graphene up to temperatures nearing 1100°C, suffering no material loss through the mesh or its edges. Ab-initio calculations demonstrate that intercalated Ar undergoes extreme pressures, up to few tens GPa. The nanobubble ripening process turns out to be driven by the minimization of the energy cost of film distortion and loss of adhesion [2]. The electronic properties of the ion irradiated interface will be also discussed.

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[2] G. Zamborlini, M. Imam , L.L. Patera , T.O. Menteş , N. Stojić , C.Africh , A. Sala , N. Binggeli , G. Comelli and A.Locatelli; Nano Lett. **15**(9), 6162–6169 (2015).

9:20am **SA+2D+AC+AS+TF-TuM5 Gas-source MBE Growth of 2D Materials Examined using X-ray Synchrotron Radiation***, **Hugh Bullen,** R.K. Nahm, S. Vishwanath, H.G. Xing, J.R. Engstrom,* Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. Here we report on the gas-source MBE growth of thin films of WSe_2 using $W(CO)_6$ and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of $W(CO)_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence. We have examined growth for a variety of conditions: growth with coincident fluxes of $W(CO)_6$ and Se, and growth in which one of the two reactant fluxes was gated. These experiments were conducted at several different substrate temperatures, on graphite (HOPG), and on so-called epitaxial graphene (graphene on SiC). First, for continuous exposure to $W(CO)_6$ and Se we observe, after an short incubation period, continuous growth of both the W and Se intensities. Analysis of this data indicates a stoichiometry consistent with WSe_2. We also find diffraction features consistent with the crystalline phase of WSe_2, where the basal plane is in the plane of the substrate. Particularly interesting is what we see when one of the reactants is gated: We have found that growth is halted by gating the incident flux of $W(CO)_6$, while the film is stable in the presence of a flux of Se_n. The physical properties of these thin films are essentially the same as those grown using continuous exposure to both reactants. We find a much different result when the flux of Se_n is gated: the absence of Se, but the presence of $W(CO)_6$, leads to *loss* of Se, and an increase in the amount of W. Since the termination of both fluxes does not lead to the loss of either element, it must be that $W(CO)_6$ is providing the species that leads to the loss of Se. The most likely scenario is that a ligand exchange reaction occurs producing the gas phase species, SeCO(*g*). Perhaps our most exciting result involves the growth of WSe_2 on epitaxial graphene. In these experiments, in addition to measuring the X-ray fluorescence, we also measured *in situ* and in real time the intensity at the anti-Bragg condition, which we have shown to be are very effective way to monitor thin film crystal growth. We observe strong and sustained oscillations, indicating layer-by-layer growth of WSe_2 of up to at least 5 monolayers. This is a very exciting result, and it indicates the effective use of synchrotron radiation to examine the growth of TMD thin films.

9:40am **SA+2D+AC+AS+TF-TuM6 Nanostructured Surface of Multilayer Graphene on Cubic-SiC**, ***Victor Aristov,*** ISSP RAS, Chernogolovka, Russia, Russian Federation*; H.-C. Wu,* BIT, Beijing, China*; O.V. Molodtsova, S.V. Babenkov,* DESY, Hamburg, Germany*; A.N. Chaika,* ISSP RAS, Chernogolovka, Russia, Russian Federation

The results of atomically resolved scanning tunneling microscopy, low energy electron diffraction, low energy electron microscopy, micro-LEED and angle resolved photoelectron spectroscopy studies of graphene synthesized on cubic-SiC will be presented. Uniform few layer graphene was fabricated on SiC/Si wafers using Si-atom sublimation followed by SiC surface layer graphitization during high-temperature annealing in ultrahigh vacuum. Using the new dynamic-XPS end-station, based on the Argus spectrometer installed on the high-brilliance soft X-ray P04 beamline at PETRA III (DESY) one can control layer-by-layer graphene growth in real time following the evolution of the photoemission spectra with an acquisition time of ~ 0.1 sec/spectrum. Recording spectra during graphene growth on the SiC/Si(001) wafer, one can stop the process as soon as the desired number of graphene layers is reached. Angle-resolved photoemission measurements allowed us to extract the information about the electronic structure and the stacking order of the few-layer graphene on SiC(001). The preferential directions of the nanodomain boundaries coincide with the directions of carbon atomic chains on the SiC(001)-c(2x2) reconstruction, fabricated prior to graphene synthesis. Electrical measurements conducted on the vicinal SiC(001) samples demonstrate the opening of a transport gap in the nanostructured trilayer graphene. Our measurements demonstrate that the self-aligned periodic NBs can induce a charge transport gap up to 1.3 eV at low temperatures. The transport gap opening produces high current on-off ratio of 10^4. This development may lead to new tuneable electronic nanostructures made from graphene on cubic-SiC, opening up opportunities for a wide range of new applications.

This work was supported by the RAS, RFBR grants No 140200949 and 140201234, by the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211, by a Marie Curie IIF grant No 12/IA/1264, by SPP 1459 of DFG.

11:00am **SA+2D+AC+AS+TF-TuM10 Full-field Photoelectron Spectromicroscopy of Ferroelectric Surfaces***, **Nicholas Barrett,*** CEA Saclay, France **INVITED**

Advanced low energy electron optics combined with synchrotron radiation has transformed photoelectron emission microscopy (PEEM) into a powerful technique for the microscopic study of material surfaces. High lateral, wave-vector and energy resolution makes it possible to probe spatial variations in the chemical and electronic structure of nanoscale materials.

Perovskite based ferroelectrics are one important family of oxide materials requiring such analysis. Their robust polarization, switchable by an external field, makes them extremely interesting candidates for post-CMOS electronics.

First, the principles of fully energy filtered PEEM will be presented. By a combination of both direct and reciprocal space imaging the surface charge, work function, topography, chemistry and band structure of ferroelectric materials can be studied. This will then be illustrated by several examples.

The surface charge and hence the ferroelectric polarization can be estimated from the the work function as measured in PEEM. There is a critical film thickness in $BiFeO_3$ below which the film polarization drops to zero despite constant tetragonality, suggesting the formation of stripe domains in ultra-thin films [1].

The band structure of ferroelectric domains in $BaTiO_3$(001) are studied using spatially resolved reciprocal space PEEM and synchrotron radiation. The dispersion relations can be correlated with domain chemistry and in- and out-of-plane ferrolectric polarization [2].

The ferroelectric stability as a function of temperature of piezo force microscopy written domains has been studied using threshold PEEM. A Curie temperature of 490°C is recorded which is also dependent on the poling voltage.

We will conclude with a brief demonstration of an operando PEEM experiment, opening up the perspective of studying the changes in functional oxide properties under electric stimulation.

[1] J. Rault, W. Ren, S. Prosandeev, S. Lisenkov, D. Sando, S. Fusil, M. Bibes, A. Barthélémy, L. Bellaiche and N. Barrett, Physical Review Letters 109, 267601 (2012)

[2] J. E. Rault, J. Dionot, C. Mathieu, V. Feyer, C. M. Schneider, G. Geneste, and N. Barrett, Physical Review Letters 111, 127602 (2013)

11:40am **SA+2D+AC+AS+TF-TuM12 Electron Confinement at Magnetic Oxide Interfaces: Insight from Photoemission Spectroscopy***, **Martina Mueller,*** Forschungszentrum Juelich GmbH, Germany **INVITED**

Recent advances in the fabrication of oxide heterostructures with atomic-scale precision has enabled interface and size control of complex oxide materials, for which unique phenomena with no bulk analogues have been demonstrated. In designated heterostructures, two-dimensional electron systems can be confined at oxide interfaces -- typically along the growth direction – which offer possible alternatives to conventional semiconductors in terms of functional (e.g. spin-polarized) electronic transport properties. Using redox-controlled synthesis [1, 2], the electronic properties of oxide heterostructures and interfaces can be engineered -- in terms of quality that were thought to be unique to semiconductors.

The basic idea of electron confinement applies to complex oxides just as to conventional semiconductors, but the physics is much richer. In metal oxides, confined electrons are subject to strong electron-electron interactions leading to a variety of physical phenomena that can be accessed, modified and controlled. For example, using oxides with intrinsic magnetic order allows to explore spin-related phenomena in low dimensions.

We present how to create two-dimensional electronic systems (2DES) in all-oxide heterostructures using EuO, a ferromagnetic insulator [1]. By interfacing Eu metal to $SrTiO_3$, a non-magnetic insulator, a redox reaction takes place at the interface which involves the oxidation of Eu metal into ultrathin EuO [2], and the reduction of Ti cations. This redox process strongly suggests that mobile electrons are created at the resulting interface. Using synchrotron-based soft, hard and angle-resolved photoemission spectroscopy [3] we probe the electronic structure and chemical composition at the EuO/STO interface and give a direct indication of a redox-created 2DES. The observed electronic confinement in all-oxide heterostrctures provides a route for controlling spin functionality for emerging applications.

[1] G. Prinz, T. Gerber, A. Lorke, M. Müller, submitted (2016)

[2] T. Gerber, M. Müller *et al*, J. Mater. Chem. C, 4, 1813 (2016)

[3] M. Müller *et al*, J. Electron Spectrosc. Relat. Phenom. 208, 24 (2016)

Advanced Surface Engineering
Room 101C - Session SE+NS+TF+TR-TuM

Nanostructured Thin Films and Coatings

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Robert Franz, Montanuniversität Leoben, Austria

8:00am **SE+NS+TF+TR-TuM1 Design and Predictive Synthesis of Thin Films and Coatings***, P.A. Salvador, **Gregory Rohrer,*** Carnegie Mellon University **INVITED**

A fundamental challenges in materials synthesis is to obtain a specific targeted composition in a functional crystal structure. For example, the synthesis of hexagonal BN is relatively easy, but synthesizing thick films of cubic BN is more difficult. In other words, we cannot currently predict exact synthesis conditions of many targeted polymorphs, and so their formation is often left to lengthy "design-of-experiments" (DOE) methodologies or, more commonly, basic trial-and-error practices. It is essential to improve the output of computational and physical experimental practices to move closer to predictive synthesis and design of coatings.

This talk will describe some recent results of a methodology called combinatorial substrate epitaxy (CSE), which we have used to understand the preferred epitaxial orientations (PEOs) of a wide range of heteroepitaxial structures and to fabricate various novel metastable materials. In this approach, the target compound is deposited on polished polycrystalline substrates, rather than commercial single crystals or buffer layers. The primary hypotheses underpinning CSE is that the each grain surface in the polycrystalline substrate can be treated as the equivalent of a single-crystal surface in a traditional DOE experiment, therefore providing every combination of substrate orientation in a single experiment. The local structure is probed in a scanning electron microscope using electron backscatter diffraction and automated orientation assignments. The method not only allows for hundreds of experiments to be carried out in a single growth run, it has the unique advantage of not being restricted to the use of commercially available single crystals.

This talk will focus on three important observations. First, when a film is grown on a polycrystal, the growth occurs by grain-over-grain epitaxy. In other words, films can grow on microcrystalline substrates in the same way they grow on millimeter scale substrates, or every grain is in an independent observation of growth. Second, there are PEOs, regardless of the substrate surface plane, and these can be easily predicted. For many of the cases we have observed, the PEO is the one that aligns the closest packed planes and directions in the eutactic (nearly close packed) arrangement of oxide ions in different structures. Third, we have already fabricated new and novel metastable coatings using this methodology, where novel substrates provide the epitaxial template to control phase formation. Observations relative to functional ceramics, including examples from the BO_2, B_2O_3, ABO_3, A_2BO_4, and $A_2B_2O_7$ families, will be described.

8:40am **SE+NS+TF+TR-TuM3 Nanoscale Atomic Arrangement in Multicomponent Thin Films Synthesized Far-from-Equilibrium***, V. Elofsson, G.A. Almyras, B. Lü, R.D. Boyd,* ***Kostas Sarakinos****,* Linköping University, Sweden

Synthesis of multicomponent thin films using vapor fluxes with a modulated deposition pattern is a potential route for accessing a wide gamut of atomic arrangements and morphologies for property tuning. In the current study, we present a research concept that allows for understanding the combined effect of flux modulation, kinetics and thermodynamics on the growth of multinary thin films. This concept entails the combined use of thin film synthesis by means of multiatomic vapor fluxes modulated with sub-monolayer resolution [1], deterministic growth simulations and nanoscale microstructure probes. Using this research concept we study structure formation within the archetype immiscible Ag-Cu binary system showing that atomic arrangement and morphology at different length scales is governed by diffusion of near-surface Ag atoms to encapsulate 3D Cu islands growing on 2D Ag layers [2]. Moreover, we explore the relevance of the mechanism outlined above for morphology evolution and structure formation within the miscible Ag-Au binary system. The knowledge generated and the methodology presented herein provides the scientific foundation for tailoring atomic arrangement and physical properties in a wide range of miscible and immiscible multinary systems.

[1] "*A METHOD OF CONTROLLING IN-PLANE COMPOSITIONAL MODULATION*", Patent Pending Application, PCT/EP2014/052831.

[2] V. Elofsson, G.A. Almyras, B. Lü, R.D. Boyd, and K. Sarakinos, "*Atomic arrangement in immiscible Ag-Cu alloys synthesized far-from-equilibrium*", Acta Mater. 110, 114 (2016).

9:00am **SE+NS+TF+TR-TuM4 Is *Intrinsic* Nanocrystalline Stability Practically Achievable? Insights from Investigations with Pt-Au Alloys***,* ***Nicolas Argibay****, T.A. Furnish, D.P. Adams, P. Lu, M. Chandross, M.A. Rodriguez, B.L. Boyce, B.L. Clark, M.T. Dugger,* Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been proposed recently, supported by some notable demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of stress on this stability. In this presentation we present results of an investigation on the stress and temperature dependent nanocrystalline stability of a noble-metal alloy (Pt-Au) in the form of sputter co-deposited thin films. In situ XRD and TEM annealing revealed an extraordinary degree of thermal stability, confirming literature predictions. Tribological experiments and molecular dynamics simulations were used to further explore the impact of stress as a destabilizing factor.

9:20am **SE+NS+TF+TR-TuM5 Improved Mechanical Properties In Tungsten-Molybdenum Nanostructured Thin Films***,* ***Gustavo Martinez****, C.V. Ramana,* University of Texas at El Paso

Preventing materials failure and improving the performance of materials in nuclear reactors demand novel materials to serve under extreme environment conditions. For nuclear applications, tungsten (W) has been alloyed in the past with La and Re to improve its performance and properties including low fracture and high ductile to brittle transition. In this work, molybdenum (Mo) solute atoms were added to W matrix with the intention of creating interstitial point defects in the crystals that impede dislocation motion, increasing the hardness and young modulus of the material. Nanostructured W-Mo thin films with variable Mo content were deposited by the sputter-deposition. W-Mo films were stabilized in bcc structure of W. Studies showed that as grain size formation increases the residual stress distribution will reach the maximum and stabilize after a deposition temperature of 350 °C. The residual stress still continues to follow a parabolic pattern, indicating that the stresses mainly depend on grain organization rather than atomic packing. From Nano-scratch testing, it is found that depth penetration decreases with increasing sputtering temperature. The effect of Mo on the overall mechanical properties improvement in W-Mo nanostructured thin films will be presented and discussed.

Keywords: Tungsten-Molybdenum Thin Films, Mechanical Properties, Nano-Indentation

9:40am **SE+NS+TF+TR-TuM6 Hierarchical Monolith Scaffolds for Silicon Lithium Ion Battery Electrodes***,* ***Kevin Laughlin****,* Brigham Young University

Research has shown stable high gravimetric capacity lithium ion battery anodes can be made from silicon deposited on carbon nanotubes (CNTs). High stability operation however requires nanostructuring of the silicon to alleviate stresses caused by the large expansion of the silicon upon Li alloying. At high silicon loadings even nanoscale layers of silicon result in stresses large enough to cause mechanical damage to the electrode. Here we present work on a hierarchical approach to structuring carbon nanotube based carbon monoliths that provide for electrode stress management on multiple scales.

11:00am **SE+NS+TF+TR-TuM10 Technological Developments in Coatings for Components and Cutting Tools***,* ***Roel Tietema****,* IHI Hauzer Techno Coating B.V., Netherlands*; D. Doerwald,* Hauzer, Netherlands*; R. Jacobs, G. Negrea, I. Kolev, J. Zhu, J. Landsbergen,* Hauzer **INVITED**

Nanostructured and amorphous coatings play an important role in today's industrial applications. This is the case both in applications for cutting tools, as well as in applications for components.

In cutting tools nanostructured coatings with high hardness, including hot hardness, and ductility have been extremely helpful to increase the productivity of the machining process. On one hand superlattice multilayers have shown here great benefits and on the other hand nanocrystallites in the material have been created to give the coating materials an inherent high hardness and ductility.

In automotive coatings these material properties were leading to technological breakthroughs as well. First coatings on the market were nanostructured WC-C:H sputtered coatings, developed by Prof. Dimiggen of Fraunhofer IST. These developments were soon followed by hybrid a-C:H coatings, combining the WC-C:H developments with a multilayered structure to achieve a gradual adaptation of the Young's modulus of the relatively soft steel as base material to the very hard a-C:H-DLC top layer. In this way it has been possible to produce coatings with a very high ductility, despite the high hardness. Hardness values as applied today on components are ranging from 2000-2500 HV for a-C:H coatings up to 4000-7000 HV for ta-C coatings.

The importance of petreatment and post treatment steps for cutting tools and components, being as important as the actual coating step, will be addressed in this talk.

The main focus in this talk will be on the equipment aspects. Several technologies for cutting tools and for components will be presented. The equipment design and even the selection of most suitable process technology is however also strongly determined by the productivity. Besides technological properties of the coating there is a focus on the cost reduction of the coating per coated part. Cost reduction is main driver in many fields, especially in the field of components. Reduction of the cost of ownership leads to a tendency to use fast processes in large systems, respectively application of in-line systems.

11:40am **SE+NS+TF+TR-TuM12 Influence of Transition Metal Dopants on Target Poisoning and Oxidation Mechanisms of Reactively Sputtered γ-Al_2O_3 Thin Films***,* ***Helmut Riedl****, B. Kohlhauser,* TU Wien, Institute of Materials Science and Technology, Austria*; V. Paneta,* Uppsala University, Sweden*; C.M. Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The outstanding oxidation resistance, thermo-mechanical stability and chemical inertness of Al_2O_3 attracts particular attention in various industrial applications. Especially, in the field of protective barrier coatings there are many research activities focusing on the synthesis of the different polymorphs α- and γ-Al_2O_3 (corundum and cubic), respectively. Apart from the fact that the deposition of the thermodynamically stable α-Al_2O_3 is strongly limited by the depositing temperature, the formation of electrically isolating Al_2O_3 at the target surface leads to massive arcing processes and destabilizes the deposition process. These problems could be overcome by varying the powering method to pulsed DC and especially

RF sputtering, but at the cost of decreased deposition rates and plasma densities.

Therefore, we study in detail the influence of small amounts of transition metals such as M = Cr, Nb, Mo, and W on the process stability and coating properties of reactive DC sputter deposited $(Al_{1-x}M_x)_2O_3$ thin films. To keep the influence of the alloying elements on the outstanding properties of alumina as low as possible only targets with alloying contents of x = 2 and 5 at.% are investigated. All micro-alloyed targets allow for significantly improved process stability and massively reduced arcing processes at the target as compared to the non-alloyed Al target. The morphology of all coatings deposited is highly dense, smooth and partly columnar with cubic γ-Al_2O_3 crystalline structure. The mechanical properties of the Cr, Mo, and W containing coatings are slightly enhanced by solid solution hardening in comparison to pure Al_2O_3 obtaining e.g. hardness values of about 25 GPa. In contrast, alloying contents of about 1 at.% Nb are already degrading the mechanical properties of alumina thin films. The significantly enhanced process stability when using Cr, Mo, and W alloyed Al targets, leads to coatings with improved thin film quality. Therefore, the oxidation resistance of these films even outperform the Al_2O_3 DC sputtered film.

Thin Film

Room 102B - Session TF+SA+MI-TuM

Thin Films for Synchrotron and Magnetism Applications

Moderators: Joshua Ballard, Zyvex Labs, Divine Kumah, North Carolina State University

8:00am **TF+SA+MI-TuM1 Achieving High-Temperature Ferromagnetic Topological Insulator by Proximity Coupling***, **Valeria Lauter**,* Oak Ridge National Laboratory

Topological insulators (TIs) are insulating materials that poses conducting surface states protected by time-reversal symmetry, wherein electron spins are locked to their momentum. This exclusive property offers novel prospects for creating next-generation electronic and spintronic devices, including TI-based quantum computation. Introducing ferromagnetic order into a TI system without compromising its distinctive quantum coherent properties could lead to a realization of a number of innovative physical phenomena. In particular, achieving robust long-range magnetic order at the TI surface at specific locations without introducing spin scattering centers could open up new potentials for devices. Here, we demonstrate topologically enhanced interface magnetism by coupling a ferromagnetic insulator (FMI) to a TI (Bi_2Se_3); this interfacial ferromagnetism persists up to room temperature, even though the FMI (EuS) is known to order ferromagnetically only at low temperatures (< 17 K). The induced magnetism at the interface resulting from the large spin-orbit interaction and spin-momentum locking property of the TI surface is found to greatly enhance the magnetic ordering (Curie) temperature of the TI/FMI bilayer system. Due to the short range nature of the ferromagnetic exchange interaction, the time-reversal symmetry is broken only near the surface of a TI, while leaving its bulk states unaffected [1]. The topological magneto-electric response originating in such an engineered TI could allow for an efficient manipulation of the magnetization dynamics by an electric field, providing an energy efficient topological control mechanism for future spin-based technologies. Work supported by U.S. DOE, Office of Science, BES.

[1]F. Katmis, V. Lauter, F. Nogueira, B. Assaf, M. Jamer, P. Wei, B. Satpati, J. Freeland, I. Eremi[5], D. Heiman, P. Jarillo-Herrero, J. Moodera, "Achieving high-temperature ferromagnetic topological insulating phase by proximity coupling", *Nature 2016*

8:20am **TF+SA+MI-TuM2 Soft X-ray Induced Spin Crossover Transition at Room Temperature***, **Paulo Costa**, X. Zhang, S. Beniwal,* University of Nebraska-Lincoln*; A.T. N'Diaye,* Lawrence Berkeley National Laboratory*; J-F. Létard,* Université de Bordeaux*; P.A. Dowben, A. Enders,* University of Nebraska-Lincoln

The spin crossover Fe(II) complex (SCO) of the type $[Fe(H_2B(pz)_2)_2(bipy)]$ has been previously shown to exhibit spin state transitions between its low spin (LS) and high spin (HS) states as a response to external stimulus such as electric fields, temperature changes, and light. It is well established that this SCO complex exhibits a crossover from its LS state to the HS state if the temperature is increased above approximately 150 K. It is demonstrated here that this spin crossover can be suppressed by mixing the SCO with strongly dipolar *p*-benzoquinonemonoimine zwitterion (PZI) molecules, so that unlike before, the LS state still prevails even at room temperature (RT). With the metastable LS state now locked in at RT, a spin state transition to the HS state can now be triggered optically by soft X-rays over a relatively short time of several minutes. This process is fully reversible, as cooling the mixture to 78 K has been shown to de-excite it back to its original LS state. Experiments were performed using X-ray absorption spectroscopy measurements (XAS) with synchrotron radiation tuned to the Fe L_3 absorption edge as well as accompanying magnetic moment measurements taken by a superconducting quantum interference device (SQUID). The effects of temperature, photon flux, and the stoichiometric ratio between SCO and PZI in the mixture were systematically studied, and the results will be presented here. This study provides a demonstration that the spin crossover transition temperature can be tailored to create a material that exists in a meta-stable LS state at RT wherein spin states can then be switched optically.

8:40am **TF+SA+MI-TuM3 Probing Thermochromic Phase Transitions in ALD VO_2 using Synchrotron Radiation***, **Alexander Kozen**,* U.S. Naval Research Laboratory*; H. Joress,* Cornell University*; V.D. Wheeler, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory

VO_2 is a thermochromic material, one class of "smart materials" that are receiving considerable interest due to a sharp semiconductor to metal (S-M) phase transition that occurs at a specific, material dependent temperature (T_c = 68˚C for VO_2). The S-M transition occurs as a result of a phase transition between a semiconducting monoclinic phase below T_c and a metallic tetragonal phase above T_c. While VO_2 has been widely utilized as a microbolometer material for IR detectors, current deposition processes used to fabricate thin film VO_2 (PLD, MBE, sputtering) are not adequate to realize complex device architectures. Use of ALD to deposit VO_2 thin films allows for uniform, low temperature coating of large area 3D substrates that could open the door to new applications.

Temperature dependent *in-situ* grazing incidence synchrotron XRD was utilized to probe lattice strain and structural reordering in both as-deposited (amorphous) and annealed (polycrystalline) ALD VO_2 thin films during the S-M transition. GIXRD allows us to selectively sample the bulk or the film-substrate interface of thin ALD films with excellent depth resolution, while the high flux provided by the synchrotron (10^{12} photons/s) enables fast data collection. Initial results show that as-deposited ALD VO_2 films are polycrystalline at the VO_2-sapphire interface, while the bulk of the as-deposited VO_2 is amorphous. Annealing VO_2 on sapphire in an oxygen-rich environment forms a fiber-textured polycrystalline VO_2 film with a more pronounced S-M transition. We will discuss how substrate selection, ALD growth and processing conditions, and film thickness influence VO_2 morphology and/or structure and relate these materials properties to device data.

The authors wish to acknowledge Cornell University's CHESS synchrotron facilities for GIXRD work and The Office of Naval Research for support. Dr. Kozen acknowledges support by the ASEE-NRL postdoctoral fellows program.

9:00am **TF+SA+MI-TuM4 Standing-wave Synchrotron Photoemission Studies of Electronic Structure in $SrTiO_3$-$LaCrO_3$ Superlattices***, **Ryan Comes**,* Auburn University*; S.C. Lin,* University of California, Davis*; C.T. Kuo,* Lawrence Berkeley National Laboratory (LBNL)*; L. Plucinski,* FZ Juelich*; S. Spurgeon,* Pacific Northwest National Laboratory*; D. Kepaptsoglou, Q. Ramasse,* SuperSTEM*; J.E. Rault,* Synchrotron SOLEIL*; S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; C. Fadley,* Lawrence Berkeley National Laboratory (LBNL)*; P.V. Sushko, S.A. Chambers,* Pacific Northwest National Laboratory

The polar discontinuity at the interface between $SrTiO_3$ (STO) and $LaCrO_3$ (LCO) has been shown to produce a varying band alignment between the two materials with a built-in potential gradient.[1] We have recently shown that this built-in potential gradient can be harnessed to induce a polarization in STO-LCO superlattices through interface engineering.[2] This work demonstrated that by controlling interfacial termination between layers we can induce a built-in polarization in STO, with Ti cations displaced off-center in surrounding oxygen octahedra. To further study this system, we have synthesized a series of STO-LCO superlattices with varying interfacial and surface terminations for synchrotron standing-wave x-ray photoemission measurements.[3] These measurements make use of Bragg diffraction from the superlattice to induce an x-ray standing wave that can be scanned across a single period of the superlattice. Through careful material design, we have achieved the strongest standing-wave effects to date, enabling angle-resolved photoemission measurements of electronic dispersion in both the STO and LCO layers of the material. Density functional theory models of the electronic structure of the superlattices are used to corroborate our experimental results with the expected behavior. Monochromated, aberration-corrected scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS) measurements also enable further studies into changes in electronic behavior at interfaces.

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[2] R.B. Comes, S.R. Spurgeon, S.M. Heald, D.M. Kepaptsoglou, L. Jones, P.V. Ong, M.E. Bowden, Q.M. Ramasse, P.V. Sushko, and S.A. Chambers, Adv. Mater. Interfaces, (2016). DOI: 10.1002/admi.201500779

[3] A.X. Gray, C. Papp, B. Balke, S.-H. Yang, M. Huijben, E. Rotenberg, A. Bostwick, S. Ueda, Y. Yamashita, K. Kobayashi, E.M. Gullikson, J.B. Kortright, F.M.F. de Groot, G. Rijnders, D.H.A. Blank, R. Ramesh, and C.S. Fadley, Phys. Rev. B **82**, 205116 (2010).

9:20am **TF+SA+MI-TuM5 *In Situ* Synchrotron X-ray Studies of Complex Oxide Thin Film Growth*, Dillon Fong,*** Argonne National Laboratory**INVITED**

Functional materials based on complex oxides in thin film form offer new and exciting strategies for meeting many of our outstanding energy challenges through systematic control of layer sequencing, strain, etc. However, the synthesis of such oxide films can be a major challenge even when utilizing reactive molecular-beam epitaxy (MBE), a powerful deposition technique that allows the construction of materials atomic plane by atomic plane. To understand the fundamental physics of oxide growth by reactive MBE, we present *in situ* surface x-ray diffraction results on the growth of $SrTiO_3$ and SrO-$SrTiO_3$ thin films on (001)-oriented $SrTiO_3$ substrates. For homoepitaxy, we compare sequential deposition (alternating Sr and Ti monolayer doses) with that of co-deposition of Sr and Ti, both in a background of oxygen pressure, and observe drastically different growth pathways due to the presence of a TiO_2 double layer. For heteroepitaxial growth of Ruddlesden-Popper SrO-$SrTiO_3$ films, we find that layers rearrange dynamically, resulting in layer sequences distinct from the shutter sequence. In general, the starting surface structure and composition, in combination with local thermodynamic considerations, strongly influence our ability to atomically construct new complex oxides.

Work at Argonne, including the Advanced Photon, is supported by the U.S. Department of Energy.

11:00am **TF+SA+MI-TuM10 Probing CVD Growth Mechanisms of SiC with *In Operando* Synchrotron-based X-ray Diagnostics*, Philip DePond,*** *A.A. Martin, J.H. Yoo, M. Bagge-Hansen, J. Lee, S. Elhadj, M. Matthews, T. van Buuren,* Lawrence Livermore National Laboratory

Laser chemical vapor deposition (LCVD) of ultra-hard coatings, such as SiC, offers sub-mm spatial control over composition and phase, while addressing multiple growth processes under the same conditions for comparison. Normally, optimization requires extensive and costly "cook and look" experiments. Using an in situ approach instead, we develop fundamental insights into the growth mechanisms to unravel the complex roles of deposition parameters. We have conducted a series of in operando synchrotron-based X-ray absorption experiments that interrogate the LCVD growth region during growth. SiC was grown in a compact, portable CVD system from tetramethylsilane using a CW 532nm YAG to achieve laser-based pyrolytic precursor decomposition. We will present the results of Si K-edge (1.8keV) X-ray absorption near-edge structure (XANES) measurements conducted concurrently for the film during LCVD growth with an emphasis on the effects of variation of temperature, flow, substrates, and pressure conditions.

11:20am **TF+SA+MI-TuM11 Unusual Effects in Organic Thin Film Growth as Revealed by the Use of *In Situ* Real Time Synchrotron X-ray Techniques*,*** *R.K. Nahm, H.J. Bullen, T. Suh,* ***James Engstrom,*** Cornell University

The effects of molecular scale events on the growth of crystalline thin films has been long been an active area of research as the resulting thin film properties depend sensitively on the microstructure. The growth of high quality, smooth thin films in the vast majority of these systems is favored at low rates of growth and high substrate temperatures. Here we report on the growth of thin films of tetracene, an organic semiconductor that possesses one less aromatic ring as compared to the much more studied pentacene. We examine the growth on SiO_2 using *in situ* real time X-ray synchrotron radiation and *ex situ* atomic force microscopy (AFM). First, using *in situ* X-ray reflectivity, we observe a transition from 3D island growth to 2D layer-by-layer growth as the growth rate of tetracene is *increased* on SiO_2 at room temperature, T_s ~ 30 °C. This unusual phenomenon, 2D growth favored at higher rates, has not been observed in previous work with pentacene, despite the similarities between these two molecules. Results from AFM indicate that tetracene may tend to quickly traverse "upwards" on thin film features such as the edges of islands, making these thin films susceptible to reorganization during and/or after growth. Thus, at sufficiently high rates of growth the rate of admolecule attachment at the tetracene island/SiO_2 substrate edges effectively outcompetes the rate of upward step-edge transport, and 2D growth results. We find additional evidence for this mechanism by examining the effect of substrate temperature. In particular we find that the transition to 2D growth occurs at a lower rate of growth at a substrate temperature of T_s ~ 0 °C, consistent with suppression in the rate of upward transport at lower values of T_s. Finally, we have also examined the evolution of the thin film crystal structure in real time using *in situ* grazing incidence X-ray diffraction. Many thin film organic semiconductors are known to crystallize in different structures, and tetracene is no exception. At room temperature we find that first a thin film phase grows, then, after a delay, a bulk phase begins to grow, while the growth of the thin film phase saturates. We also find that the film thickness at which X-ray scattering from the bulk phase becomes apparent is found to vary with deposition rate. These phenomena are also dependent on substrate temperature. For example, for the range of thin films thicknesses examined, we found no evidence for growth of the bulk phase at the lower substrate temperature, T_s ~ 0 °C. These results highlight the potential complexity of crystalline thin film growth in what appears to be a very simple system, tetracene on SiO_2.

11:40am **TF+SA+MI-TuM12 Understanding the Effect of Nitrogen Plasma on Plasma Assisted Atomic Layer Epitaxy of InN Monitored by Real Time GISAXS*, Neeraj Nepal,*** *V. Anderson, S.D. Johnson, D.J. Meyer, B.P. Downey, A.C. Kozen,* US Naval Research Laboratory*; Z.R. Robinson,* SUNY College at Brockport*; D.R. Boris, S.C. Hernández, S.G. Walton,* US Naval Research Laboratory*; K.F. Ludwig,* Boston University*; C.R. Eddy, Jr.,* US Naval Research Laboratory

III-N semiconductors have found application in a variety of technologies such as high power transistors, emitters, detectors, and solar-cells. The relatively high growth temperature of common III-N synthesis techniques has impeded further development and application of the materials due to challenges with miscibility gaps and strain related to thermal expansion mismatch with non-native substrates. To address these challenges, Plasma assisted atomic layer epitaxy (PA-ALE) offers a new approach to low temperature III-N growth and can be used to epitaxially grow InN by using alternative pulses of trimethylindium and nitrogen plasma [1]. Since growth using this technique is far from thermodynamic equilibrium, understanding how nitrogen plasma affects nucleation and growth kinetics is essential for development.

Real-time grazing incidence small angle x-ray scattering (GISAXS) measurements at the Cornell High Energy Synchrotron Source were used to study the effect of variation in nitrogen plasma pulse conditions on PA-ALE of InN at 250 °C. Current results show the evolution of GISAXS characteristics such as the correlated peak (CP) length scale in the Yoneda Wing (YW) directly relates to the surface roughness, impurities, and electrical properties of the material. During the initial cycles of InN growth, the diffuse specular reflection broadens and CPs start to evolve along the YW with different correlated length scales. For the nitrogen plasma pulse time (t_p) of 15 seconds, the CPs have two different correlated length scales of 33.36 and 8.38 nm. With increasing t_p to ≥ 20s (the empirically optimal pulse length), a YW with only one CP evolves and the longest correlated length scale of 11.22 nm is for T_p = 25s. The correlated length scale of this single CP decreases to 10.75 nm for t_p = 30s. Additionally at t_p = 25s, the growth rate is largest (0.035nm/cycle – consistent with previously reported self-limited growth [1]) with root mean square surface roughness and carbon impurity at or below AFM and XPS sensitivity limits, respectively. The nature of GISAXS CP correlated length scale directly relates to the material quality. GISAXS also shows that the N_2/Ar flow ratio significantly affect the nucleation and growth of InN. Based on various *ex situ* characterization methods, the quality of the PA-ALE grown films is similar or better than the material grown by conventional growth methods, for example, molecular beam epitaxy at higher temperature (>400 °C).

[1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).

12:00pm **TF+SA+MI-TuM13 Spintronics Based on the Chiral Induced Spin Selectivity (CISS) Effect*, Yossi Paltiel,*** The Hebrew University, Israel*; R. Naaman,* The Weizmann Institute of Science, Israel

The high level of energy dissipation associated with the present semiconductor-based integrated-circuit technology limits the operating frequency of the devices. Therefore there is interest in new concepts that may solve this problem. One such concept that attracts considerable attention nowadays combines spins with electronics (spintronics). In principle, the application of spintronics should result in reducing power consumption of electronic devices and efficiency should be closer to the thermodynamic limit.

Two major issues complicate the use of spintronics; material problems and the inefficiency in producing spin-polarized current. Spintronics devices usually require the use of complicated structures of magnetic material layers and the need for permanent magnetic layers puts constrains on the miniaturization of these devices. In addition, high currents are required to produce highly polarized spin current which results in induced heating.

We present a new concept in which spin current is produced by using the spin selectivity in electron transport through chiral molecules, termed Chiral-Induced Spin Selectivity (CISS). The CISS effect allows realization of simple local and power efficient spintronics devices. Studying the CISS effect, we found that chiral molecules, especially helical ones, can serve as very efficient spin filters at room temperature, with no need for a permanent magnetic layer. Recently, by utilizing this effect we demonstrated a simple magnetless spin based magnetic memory. Moreover, we show that when chiral molecules are adsorbed on the surface of thin ferromagnetic film, they induce magnetization perpendicular to the surface, without the application of current or external magnetic field.

The CISS-based spintronics technology has the potential to overcome the limitations of other magnetic-based memory technologies and to facilitate the fabrication of inexpensive, high-density memory and other spintronics elements.

Thin Film
Room 105A - Session TF-TuM

Advanced CVD and ALD Processing, ALD Manufacturing and Spatial-ALD

Moderators: Steven M. George, University of Colorado at Boulder, Jesse Jur, North Carolina State University

8:00am **TF-TuM1 An Analytic Expression for Reactant Utilization in CVD and ALD Chambers***, **Edward McInerney**,* Lam Research Corporation

Recent advances in semiconductor device performance have depended, in part, on the adoption of new materials into the fabrication process. One of the challenges introduced with these materials is cost. In particular exotic reactants for CVD and ALD processes are often quite expensive. To use these materials efficiently, deposition chambers and processes must be designed to maximize reactant utilization while maintaining good deposition uniformity and film properties. In this presentation, an analytic expression for reactant utilization will be developed for CVD and ALD processes in parallel plate stagnation flow reactors. This expression will then be used to highlight the various approaches to achieving good utilization.

8:20am **TF-TuM2 Growth of Silicon Films at Room Temperature Using Electron Enhanced Atomic Layer Deposition***, **Jaclyn Sprenger**, A.S. Cavanagh, H. Sun, S.M. George,* University of Colorado, Boulder

Electron enhancement can dramatically reduce the temperatures required for ALD. Electrons can desorb surface species, such as hydrogen, and create “dangling bonds”. These “dangling bonds” can facilitate reactant adsorption. Using sequential electron and reactant exposures, low temperature growth should be possible for the ALD of Si, SiN_x, SiC_x, C, and CN_x films that can be grown with hydride precursors. In this work, silicon films were deposited at room temperature using sequential Si_2H_6 (disilane) and electron exposures.

Silicon film growth using an electron flood gun was monitored with an *in situ* spectroscopic ellipsometer in the high vacuum chamber. A silicon growth rate of 0.2 Å/cycle for sequential Si_2H_6 and electron exposures was observed at room temperature with electron energies of 50 eV. *In situ* Auger electron spectroscopy (AES) revealed strong silicon AES signals with ~15 at.% carbon and <4 at.% oxygen impurities. *Ex situ* x-ray photoelectron spectroscopy (XPS) analysis was consistent with the *in situ* AES measurements.

Silicon films were also grown using electrons from a DC glow discharge plasma in a spatial ALD chamber. Deposition was performed at room temperature on 150 mm Si wafers. *Ex situ* spectroscopic ellipsometry measurements obtained a linear growth rate of 0.24 Å/cycle for sequential Si_2H_6 and electron exposures. This growth rate is in excellent agreement with the growth rate measured in the high vacuum chamber. Uniform silicon film thicknesses were obtained with a variation of only 3.0% along the axis of the slit from the DC glow discharge plasma. XPS depth-profiling analysis revealed that the silicon films contained ~10 at.% carbon.

8:40am **TF-TuM3 Chemical Vapor Deposition within the ALD window – Quantitative Analysis of Precursor Surface Kinetics in Thin Film Formation***, **Michael Reinke**, Y. Kuzminykh, P. Hoffmann,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

All chemical vapor deposition (CVD) processes rely on the decomposition of precursors on the substrate to deposit the desired material. While in thermal CVD, high substrate temperatures are employed to induce pyrolytic decomposition of the adsorbed precursor molecules, lower temperatures are applied in atomic layer deposition (ALD) to deliberately avoid pyrolysis of the precursor and favor self-saturating surface reactions between two or more reactive partners.

A crucial aspect in ALD processes is the proper separation of reactive partners in order to prevent spontaneous gas phase condensation; this is most commonly achieved in a vacuum process where the reaction volume is sequentially filled with one of the different reactive partners and their exposure is separated by a purge time. Contrary, in spatial ALD the substrate is moved through different reaction volumes that are continuously filled with one reactive partner allowing decreased cycle times and, consequently, increased growth rates.

An alternative way of separating reactive precursor molecules is realized in a high vacuum chemical vapor deposition (HV-CVD) process. If the background pressure during the deposition is sufficiently low, the free mean path of precursor molecules exceeds their trajectory length between effusion source and substrate – in this way gas phase reactions are avoided and the substrate can be simultaneously exposed even to reactive ALD chemistries.

Exemplary, we will review in detail the thin film deposition process of titanium dioxide utilizing titanium tetraisopropoxide (TTIP) and water. We demonstrate the continuous CVD growth of titanium dioxide thin films within the ALD window and show that even selective growth methods applicable in ALD are suitable for HV-CVD processes.

We will discuss a comprehensive surface kinetic model of the TTIP surface reactions, including hydrolysis and pyrolysis. The model was fitted to the large number of experimental results and can describe the experimental observations ranging from thermal CVD depositions to co-depositions with water in the ALD window. The model’s good agreement with the experimental data in a wide parameter range suggests its high relevance.

The proposed model and the derived process parameters can be used for quantitative predictions of the precursor behavior in CVD processes, such as prediction of growth rates, deposition efficiencies and pyrolytic decomposition threshold. It reveals furthermore insight in the ALD process itself and allows modelling of the ALD growth rates - including the position of the ALD window.

9:20am **TF-TuM5 A Rotation Fluidization Coupled Atomic Layer Deposition Reactor for Nanoparticle Coating***, C.L. Duan,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, School of Optical and Electronic Information, Huazhong University of Science and Technology, China*; **Kun Cao**,* Huazhong University of Science and Technology, Wuhan, China

Atomic layer deposition (ALD) is an attractive approach for atomically controllable and conformal coatings on nanoparticles (NPs) for the fields of catalysts, optical detections, biomedicines, etc. There have been many kinds of ALD reactors for particles. Some of these designs are static reactors which rely on long time precursor diffusion to coat particles. Fluidized bed reactors utilize gas flow to disperse nanoparticles for enhanced gas-solid interactions, though obtaining steady fluidization of nanoparticles and limited precursor residence time are challenges. Rotary reactors disperse particles through rotary agitation and increase precursor usage by a static exposure stage.

In this talk, a rotation fluidization coupled atomic layer deposition reactor will be introduced. Such design allows the fluidization to facilitate the precursor transport in the particle bed and intensify the dynamic breaking up of the particle agglomerates to expose particle surfaces to precursors. In the deposition procedure, the coating process could be expedited due to the enlarged and homogenized void fraction in the particle bed, large gas distribution area and higher particle concentration in the rotating fluidized bed. The rotation not only enhances the gas-solid interactions to stabilize fluidization, but also provides large centrifugal force to break up soft agglomerates together with the fluid drag force derived from gas-solid interactions and the collision between particles. In situ mass spectrometry monitoring of the reaction was performed to optimize the coating process. Under high precursor feed rate, the precursor utilization was improved from below 80% to nearly 100% with thicker rotating bed. The microscale morphology of the coating layers, the macro statistical element mass concentrations and the changes of specific surface area as well as the size distribution after coating confirmed the uniformity and conformity of coatings on individual particles. As an example, magnetic Fe_3O_4 nanoparticles have been uniformly coated with ultrathin Al_2O_3 passivation layers using this reactor. With 5nm coating layer, the nanoparticle could be stable under oxidation resistance with minimum magnetization loss (less than 10%). This is quite attractive in practical magnetic based biomedical applications. Well controllable amorphous Al_2O_3 passivation layers were also deposited on crystalline AlH_3 particles to postpone their decompose process, which could enhance the safety storage or transportation of these energetic materials.

9:40am **TF-TuM6 Atmospheric Pressure ALD in Porous Substrates: The Effect of Pressure on Step Coverage**, *E. Balder, F. Roozeboom,* ***Paul Poodt,*** Holst Centre / TNO, Netherlands

ALD is renowned for its ability to deposit thin films into high aspect ratio structures with step coverages realized that are unparalleled by other gas-phase deposition techniques. This is one of the reasons ALD has become a key deposition technique in microelectronics fabrication. In the past years, Spatial ALD concepts have evolved for high throughput, large-area and roll-to-roll ALD applications in e.g. photovoltaics and flexible electronics. A new challenge for Spatial ALD is coating inside porous and 3D substrates, e.g. for applications in energy storage, catalysis and membranes. In many cases, Spatial ALD is performed at atmospheric pressure.

There are several studies where the relation between precursor dose and step coverage has been investigated. The most famous one is the kinetic model derived by Gordon *et al.* [1] that gives an analytical estimation of the precursor dose required to conformally coat a pore as a function of its aspect ratio. The pressure dependence of conformal coating in pores is in the transport of precursor molecules by diffusion along the length of the pore, given by the diffusion coefficient. Unfortunately, the diffusion coefficient is not a variable in the Gordon model.

We have derived an alternative kinetic model that makes use of similar assumptions as used in the Gordon where the pressure dependence of the diffusion coefficient was included. Three regimes can be identified for diffusion inside pores: *pressure dependent* Fickian diffusion for large diameter pores, *pressure independent* Knudsen diffusion for small pore diameters and a transition regime between the two. Combining the pressure dependence of the diffusion coefficient, the kinetic model and experimental data we can calculate the required precursor dose required to conformally coat a pore as a function of pore diameter and reactor pressure. A similar analysis can be performed on the required purge time to empty a pore of reactants.

The main results we will show are that 1) for pores smaller than ~1 µm diameter, there is no difference in atmospheric and low pressure ALD with respect the required precursor dose, 2) for larger pores there is a pressure dependence of the diffusion coefficient and 3) in terms of *deposition rate* it is beneficial to use higher reactor pressures to allow high precursor partial pressures leading to high diffusion- and reaction rates. Based on these experimental and modeling results we will finally give an outlook to the feasibility of large-area or roll-to-roll atmospheric pressure Spatial ALD of conformal coatings in high aspect ratio substrates.

11:00am **TF-TuM10 New Spatial ALD platform for Semiconductor Manufacturing**, ***Joseph Yudovsky,*** Applied Materials, Inc. **INVITED**

Adoption of Atomic Layer Deposition (ALD) for semiconductor manufacturing has more than doubled over the past 3 years driven by inflections in both logic and memory devices from planar to 3D structures requiring conformal deposition and is set to double again over the next 3 to 5 years as the need for continued device scaling is expected to drive the need for unique and differentiated ALD films. The use of Spatial ALD techniques serves as a disruptive means compared to conventional ALD processes to address the needs of this rapidly growing market. Though Spatial ALD is not new, having been used in volume production for solar cells and Roll-to-Roll systems, adapting spatial ALD technology for the semiconductor market where device performance requirements demand a magnitude higher level of film deposition control faces numerous challenges. In this presentation, we will review the hardware challenges associated with adapting spatial ALD technology to high volume semiconductor manufacturing, and our design approach used in developing a new ALD platform to address those challenges.

11:40am **TF-TuM12 Spatial MLD of Polyamide Films on Flexible Substrates using a New Rotating Cylinder Reactor in a Custom Oven**, ***Daniel Higgs***, University of Colorado Boulder*; S.M. George,* University of Colorado at Boulder

Molecular layer deposition (MLD) is usually restricted by the low vapor pressure of the organic reactants. This low vapor pressure could be especially problematic during spatial MLD when rapid substrate speeds limit the reactant exposure times. To address this problem, we have developed a new spatial MLD reactor. The new spatial MLD reactor is based on a rotating cylinder inside an outer fixed cylinder with dosing, pumping and purging modules. In addition, the spatial MLD reactor and the reactants are both located in an isothermal environment using a custom oven. This isothermal environment avoids any possible cold spots in the apparatus.

We have used the new spatial MLD reactor to deposit a polyamide network polymer on a metalized PET polymer substrate. The polyamide network polymer is derived from trimesoylchloride and m-phenylenediamine. This polyamide network polymer has application as a reverse osmosis membrane for desalination. We observed polyamide MLD growth rate of 4.5 Å/cycle at 115°C. The rotating cylinder can be rotated at up to 200 RPM and achieves substrate speeds up to 3 m/s. This reactor can produce growth rates of up to 14 Å/s. The growth of the polyamide MLD film is linear with number of MLD cycles. We could routinely grow polyamide MLD films with thicknesses of 4000 Å in 5 minutes. Polyamide MLD film growth was confirmed using transmission Fourier transform infrared spectroscopy (FTIR) and microRaman spectroscopy.

In addition to the desalination membrane application, these polyamide network polymer films will be useful for flexible gas diffusion barriers. One major difficulty for ALD gas diffusion barriers on polymers is the presence of particles on the initial polymer substrate. These particles mask the polymer surface during ALD and then “fall off” leaving behind pin-hole defects in the ALD film. One solution is to bury all the particles in a thick MLD film and then perform ALD on the surface of the MLD film. We have recently coated a PEN polymer substrate with a MLD polyamide film with a thickness of ~1 µm. After deposition of a 50 nm Al_2O_3 ALD gas diffusion barrier film, the number of pin-hole defects in the Al_2O_3 gas diffusion barrier film reduced by an order of magnitude.

12:00pm **TF-TuM13 Spatial Atomic Layer Deposition for Porous and Fibrous Materials**, ***Gregory Parsons****, A.H. Brozena, C.J. Oldham,* North Carolina State University

Although there are few thin film deposition methods which can coat complex substrates, such as fibers and membranes, with as high a degree of conformality as atomic layer deposition (ALD), slow growth rates and other scaling limitations have prevented the industrial application of ALD to these materials.

To increase the speed of thin film deposition, researchers have developed spatial ALD as way to scale up traditional ALD systems. By flowing reactants continuously through alternating channels and moving the substrate beneath these reactant flows, thin films can be deposited at rapid speed. However, current spatial ALD systems are designed for solid or solid-backed substrates, such as silicon wafers. The technique has not yet been demonstrated on porous or fibrous substrates, such as woven or non-woven textiles.

To achieve rapid spatial ALD growth on these kinds of porous materials, we modeled and built a flow-through spatial ALD reactor for roll-to-roll deposition of Al_2O_3, using non-woven polypropylene fabric as the test substrate. The tool is operated under open atmospheric conditions and does not use expensive vacuum equipment. The reactor’s shower-head design utilizes alternating gas-flows of nitrogen, trimethyl aluminum, and water to produce three complete ALD cycles for a single traversal of the substrate. More ALD cycles can be additively deposited with increasing passes of the substrate. The gases flow through the material and are vented away using a slight negative pressure generated by facility exhaust. With this prototype flow-through spatial ALD reactor, we study how gas flow rates, fabric porosity, and web speed affect self-limiting ALD growth. By monitoring changes to the surface energy of the polypropylene using water contact angle and comparing the spatial ALD coated materials to batch-coated samples, we learn what conditions are necessary to achieve high-throughput, roll-to-roll ALD coatings on porous samples.

Advanced Surface Engineering
Room 101C - Session SE+MS+TF-TuA

Innovations in PVD, CVD, Atmospheric Pressure Plasma and Other Surface Technologies

Moderators: Michael Stueber, Karlsruhe Institute of Technology, Germany, Robert Franz, Montanuniversität Leoben, Austria

2:20pm **SE+MS+TF-TuA1 Investigation of Critical Processing Parameters on Laser Surface Processing of Mg-Al-Zn Alloys: Impact on Corrosion Kinetics***, **Michael Melia**, D.C. Florian, J.R. Scully, J.M. Fitz-Gerald,* University of Virginia

Magnesium (Mg) and its alloys have been the topic of intense research over the past 15 years as the automotive and aeronautic industries strive to increase fuel efficiency by reducing the weight of vehicles. However their wide spread implementation is currently limited by poor intrinsic corrosion resistance. Preferential dissolution of the Mg matrix occurs due to the electrochemically noble secondary phases formed during traditional processing routes of Mg alloys. To mitigate the impact secondary phases (e.g. γ-Al$_8$Mn$_5$) have on corrosion, pulsed laser surface processing was employed in the ns time regime. Lasers operating in this time regime are capable of melting and solidification rates on the order of 10^9 K/s with the ability to extend the solid solubility limit of the alloying elements. The research herein shows the impact laser processing parameters have on the dissolution of the secondary phases and corrosion resistance in the Mg-Al-Zn alloy, AZ31B.

A KrF excimer laser (λ = 248 nm, pulse duration = 25 ns FWHM) was utilized with a cylindrical focusing lens, a laser spot size of 27 mm x 1.2 mm, and a pulse overlap of 95%. The processing parameters investigated include the laser fluence (0.7, 0.8 and 1.5 J/cm^2), irradiation dosage (pulse per area (PPA) = 20 to 400), and processing pressure (1 to 1280 Torr Ar). The dissolution of the γ-Al$_8$Mn$_5$ particles was observed by scanning electron microscopy equipped with a backscatter electron detector. Fiduciary image recognition was utilized to observe the change in γ-Al$_8$Mn$_5$ particle size before and after processing. Analysis of the H$_2$ evolution reaction rate, related to the quantity and density of electrochemically noble secondary phases, was performed by potentiodynamic polarization measurements in 0.6 M NaCl solution.

Results from the fluence study revealed significant dissolution of the γ-Al$_8$Mn$_5$ particles when processing was performed above the ablation threshold suggesting that material transport was afforded by a laser induced plasma pressure acting on the irradiated layer, increasing the extent of dissolution. This was also observed by an order of magnitude reduction in H$_2$ evolution reaction rate. The lowest pressure of Ar investigated, 1 Torr, consistently exhibited the smallest reduction in H$_2$ evolution reaction rate from the bulk material. All other processing pressures showed an order of magnitude reduction in H$_2$ evolution reaction rate when a fluence above the ablation threshold was used. The PPA study revealed a plateau in the reduction of the H$_2$ evolution reaction rate, observed dissolution of γ-Al$_8$Mn$_5$ particles, and time to breakdown of the corroding surface after 100 PPA.

2:40pm **SE+MS+TF-TuA2 Engineering a WC/Co Carbide Surface for PVD and CVD coatings***, **Aharon Inspektor**, P.A. Salvador,* Carnegie Mellon University*; D. Banerjee, C. McNerny, M. Rowe, P. Mehrotra,* Kennametal Inc.

The emergence of new coating technologies is driving the development of new cutting tools and improved metal cutting techniques. However, to reach these goals, the coating has to work in concert with the tool substrate material. Hence, building a functional surface that consists of coating and substrate working together, is a key step in the development of new cutting tool. In this paper we will look at the substrate side of the coating - surface interface and discuss how it affects the properties of the subsequent coating. The focus will be on surface engineering of WC/Co carbide surface for Physical Vapor Deposition, PVD, for Chemical Vapor Deposition, CVD, and for CVD diamond coatings. Specifically, Co mobility in the subsurface zone for CVD coatings and surface treatment for PVD coatings. Structure and properties of the resultant surface - coating combination will be presented and discussed.

3:00pm **SE+MS+TF-TuA3 Room-Temperature Ductility in Refractory Transition-Metal Carbides: Potential to Create Ultra-Tough, Flexible Thin Films***, **Suneel Kodambaka**,* University of California at Los Angeles **INVITED**

Transition-metal carbides are high-melting (> 3000 K), extremely hard (10s of GPa), mechanically robust, and chemically resilient compounds capable of operating in extreme environments and are attractive for aerospace and other industries. These hard materials are generally considered to be brittle at low temperatures. Improving their ductility, and hence toughness, is highly desirable but progress thus far has been limited by the lack of a basic understanding of the intrinsic deformation mechanisms in this class of materials. Here, using *in situ* transmission electron microscopy (TEM) coupled with uniaxial compression tests conducted on sub-µm-size pillars, in combination with density functional theory (DFT) calculations, we show that dislocations are mobile at room-temperature and lead to plastic deformation in NaCl-structured group IV and group V transition-metal carbide single crystals, zirconium carbide (ZrC) and tantalum carbide (TaC). We find that the yield strengths of ZrC crystals increase with decreasing size and ZrC(111) is softer than ZrC(100) crystals, an unexpected finding for NaCl-structured compounds. We attribute this anomalous behavior to surprisingly easy dislocation motion and low shear stresses along {001}<1-10> rather than along the commonly assumed {110}<1-10> slip systems. For TaC, in contrast to ZrC, the yield strengths are found to be independent of crystal size and orientation. Our observations suggest that multiple slip systems can be active and operate at room temperature in these hard, refractory ceramics and we expect similar behavior in other transition-metal carbides and nitrides. The insights gained from these studies may help in the development of new material architectures, such as tough and flexible membranes, for new small-scale structural applications.

4:20pm **SE+MS+TF-TuA7 Spray-Coated Carbon-Nanotubes for Crack-Tolerant Metal Matrix Composites as Photovoltaic Gridlines***, **Omar K. Abudayyeh**,* University of New Mexico*; N.D. Gapp, G.K. Bradshaw, D.M. Wilt,* Air Force Research Laboratories*; S.M. Han,* University of New Mexico

Microcracks developing in photovoltaic cells, due to growth defects or due to external mechanical factors, can lead to substantial power loss in solar cells. Microcracks can be critical as they propagate from the semiconductor bulk to the metal gridlines isolating portions of the cell and leading to decreased cell performance. In this work, multiwalled carbon nanotubes are being investigated for reinforcement of metal contacts on photovoltaic solar cells that serve as a secondary conductive network in the presence of cracks. In this effort we have focused on a silver-carbon-nanotube layer-by-layer microstructure. We present the use of a simple, cost-effective, and manufacturable method of depositing carbon nanotubes onto electroplated metal films to create metal matrix composite gridlines for photovoltaic cells. Carbon nanotubes are deposited using a spray coating method to create layer-by-layer microstructure composites. To increase adhesion strength to metal and achieve efficient metal-nanotube stress transfer, carbon nanotubes are chemically functionalized with carboxylic group prior to deposition. Initial strain failure tests show the ability of composite lines to remain electrically connected with fractures up to 28-µm-wide on average, where carbon nanotubes electrically bridge the gap. The metal-carbon-nanotube composites are electrically characterized though current-voltage (*I-V*) sweeps. Our composite lines can carry current densities ranging from 500 to 2500 A/cm^2 in the presence of cracks (5, 10, and 15-µ m-wide). MMC gridlines are successfully integrated on commercial triple-junction solar cells with measured fill factor and efficiency 86% and 26.8% respectively, closely comparing to current triple-junction cells with standard metallization. Dark *I-V* measurements indicate further improvement in the series and shunt resistances of the cells with the optimization of MMC integration process.

4:40pm **SE+MS+TF-TuA8 Atmospheric Pressure Plasma Enhanced CVD of High Quality Silica-Like Bilayer Encapsulation Films***, **Fiona Elam**,* FUJIFILM Manufacturing Europe B.V., Netherlands*; A.S. Meshkova,* DIFFER, Netherlands*; S.A. Starostin, J.B. Bouwstra,* FUJIFILM Manufacturing Europe B.V.*; M.C.M. van de Sanden,* Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands*; H.W. de Vries,* DIFFER, Netherlands

Atmospheric pressure-plasma enhanced chemical vapour deposition (AP-PECVD) is an innovative technology that can be integrated into many existing manufacturing systems to facilitate the mass production of functional films; specifically encapsulation foils. These barrier films are essential to the flexible electronics industry, envisioned to protect devices such as flexible solar cells and organic light emitting diodes against degradation from oxygen and water.

Roll-to-roll AP-PECVD was recently used to produce smooth, 90 nm silica bilayer thin films comprising a ‘dense layer’ and ‘porous layer’ that demonstrated exceptionally good encapsulation performance with effective water vapour transmission rates in the region of 6.9×10^{-4} g m^{2} day^{-1} (at 40°C, 90% relative humidity). By using the same material in the multilayer film architecture, and by having AP-PECVD as the deposition method, rendered this investigation highly industrially and commercially relevant to the eventual large scale production of flexible encapsulation foils. It was discovered that increasing the input energy per precursor gas molecule during the deposition of the dense layer, resulted in an improved encapsulation performance. However, the individual role performed by each layer in the overall success of the bilayer films is not yet fully understood, nor is the potential for energy conservation by varying process throughput.

A glow-like AP dielectric barrier discharge in a roll-to-roll set-up was used to deposit silica bilayer thin films onto a polyethylene 2,6 naphthalate substrate by means of PECVD. Tetraethyl orthosilicate (TEOS) was used as the precursor gas, together with a mixture of nitrogen, oxygen and argon. In each case, the deposition conditions for the synthesis of the dense layers were varied in order to study the effect of input energy per TEOS molecule and process throughput on the chemical composition and porosity of the layer. Deposition conditions for the porous layers were kept constant, with process throughput the only exception. Each film was characterised in terms of its water vapour transmission rate, its chemical composition and its morphology as a function of the input energy per TEOS molecule during the dense layer deposition and overall process throughput.

For the first time in AP-PECVD, it was found that the porous layer plays a critical role regarding encapsulation performance and surface smoothening of silica bilayer films. Due to increased throughput, the bilayer architecture also enables a 50% reduction in deposition energy consumption per barrier area, with respect to single layer silica films of equivalent encapsulation performance and thickness.

5:00pm **SE+MS+TF-TuA9 Plasma Polymerization of Organic Coatings at Atmospheric Pressure: Relationship between the Precursor Chemistry, the Plasma Chemistry and the Final Coating Chemistry***, B. Nisol, N. Vandencasteele, J. Hubert, C. De Vos, J. Ghesquière, D. Merche,* ***François Reniers,*** Université Libre de Bruxelles, Belgium

The synthesis of organic coatings using plasma technologies has been developed since many decades. This paper investigates a full series of organic coatings, synthesized in the same dielectric barrier discharge system, in the same operational conditions. The >10 precursors vary from fully saturated molecules, with or without heteroatoms (hexamethylnonane, CxCly, CxFy), to anhydrides, acrylates, with or without double or triple bonds. It is shown that the presence of double bonds not only significantly increase the polymerization rate, but also protect the ester function in acrylates. A combined effect of the plasma power and the presence of double bonds on the C/O ratio is observed for all the relevant precursors used. Correlation between the plasma chemistry and the fragment pattern in the gas phase, as recorded by atmospheric mass spectrometry, with the final chemical composition of the coatings, determined by XPS and FTIR is established. Coatings properties can be easily tuned either by combining precursors, by varying the plasma power or by changing the main plasma gas. By an appropriate combination of the plasma parameters and the precursor, very high deposition rates can be achieved, highly hydrophobic or hydrophilic coatings can be synthesized. These macroscopic results are interpreted in terms of plasma properties, and chemical reactivity.

This work was supported by the Belgian Federal Government (IAP research project P7/34 – Physical Chemistry of Plasma Surface Interactions).

5:20pm **SE+MS+TF-TuA10 Innovations in Atmospheric Pressure Plasma Technologies for Surface Engineering***,* ***David Ruzic,*** *Y.L. Wu, L. Na, S. Hammouti, I.A. Shchelkanov,* University of Illinois at Urbana-Champaign **INVITED**

The growing need for high efficiency-low cost coating tools for large area surfaces drives research efforts for development of innovative techniques. One of the options is an Evaporative Coating at Atmospheric Pressure process (ECAP). The principal of this deposition method is an evaporation of a material, with-in a plasma environment. The appealing advantage of this deposition technique is its atomic nature, and its environmentally safe process as no harmful chemicals compounds are used. With ECAP the evaporated material atoms end up deposited molecule-by-molecule or atom-by-atom as in a Physical Vapor Deposition but without the need for a vacuum chamber. This effect is achieved by using a thermal energy from the microwave plasma, when solid 99.99%+ purity metallic and ceramic target such as Al, Sn, Cr, Au, Ag and $AlCl_3$ could be evaporated and then produce a PVD-like coating on a work piece. The tool is designed to have the evaporated material being submerged into the center of the atmosphere microwave discharge. As the result evaporation occur in a controlled environment where a pure metals can be deposited or their compounds. For example in the aluminum case, a pure alpha phase of Al_2O_3 can be deposited using oxygen from the environment, or if a metallic coating of such a reactive metal as Al, is desired, the deposition can be performed in an pure Ar argon environment with the help of a special gas curtain. The tool provides deposition rate for metals as high as 1-5 um/min with high adhesion. The measured adhesion for copper on steel was at least 250 g/mm^2. The ECAP technology opens broad possibilities for surface processing at atmosphere without environmental impact.

6:00pm **SE+MS+TF-TuA12 Solid-state Dewetting: Control and Applications***,* ***Lukasz Borowik,*** *Y. Almadori, N. Chevalier, J.-C. Barbé,* CEA, LETI, MINATEC Campus, France

The dewetting of ultrathin silicon layers, induced by the thermal budget, is an issue to develop Silicon On Insulator (SOI) and Silicon Germanium On Insulator (SGOI) based technologies. However, dewetting can be controlled to obtain well-arranged agglomerates with similar size or even inhibited. This experimental study aims at demonstrating: the effect of the strain, surface contamination, ion sputtering on the dewetting mechanism, and further applications of dewetting thanks to interfacial reaction between agglomerates and the silicon dioxide. For that purpose, we present the results obtained on: (1) (001) oriented ultrathin (8-22 nm) silicon layers on silicon dioxide, (2) (001) oriented 12 nm silicon-germanium layers on silicon dioxide. In order to understand the dewetting mechanism, samples were heated up to ~800°C under ultra-high vacuum (1×10^{-9} mBar) during tens of minutes. The dewetted samples were characterized by Atomic Force Microscopy (AFM) to put in evidence the influence of the different factors on dewetting mechanism.

In first part of our presentation we will present various methods to control dewetting process by using different parameters such as: strained silicon, [1] surface contamination [2] or argon pre-sputtering. [3] These parameters allow tuning agglomerates size, shape and density. In second part of the talk we will show possible applications of dewetting to form porous silicon dioxide via agglomerates interfacial reaction, and finally how to master stoichiometry of silicon germanium agglomerates. [4] All these methods are promising since permit an easy and fast implementation, it is thus of real interest, since it opens up Si and SiGe agglomerates with tuned Ge concentration to application in innovative technologies.

This work was performed in the frame of the ANR LOTUS project. The measurements were realized on the CEA Minatec Nanocharacterization Platform (PFNC).

References:

[1] Ł. Borowik et al. Journal of applied physics 114, 063502 (2013)

[2] Ł. Borowik et al. Thin solid films 527, 133–136 (2013)

[3] F. Leroy et al. Surface Science Reports accepted

[4] Y. Almadori et al., 120, 7412–7420 (2016)

Thin Film
Room 105A - Session TF-TuA
Thin Film Photovoltaics

Moderators: Eray Aydil, University of Minnesota, Colin Wolden, Colorado School of Mines

2:20pm **TF-TuA1 Perovskite Solar Cells: Material Synthesis, Device Operation and Charge Carrier Dynamics***,* ***Kai Zhu,*** National Renewable Energy Laboratory **INVITED**

Organic-inorganic hybrid halide perovskites have rapidly become a focal point of the photovoltaic (PV) community as a promising next-generation PV technology. Various perovskite absorbers (e.g., $CH_3NH_3PbI_3$ and $HC(NH_2)_2PbI_3$) and device architectures (e.g., mesoporous, planar, and mesoporous-planar hybrid cell configurations) have been examined with promising results by using either solution processing or thermal evaporation. The certified efficiency of a single-junction perovskite solar cell (PSC) has reached 22% after only a few years of active research. In addition to solar cell application, the fascinating optical and electronic properties of these perovskite systems have enabled their usage for various electronic devices including light emitting diodes, photodetectors, and transistors. Despite this remarkable progress associated with perovskites, there are still many fundamental questions to be addressed at both material and device levels. Further improvements are required to advance our understanding on the material effects on the fundamental physical and chemical processes that are important to device operations. In this presentation, I will present our recent studies toward a better understanding and control of perovskite nucleation, grain growth, and microstructure evolution using solution processing. The precursor chemistry and growth conditions are found to affect significantly the structural and electro-optical properties of perovskite thin films. Devices based on different grain sizes and film thicknesses were investigated to correlate the grain sizes with device performance. The impact of grain size on charge carrier dynamics was also studied. Tuning tolerance factor through solid state alloying is shown as an effective way for stabilizing perovskite structures. In addition, I will discuss briefly the role of grain boundary on charge carrier dynamics and device characteristics. These results and others will be discussed.

3:00pm **TF-TuA3 Perovskite Film Growth And Degradation Mechanisms In Graphene-Based Perovskite Solar Cells By In Situ Spectroscopy***, **Muge Acik**,* Argonne National Laboratory*; S.B.D. Darling,* Argonne National Laboratory, University of Chicago

High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. Hybrid organic-inorganic methylammonium lead halides, $MAPbX_3$ (X=I, Br, Cl)/mixed-halides ($I_{3-x}Cl_x$, $I_{3-x}Br_x$) have been reported as light harvesting layers with tunable bandgaps, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination (1). Graphene-derived hybrids has recently emerged as an ETL/HTL replacement in these devices. Graphene/perovskite structure-property relationships are, however, not well understood due to unclear chemistry at the ETL/perovskite/HTL interfaces. Moreover, effect of film thickness, lead content, stoichiometry control, overlayer/underlayer morphology/composition, and cation-anion electrostatic interactions ought to be examined for better charge transport at the graphene/perovskite interfaces. Stability factors also need to be studied for charge mechanisms to unravel device performance challenges. Indeed, underlayer ETLs (TiO_2/Al_2O_3) and overlayer HTLs (spiro-OMeTAD) were rarely studied with graphene. To address scalability and stability issues, we investigated degradation, nucleation and growth mechanisms in reduced graphene/graphite oxide (RGO) upon halide-based (I, Cl, Br) perovskite deposition. Chemical interactions were interpreted at perovskite/RGO interfaces for the grain size, orientation, boundaries, and surface/bulk effects using variable-temperature (≤600°C, Ar(g)) *in situ* spectroscopy (infrared absorption, micro-Raman, UV-vis-NIR, luminescence). Controlled perovskite formation was achieved at room temperature for bromide/chloride-based perovskites resulting in improved chemical stability with heat (vs. iodide derivative). Perovskite decomposition was observed at ~150°C. Oxygen-induced chemical reactions occurred at ≤150°C, eliminated hydroxyls/ carboxyls in RGO, and maintained ethers/epoxides upon perovskite decomposition (2). Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air (O_2, H_2O). Film morphology was explored by SEM, XRD, XPS, TEM, and AFM.

(1) M Acik, SB Darling. J. Mater. Chem. A (2016) Advance Article. Doi: 10.1039/C5TA09911K (2) M Acik, G Lee, C Mattevi, M Chhowalla, K Cho, YJ Chabal. Nature Mater. (2010) 9 (10), 840-845

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3:20pm **TF-TuA4 ALD Processing for Organo-Metal Halide Perovskite Solar Cells: Opportunities and Challenges***, V. Zardetto,* Eindhoven University of Technology, Netherlands*; F. di Giacomo, R. Andriessen,* Solliance/TNO, Netherlands*; T.M. Brown, A. di Carlo,* University of Rome "Tor Vergata", Italy*; W.M.M. Kessels, **Mariadriana Creatore**,* Eindhoven University of Technology, Netherlands

Within the class of emerging photovoltaic technologies, organo-metal halide perovskite solar cells have exhibited a sky-rocketing conversion efficiency above 20% in just a few years. In this contribution we will address the opportunities which ALD offers to perovskite solar cells by highlighting its merits of low temperature processing and compatibility with 3D-structures.

Specifically, we will present two studies aimed at the suppression of charge carrier recombination processes at the complex interface ITO/mesoscopic TiO_2 scaffold/ mixed halide perovskite absorber.

In the first study we investigate the role of thin plasma-assisted ALD TiO_2 blocking layers on PET/ITO substrates, developed at a substrate temperature of 150°C [1,2]. The ALD TiO_2 layer is found to exhibit an excellent blocking behaviour towards charge carrier recombination at the above-mentioned interface, leading to open circuit voltage (V_{oc}) values as high as 900 mV (with respect to the pristine PV device exhibiting no rectifying behaviour with a V_{oc} of 50 mV) and superior device performance (9.2%) with respect to a sol-gel TiO_2 blocking layer (4%).

In the second example we carry out few ALD cycles of Al_2O_3 in a 250 nm-thick mesoscopic TiO_2 scaffold. Next to the conformality of the process, we demonstrate by means of electrochemical impedance spectroscopy that just one ALD cycle is sufficient to suppress the charge recombination processes. Specifically, the V_{oc} is found to increase from 860 to 960 mV upon 1 ALD cycle of Al_2O_3.

This contribution will end by discussing the challenges yet to be met by ALD processing directly on perovskite. In all these cases, a careful interface engineering needs to include several aspects potentially affecting the opto-chemical and morphological stability of the active components of the device. For example, methylammonium lead iodide perovskite solar cells already degrade under prolonged (i.e. few hours) annealing at 80°C, as witnessed by the appearance of a PbI_2-related peak in the XRD spectrum. However, when the Al_2O_3 plasma-assisted ALD process at 30°C is compared with the thermal process at 80°C, the plasma step is found to be responsible for abstraction of the methylammonium cation and the formation of iodate species. Instead, the thermal ALD process does not affect the chemistry of the perovskite. These selected examples point out that processing temperature and choice of reactant (moisture or plasma radicals) need to be carefully considered when dealing with processing of hybrid materials, such as perovskite solar cells.

[1] F. Di Giacomo *et al*., Adv. Energy Mat. 5, 1401808 (2015)

[2] V. Zardetto *et al*., ECS Transactions 69 (7), 15 (2015)

4:20pm **TF-TuA7 Identification of Critical Defects in Thin Film CdTe Solar Cells Deposited by Magnetron Sputtering***, P.M. Kaminski, A. Abbas, S. Yilmaz, **John Walls**,* Loughborough University, UK

The exceptional uniformity of deposition provides magnetron sputtering with important advantages as a deposition technique for some applications of thin film cadmium telluride (CdTe) solar cells. Efforts to develop a viable sputtering process for CdTe have been conducted in many laboratories around the world. These efforts have been moderately successful but the conversion efficiency achieved has not matched that obtained using lower energy deposition techniques such as Close Space Sublimation or Vapour Transport Deposition. In particular, sputtered CdTe is less tolerant to the cadmium chloride activation process. Delamination of the films at the cadmium sulphide junction is often observed. Catastrophic void formation within the CdTe layer has also been reported. This behaviour has often been attributed to film stress even though this can be mitigated in the as-deposited films. Using state-of-the-art High Resolution Transmission Electron Microscopy, we will report on the identification of the nanoscale defects that are responsible for the poor response of sputtered CdTe films to the cadmium chloride treatment. Identification of the atomic scale mechanisms at work provides a way to significant process improvement.

4:40pm **TF-TuA8 Solar Energy Conversion Properties and Defect Physics of $ZnSiP_2$***, **Aaron Martinez**,* Colorado School of Mines*; E.L. Warren, P. Gorai,* National Renewable Energy Laboratory*; K.A. Borup,* Aarhus University, Denmark*; D. Kuciauskas, P.C. Dippo,* National Renewable Energy Laboratory*; B.R. Ortiz,* Colorado School of Mines*; R.T. Macaluso,* University of Texas at Arlington*; S.D. Nguyen,* University of Northern Colorado*; A.L. Greenaway, S.W. Boettcher,* University of Oregon, Eugene*; A.G. Norman,* National Renewable Energy Laboratory*; V. Stevanovic, E.S. Toberer,* Colorado School of Mines*; A.C. Tamboli,* National Renewable Energy Laboratory

Implementation of an optically active material on silicon has been a persistent technological challenge. For tandem photovoltaics using a Si bottom cell, as well as for other optoelectronic applications, there has been a longstanding need for optically active, wide band gap materials that can be integrated with Si. $ZnSiP_2$ is a stable, wide band gap (2.1 eV) material that is lattice matched with silicon and comprised of inexpensive elements. From bulk single crystal growth, we have demonstrated the first $ZnSiP_2$ photovoltaic device, and shown that $ZnSiP_2$ has excellent photoresponse and high open circuit voltage of 1.3 V, as measured in a photoelectrochemical configuration. The high voltage and low band gap-voltage offset are on par with much more mature wide band gap III–V materials. Photoluminescence data combined with theoretical defect calculations illuminate the defect physics underlying this high voltage, showing that the intrinsic defects in $ZnSiP_2$ are shallow and the minority carrier lifetime is 7 ns. The favorable results obtained from characterization of bulk material encourage the development of $ZnSiP_2$ as a photovoltaic absorber material. To pursue this development, we have constructed a thin film growth reactor. This reactor employs a combination of ultra high vacuum chemical vapor deposition, using silane and phosphine as precursor gases, and physical vapor deposition, using an effusion cell to evaporate elemental Zn. The preliminary results of the first stages of thin film growth will be presented in addition to an overview of our characterization of bulk $ZnSiP_2$.

5:00pm **TF-TuA9 Controlling the Composition of Zn(O,S) Alloys Grown by Atomic Layer Deposition***, **Diane K. Lancaster**, H. Sun,* University of Colorado, Boulder*; S.M. George,* University of Colorado at Boulder

Zn(O,S) alloys are promising conduction band buffers for solar cells. The tunable conduction band of Zn(O,S) alloys improves electron transfer between electron absorber and electron transport materials. Zn(O,S) alloys are produced with atomic layer deposition (ALD) by alternating between ZnO ALD and ZnS ALD using diethylzinc (DEZ) and H_2O or H_2S as the reactants. However, controlling the composition of Zn(O,S) alloys is complicated by an efficient exchange reaction between H_2S and ZnO to produce H_2O and ZnS. This H_2S + ZnO -> H_2O + ZnS exchange reaction dramatically increases the sulfur content of the Zn(O,S) alloys. Because of this exchange reaction, the growth temperature and the H_2S exposure have an effect on the Zn(O,S) alloy composition that is nearly equivalent to the ratio between the alternating numbers of ZnO ALD and ZnS cycles. For example, the exchange reaction is much more efficient at higher temperatures. Increasing the growth temperature from 100°C to 225°C changed the composition for films grown with an alternating sequence of 3 ZnO ALD cycles and one ZnS ALD cycle from 65% ZnS to 90% ZnS, respectively. To overcome the complexity of the exchange reaction, we have developed a new method of growing Zn(O,S) alloy films that avoids alternating between numbers of ZnO ALD and ZnS ALD cycles. This new growth method exposes the H_2O and H_2S simultaneously in sequence with the DEZ exposures. The simultaneous H_2O and H_2S exposures allow competition between the forward exchange reaction (H_2S + ZnO -> H_2O + ZnS) to produce ZnS and the reverse exchange reaction (H_2O + ZnS -> H_2S + ZnO) to recreate ZnO. Film composition using this method was determined by the mole fraction of the H_2S in the dosing mixture. The bandgaps of the Zn(O,S) alloys were measured versus film composition. Composition determined the bandgaps of the Zn(O,S) alloys regardless of growth conditions. Controlling the Zn(O,S) band gap was also much more reproducible using the simultaneous H_2O/H_2S exposures. Bandgaps varied linearly from 3.06 eV to 3.39 eV for H_2S mole fractions in the H_2O/H_2S dosing mixture from 0.03 to 0.39, respectively. We are now able to prepare tunable conduction band buffers for solar cell applications.

5:20pm **TF-TuA10 ALD Ta-doped ZnO Transparent Conducting Oxide***, **Zhengning Gao**, Y. Myung, R. Mishra,* Washington University in St. Louis*; R. Kanjolia,* SAFC, Sigma*; J. Park,* Korea University, Republic of Korea*; P. Banerjee,* Washington University in St. Louis

ZnO based transparent conducting oxides (TCOs) offer earth abundant alternatives to conventional indium tin oxide (ITO) films. At the same time, ALD enables discretized doping of substitutional cations at a monolayer level, providing fine and exquisite control over dopant concentration and resultant properties. In this work, we present the ALD of tantalum (Ta) doped ZnO (TZO) films. Compared to dopants such as Ga^{3+} and Al^{3+}, a Ta cation exists in +5 oxidation state and thus, can ideally transfer 3 electrons by substitutionally doping a Zn^{2+} site. We show that 30 nm TZO films with 2 at% Ta provides a minimum resistivity of 4 mW.cm and optical transmissivity of > 86% in the visible range.

The precursors used for Zn, O and Ta are diethyl Zn (DEZ), H_2O and pentakis-dimethylamido Ta (PDMAT). The targeted % Ta is varied from 2 to 20% by introduction of PDMAT pulse between DEZ and H_2O pulses. Downstream quadrupole mass spectrometry (QMS) tracks the interaction chemistry of the PDMAT with Zn-ethylated surface and the DEZ with a Ta-dimethyl amido saturated surface. Electron concentration and mobility are measured using Hall measurements. A minimum resistivity of 4 mW.cm with carrier density of $9.0x10^{19}$ cm^{-3} and a mobility of 17.7 cm^2/V-sec is observed at 2 at% Ta. UV-Vis spectroscopy indicates a monotonic increase in bandgap of ZTO from 3.2 to 3.4 eV upon addition of Ta. Photoluminescence (PL) shows a quenching of the green band emission of ZnO associated with oxygen defects upon the addition of 2 at% Ta. Upon further Ta addition, a red shifted defect peak appears which is attributed to formation of new Zn vacancies. This data is supported by X-ray photoelectron spectroscopy (XPS), showing removal of O vacancies and a clear Ta-O-Zn bond formation for higher Ta doping. The results provide a clear understanding on the mechanism of Ta doping in ZnO and its direct impact on vacancies and resulting electronic and optical properties.

Finally, ALD TZO is deposited on flexible glass substrates and inside nanoporous anodic alumina templates to demonstrate formation of transparent conducting electrodes, conformally on a variety of platforms of relevance to photovoltaic research.

5:40pm **TF-TuA11 Leveraging Small Molecules to Control Interfacial Stability of Transparent Conductive Oxides***, **Ina Martin**, R. Matthews, E.B. Pentzer, T.J. Peshek,* Case Western Reserve University

Transparent conductive oxide (TCO) degradation is a known failure mode in thin-film photovoltaic (PV) devices through mechanisms such as resistivity increase and delamination. Degradation studies encompassing accelerated aging of the individual TCO, material combinations (e.g. the TCO interacting with an encapsulant) and full devices are necessary to elucidate the complicated mechanistic pathways of degradation that occur in thin-film PV devices. We have previously demonstrated quenching of the damp-heat-induced degradation of Al:ZnO (AZO), used as a front contact in CIGS modules, by depositing a mere 1 nm of a silane modifier, 3-aminoproplytriethoxysilane (APTES). Here we present results on the effect of the application of thin interfacial modifiers on AZO degradation, for thin films and within full CIGS ($Cu(In,Ga)Se_2$) thin film PV devices. Accelerated aging was performed under damp-heat (DH) and thermal-cycling protocols (from the IEC 61646 testing protocol for PV modules), ASTM G155 and outdoor testing. Modifiers include a monofunctional amine terminated silane (APDMES, 3-aminopropyldimethylethoxysilane), and a trifunctional amine terminated silane (APTES, 3-aminopropyltriethoxysilane).

6:00pm **TF-TuA12 Thickness Dependence of Electro-optical Properties of $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ Thin Films for Photovoltaic Applications***, **Vaishali Batra**, S. Kotru,* The University of Alabama

Exploring the viability of alternate materials to increase efficiency of the solar cells, and to decrease the fabrication cost, has gained momentum in the past decade. Ferroelectric materials are one of those materials which have become a subject of intense research for future energy applications. These materials are well established in memory and MEMS industry and nowadays are being investigated to design photovoltaic (PV) devices. These materials show PV effect without a need of p-n junction as required in semiconductor devices. Additionally they exhibit bulk PV effect due to internal electric field originating from electric polarization. Of all the materials, lanthanum doped lead zirconate titanate ($Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$/PLZT) of perovskite type crystalline structure is considered to be promising ferroelectric material for solar cell applications. The practical realization of these devices requires high PV response which is still a challenge. In this work, an innovative method based on orientation control of PLZT thin films is used to improve the PV response.

Promoting (001) orientation and suppressing (110) orientation in the PLZT films is observed to improve the electrical and optical properties of these films. This work focusses on effect of varying thickness of PLZT films on their electrical and optical properties. The reflectance and band gap energies strongly depend on film thicknesses and are found to be in the range of 3.30-3.57 eV. AFM demonstrates the change in morphology and improvement in roughness with respect to orientation. The roughness in the films is observed to increase with the increase in film thickness in the range of 2.92 nm to 4.06 nm. Raman spectroscopy reveals the shift in longitudinal and transverse optical modes with the change in film thickness suggesting the change in ferroelectric phases and crystallinity in the films. The electrical properties were studied using the model for metal-ferroelectric-metal (MFM) heterostructures with Schottky contacts using Pt electrodes. High polarization, free carrier concentration and higher photovoltaic properties are obtained from thicker PLZT films. The photovoltaic efficiency is observed to increase by ~4-10 times by controlling the orientation of the films.

2D Materials Focus Topic
Room 103B - Session 2D+TF-WeM
2D Materials: Growth and Fabrication

Moderator: Masoud Mahjouri-Samani, Oak Ridge National Laboratory

8:00am **2D+TF-WeM1 Synthesis and Characterization of Two-dimensional WSe_2 Grown using Chemical Vapor Deposition***, **Avra S. Bandophadyay**, G.A. Lara Saenz, C. Biswas, A.B. Kaul,* University of Texas at El Paso

Semiconducting Transition Metal Dichalcogenides (TMDCs) have attracted a lot of attention recently, because of their interesting electronic, optical, and mechanical properties [1]. Among large numbers of TMDCs, monolayers of tungsten diselenides (WSe_2) are of particular interest since WSe_2 possesses a direct band gap (~1.6eV) and tunable charge transport behavior, which makes it suitable for a variety of electronic and optoelectronic applications. Direct synthesis of large domains of monolayer WSe_2 and their growth mechanism studies are important steps toward applications of WSe_2. In this work, we have synthesized Tungsten Diselenide via Chemical Vapor Deposition Method using WO_3 powder and Se pellets as the precursors. Selenium was placed at the upstream side of the furnace at a temperature zone of 260-270°C. The temperatures and distances of these two sources were carefully controlled and adjusted. We used silicon with 300 nm thermally grown SiO_2 as the substrate and it was placed at some distance from the WO_3 source. The substrates for growing WSe_2 are put at the downstream side, where the Se and WO_3 vapors were brought to the targeting substrates by an Ar/H_2 (4:1) flowing gas with a flow rate of 120sccm. The pressure was maintained at 5Torr throughout the experiment. The temperatures at the Se source, WO_3 source and Substrates are maintained 260°C, 950°C and 750-850°C respectively. After the growth, the temperature of the furnace was naturally cooled down to room temperature and the samples were taken out for characterization. The size and shape of the as-grown flakes were observed under an Optical Microscope. Raman spectroscopy was used to determine the number of layers by noting the location of the Raman peaks and the relative Raman shift. In this paper we will discuss our work on the synthesis and characterization of 2D WSe_2, where we have also succeeded in forming monolayer structures for electronic device applications.

References:

[1] A. B. Kaul, *Journal of Materials Research*, vol. 29, pp. 348-361, 2014.

[2] H.Sahin et al, Physics Review B, vol. 87, pp. 1654091-1654096, 2013.

8:20am **2D+TF-WeM2 Reduction of Graphene Oxide by a Selective Surface Modification Process via Chemical Route for Achieving Higher Proportion of Graphene***, K. Dave,* CCMB, India; ***KyungHee Park****,* Chonnam National University, Republic of Korea*; M. Dhayal,* CCMB, India

The primary objective of the study was to target the removable of remaining oxygen available as carboxylic acid functionalities from the surface of first level of reduced graphene oxide. Hence, first we describes preparation of highly exfoliated graphene oxide (GO) from graphite which was further reduced by hydrazine and sodium borohydride. Further we used soda lime for removing carboxylic functional group from the surface of reduced GO by decarboxylation. X-ray photoelectron spectroscopic analysis confirm the synthesis of exfoliated graphene oxide by chemically introduced oxygen as -COOH), –OH and C-O-C. A very high % proportion of carbon atoms as carboxylic functionality observed in the synthesized GO whereas the reduction of it with NaBH4 and Hydrazine significantly reduced it. The use of soda lime had further reduced the carboxylic group in both the $NaBH_4$ and N_2H_4 reduced GO. Raman spectroscopic analysis showed two distinct peaks of graphene oxide and reduced graphene in Raman spectra which were correlated with breathing mode of sp^2 atom and graphitic carbonic sp2 of carbon atoms. A strong red shift in the G-band position was observed after oxidation of graphite into GO due to increase in the number of layers of graphene whereas the reduced GO by both reducing agent $NaBH_4$ and N_2H_4 had showed a decrease in the red shift of the D-band. Above finding confirms better conversion of GO into graphene due to increased SP_2 carbon proportion after selective reduction of the GO. In the future we planned to use these materials for biomedical applications.

8:40am **2D+TF-WeM3 Scalabale Production of Molybdenum Disulfide-based Biosensors***, **A.T. Charlie Johnson**,* University of Pennsylvania **INVITED**

We demonstrate biosensor arrays based on CVD-grown molybdenum disulfide (MoS_2) field effect transistors (FETs) coupled to a computationally-redesigned soluble variant of the μ-opioid receptor (MOR). By transferring dense films of monolayer MoS_2 crystals onto prefabricated electrode arrays, we obtain clean, high-quality FETs that allow reproducible protein attachment. The yield of MoS_2 FETs and biosensors exceeds 95%, with average mobility of 2.0 $cm^2V^{-1}s^{-1}$ (36 $cm^2V^{-1}s^{-1}$) under ambient (in vacuum). An atomic length linker chemistry enables target binding very close to the MoS_2 surface to maximize sensitivity. The biosensor calibration curve for a synthetic opioid peptide target indicates binding affinity that matches values determined using traditional techniques and a limit of detection ~ 3 nM. The combination of scalable array fabrication and rapid readout enabled by MoS_2 transistors offer the prospect of a solid-state drug testing platform for rapid readout of the interactions between novel drugs and their intended protein targets.

9:20am **2D+TF-WeM5 Growth of Graphene on Cubic Silicon Carbide on Silicon Substrates***, **Mehdi Rezaee**, G.L. Harris, J. Griffin, C. Taylor,* Howard University*; E. Hu, D. Bell,* Harvard University

Graphene is a two-dimensional sheet of sp^2 carbon atoms with extraordinary high mobility and quantum properties that makes it a promising candidate for future electronics. Large-scale production of graphene is paramount for the development of graphene-based electronics. This thesis focused on the synthesis and characterization of graphene layers. Two methods were used to grow graphene films. First, graphene films were epitaxially grown on silicon carbide substrates by thermal decomposition of SiC at high temperatures and low pressures. An in-house built reactor consisting of an induction furnace was used to form epitaxial films for electronic applications. Second, chemical vapor deposition was used for direct graphene synthesis on 3C-SiC using copper as a catalyst. In the thermal CVD processes, hydrogen and methane gases were used as precursors. Methane acts as a carbon source, while annealing and cooling were done in a hydrogen environment. Different polytypes of silicon carbide (6H-SiC and 3C-SiC) and their crystal orientations were exploited as substrates to form epitaxial graphene. A hetero-epitaxial 3C-SiC epilayer was first deposited on Si substrate using the chemical vapor deposition technique in the cold wall, low-pressure horizontal CVD reactor. The reactor temperature, argon pressure, flow rate and concentration of different gases (propane, silane, hydrogen and argon) was investigated to control the growth of 3C-SiC and graphene sublimation rate. The resulting graphene films were confirmed using Raman spectroscopy. Further, graphene films have been characterized with the tools of atomic force microscopy (AFM) and scanning electron microscopy (SEM). Mobility, electrical resistivity and carrier density measurements were taken using Hall effect measurements.

This work was supported by the STC Center for Integrated Quantum Materials, NSF Grant No. DMR-1231319 and the PREM NSF Program.DMR-1205608 grant.

9:40am **2D+TF-WeM6 Growth of Graphene on Cu Single Crystal Substrates***, **Tyler Mowll**,* University at Albany-SUNY*; Z.R. Robinson,* College at Brockport-SUNY*; C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Copper foils are frequently used to grow single-layer graphene by chemical vapor deposition (CVD). The primary reasons for this are the low costs of the Cu foils, the low solubility of carbon in Cu, and the relatively low cost of the equipment needed to grow the films. However, the polycrystalline nature of Cu foils can lead to numerous crystalline defects in the graphene, resulting in a reduction in the transport properties. To provide a systematic study of the CVD graphene growth process, a study of the growth of graphene on single crystal Cu substrates, with terminations along the (100), (110), and (111) planes, was performed. Synthesis was performed in an ultra-high vacuum (UHV) chamber using a modified setup to allow growth at pressures as high as 1 Torr. Ethylene was used as the precursor gas. To control Cu sublimation at the elevated growth temperatures, an Ar overpressure was used. This arrangement allowed for the preparation of clean Cu surfaces by sputtering and annealing the Cu crystals in UHV, followed by graphene growth at low pressure, and analysis with low energy electron diffraction in UHV without breaking vacuum. This avoided exposure of the crystal to atmospheric contaminants. It was found that surface termination plays a strong role in the rotational alignment of the nucleating graphene grains and the decomposition rate of the ethylene. It was observed that single-domain epitaxy is possible on Cu(111) when the ethylene pressure is 5 mTorr or less. However, growth on both Cu(100) and Cu(110) result in a minimum of two domains. In addition, ex-situ EELS is currently being performed on well-ordered epitaxial graphene films grown on Cu(111) and Cu(100) to determine the effect of the graphene-Cu interaction on the electronic properties of the graphene.

11:00am **2D+TF-WeM10 Atomic Layered Large Area Growth of 2D Monolayers Over Different Substrates***, **Joseph Waters**, S. Garg, S. Balci, S. Kim, P. Kung,* University of Alabama

Atomically-thin transition metal dichalcogenides (TMDCs) such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) are of great interest because of their unique semiconducting and optical properties. For example, unlike graphene, MoS_2 is a semiconductor whose band gap changes from indirect (~1.2 eV) to direct (~1.85 eV) as the material thickness reduces from bulk to a monolayer state. This makes MoS_2 promising for numerous optoelectronic and biosensing applications. TMDC monolayers have originally been realized through exfoliation. However, the ability to synthesize monolayers over larger areas than those achievable with exfoliation requires scalable techniques such as chemical vapor deposition.

Here, we report the large area growth of monolayer thin films of TMDCs, such as MoS_2 and WS_2, by low-pressure chemical vapor deposition in an oxygen-free inert argon atmosphere. The growth of these materials has been compared on various substrates, such as basal plane sapphire, (001) SiO_2/Si, and GaN/sapphire substrates. The effects of growth conditions, including growth temperature, on the characteristics of the resulting material have been studied. The physical properties of the monolayers have been characterized using electron microscopy and atomic force microscopy to study their topology over the various substrates, in conjunction with confocal micro-Raman and micro-photoluminescence spectroscopy to correlatively assess their optical characteristics. The terahertz time domain spectroscopy of MoS_2 and WS_2 monolayer thin films will also be presented. We will further discuss the impact of these monolayer materials for robust optoelectronic device applications.

11:20am **2D+TF-WeM11 Growth of Doped Graphene from Fullerene Precursors***, X. Fei, J. Neilson, V. Lopez,* California State University Northridge*; H.J. Gao,* Chinese Academy of Sciences, People's Republic of China*; L. Gan,* Peking University, People's Republic of China*; **Li Gao**,* California State University Northridge

Heteroatom-doped graphene materials have potential applications in electronic devices, energy storage and conversion systems, and gas storage. Chemical doping with various heteroatoms is an effective strategy for tuning the properties of graphene in order to expand its applications. Toward the practical applications as well as fundamental studies of doped graphene materials, it is an urgent task to explore effective approaches to synthesize these materials with a high level of control over their doping properties. In this talk, we will discuss the synthesis of heteroatom-doped graphene materials from fullerene precursors. Initial success has been achieved on the iridium and ruthenium surfaces. The growth process and the properties of grown doped graphene materials are characterized by using scanning tunneling microscopy on the atomic scale. We will discuss how the growth process and the properties of grown doped graphene depend on precursor/metal systems and experimental conditions. This new synthesis approach is an important complement to the existing strategies for the preparation of heteroatom-doped graphene.

11:40am **2D+TF-WeM12 Evaluation of Precursor Chemistry for Controllable Growth of Molybdenum Disulfide by Pulsed Chemical Vapor Deposition***, **Berc Kalanyan**, J.E. Maslar, W.A. Kimes, B.A. Sperling, E. Garratt, B. Nikoobakht, R. Beams, S.J. Stranick, A.V. Davydov,* National Institute of Standards and Technology (NIST)

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs), e.g., MoS_2, are of increasing interest for next-generation nanoelectronic and optoelectronic devices due to their thickness dependent optical and electrical properties. For many applications, high volume manufacturing of devices based on TMDs will require deposition techniques that are capable of reproducibly growing wafer-scale films with monolayer control. To date, TMD deposition processes largely rely on powder vaporization and transport, with minimal control over precursor fluxes and chemistry. A detailed understanding of metal and chalcogen precursor chemistry in relation to film properties remains an important step toward the design of highly-controllable deposition processes suitable for large-scale 2D synthesis.

We aim to identify promising chemistries for chemical vapor deposition (CVD) processes for TMDs. We focus on MoS_2 CVD using organometallic and organosulfur compounds in a research grade single-wafer deposition system equipped with *in situ* optical diagnostics. The precursor flux is measured using optical mass flow meters installed on the delivery lines while deposition chemistry is characterized in the reactor volume above the deposition surface using *in situ* Fourier transform infrared (FTIR) spectroscopy. As-deposited and annealed films are characterized with *ex situ* techniques, including Raman and photoluminescence spectroscopy, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy.

Large-area thin films of MoS_2 were prepared from (η^5-ethylcyclopentadienyl)-dicarbonylnitrosyl molybdenum, cycloheptatriene tricarbonyl molybdenum, bis(ethylbenzene) molybdenum, 1-propane thiol, and diethyl disulfide sources. Film composition and growth rates on SiO_2 and c-plane Al_2O_3 were characterized for each compound as a function of precursor exposure time. Gas phase reaction chemistry and thermal stability of precursors were evaluated using FTIR spectroscopy. The full-width at half-maximum values for in-plane (E_{2g}^1) and out-of-plane (A_{1g}) Raman modes for MoS_2 were used as indicators of film quality. By relating film properties to gas-phase chemistry for various metal precursors, we will highlight precursor design and process conditions that lead to high quality CVD films.

12:00pm **2D+TF-WeM13 *In-situ* Scanning Tunneling Microscopy Studies of Chemical Vapor Deposition of hexagonal Boron Nitride Monolayers on Pd(111)***, **Pedro Arias**, A. Ebnonnasir, F. Fankhauser,* University of California at Los Angeles*; C. Ciobanu,* Colorado School of Mines*; S. Kodambaka,* University of California Los Angeles

Using *in-situ* ultra-high vacuum variable-temperature scanning tunneling microscopy (STM), we investigate the chemical vapor deposition kinetics of hexagonal boron nitride (hBN) monolayer growth on Pd(111) substrates as a function of substrate temperature, borazine flux, and deposition time. All of the experiments were carried out on sputter-deposited Pd(111)/Al_2O_3(0001) thin films. In each experiment, STM images were acquired while resistively heating the Pd(111) samples on the STM stage at temperatures between 300 K and 773 K and in the presence of borazine (10^{-7} ~ 10^{-6} Torr) for times between 60 s and 2500 s. We observe the nucleation and growth of chemisorbed (and presumably partially dissociated) borazine islands on the Pd surfaces. From the STM images, we measured the island density and size as a function of time, temperature, and borazine flux. We find that both the island density and size increase with increasing borazine flux and deposition time. We also find that borazine islands form on Pd(111) 'up-steps.' After achieving monolayer coverage of borazine, the samples are annealed in ultra-high vacuum at 1020 K for 60 seconds to form hBN monolayers. We then determined of the number density of rotational domains in the hBN layers, based upon which we identify the deposition parameters critical to the growth of single-domain hBN layers on Pd(111).

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

Atomic Layer Etching

Moderator: Eric A. Hudson, Lam Research Corporation

8:00am **PS+TF-WeM1 Selective Cyclic Plasma Etching of Thin Films in Two Heating Way, Ion Bombardment and Infrared Irradiation.***, M. Izawa,* Hitachi High-Technologies Corp., Japan*; **Kazunori Shinoda**, N. Miyoshi, H. Kobayashi,* Hitachi, Japan*; N. Yasui, M. Tanaka, Y. Sonoda, K. Kuwahara,* Hitachi High-Technologies Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan **INVITED**

With shrinking device size and introduction of 3D FinFET transistor structure, cyclic Atomic Layer Etching (ALEt) becomes one of the key technologies in thin film etch. To achieve extreme high selectivity against mask and etch-stop layers, atomic level etching as a method to meet these etching requirements and eliminate physical damage has been investigated. Further, isotropic ALEt will be required for use in nanoscale patterning for formation of more complex 3D structures. In cyclic ALE technology, a modification layer is formed on a thin film layer by supplying etching species. After that, the modification layer is removed by heating. We investigated two types of ALEt tools; one is a anisotropic ALE tool based on Microwave ECR plasma and the other is a isotropic ALE based on ICP type down-flow plasma.

Recently, we have reported results of isotropic ALEt of Silicon Nitride (SiN) film [1]. High-throughput and high-selectivity ALEt of SiN using IR irradiation and down-flow plasma was also demonstrated [2]. Modification layer, ammonium hexafluorosilicate ($(NH_4)_2SiF_6$), was synthesized by fluorocarbon gas plasma and nitrogen supplied from SiN flim. Because the modification layer is formed only on SiN film, SiN film can be removed with high selectivity at IR radiation heating step. This technology can be also applicable to ALEt of TiN.

Anisotropic ALEt was also investigated by using Microwave-ECR plasma [3]. In this study, Ar ion irradiation was utilized instead of heating. To achieve high selectivity, the ion energy lower than sputtering threshold is required. Because microwave-ECR plasma has low plasma potential and is not fluctuated by wafer RF power, lower ion energy is available. In addition, It is known that excessive dissociation of gases and by-products causes reverse reaction and degradation of selectivity. We therefore used high gas flow rate and pulsed plasma to reduce dissociation. This ALEt technology has been applied to high selective etching of Si, HfO_2, and SiN film.

[1] K. Shinoda *et al*., AVS Atomic Layer Etching workshop 2015.

[2] N. Miyoshi *et al*., 62 nd AVS, , PS+SS+TF-WeM5, 2015.

[3] M.Tanaka *et al*. , SPIE Advanced Litho., 9428-23, 2015.

8:40am **PS+TF-WeM3 Concurrent Engineering of Atomic Layer Etch Patterning Processes Involving Oxide and Nitride Materials*, Mingmei Wang***, *P. Chan,* TEL Technology Center, America, LLC*; P. Ventzek,* Tokyo Electron America*; A. Ranjan,* TEL Technology Center, America, LLC

Atomic layer etching (ALE) of Si has been the focus of extensive research and development for over two decades. [1] However, the precision etch of dielectric materials (SiO_2, Si_3N_4) in patterning schemes employing self-aligned contacts (SACs) and self-aligned multiple patterning (SAMP) at the 10nm technology node and beyond are where ALE has significant potential. In both SAC and SAMP schemes, an oxide layer must be etched selective to a thin nitride layer with a corner with a thickness and radius of curvature of less than 10 nm. Fortunately precision etch using cyclic deposition/etch schemes have been proven effective at preserving the thin nitride corner. Unlike atomic layer etching of silicon using chlorine, fluorocarbon chemistry etching of nitride and oxide is not self-limiting process. The thin fluorocarbon polymer layers that protect the nitride layer corner deep in a feature are difficult to measure with common in-line metrology. Both these facts make trial-and-error development of processes for cyclic etch of oxide materials selective to nitride underlayers challenging. We have used concurrent engineering approaches including both modeling and experiment to bypass these difficulties. The core of the approach is a new integrated chamber (HPEM)-feature scale MCFPM (Monte Carlo Feature Profile Model) model [2] for oxide nitride etch experiments conducted on a dual frequency plasma source using a benchmark $Ar/C_4F_6/O_2$ chemistry. The concurrent engineering approach comprises stages of development and prediction tests using both blanket wafer and patterned coupon data and finally process parameter optimization. By using this approach, we have minimized nitride corner loss and optimized nitride/oxide etch selectivity with a minimum of engineering resources. The presentation will survey both experimental and computational results representing a case study in SAC process development. Furthermore, insights into the relationship between chamber function and critical surface processes will be discussed.

[1] A.Ranjan, M.Wang, S.Sherpa, V. Rastogi, A. Koshiishi, and P.Ventzek, J. Vac. Sci. Technol. A34, 2016.

[2] M.Wang and M.Kushner, J. Appl. Phys 107, 2010.

9:00am **PS+TF-WeM4 System Trade-offs of Atomic Layer Etching (ALE) of High Aspect Ratio 3D Features*, Chad Huard,*** University of Michigan*; Y. Zhang, S. Sriraman, A. Paterson,* Lam Research Corp.*; M.J. Kushner,* University of Michigan

Atomic layer etching (ALE) is a method for decoupling process parameters that, with continuous etching, are usually difficult to separately control. ALE does so at the trade-off of decreased etch rate. Of particular interest is the ability of ALE to separate the consequences of plasma parameters, such as ion to neutral flux ratios and ion energies, from issues of transport into and out of the feature. By using separate and self-limited reactions for surface passivation and material removal, ALE offers a way to deliver the optimum neutral/ion ratio at any aspect ratio at the trade-off of increasing etch time.

Using a 3-dimensional voxel based Monte-Carlo feature profile model, the trade-off between etch time and etch fidelity encountered in the ALE regime has been investigated. The poly-silicon gate etch process of a high-k metal replacement finFET is the base case for this study. The time-multiplexed scheme to achieve ALE is an Ar/Cl_2 plasma passivation step followed by an Ar plasma step having higher ion energies to remove Si. We found that the change in neutral conductance of the feature as the aspect ratio increases requires adjusting process step times to optimize etch rates. We also found that ALE is able to clear corners in 3D features more effectively than continuous etching, requiring less over-etch. A measure of clearing efficiency is the amount of over-etch required to clear the corners compared to the total etch time. The clearing efficiency was investigated for an entirely ALE process and a hybrid approach using a continuous main etch followed by an ALE clearing etch, over a range of geometries including varying fin spacing and side-wall slope.

Work was supported by Lam Research Corp., Department of Energy Office of Fusion Energy Science and the National Science Foundation.

9:20am **PS+TF-WeM5 Molecular Dynamics Simulations of Atomic Layer Etching*, Jun-Chieh Wang,*** *S. Rauf, J.A. Kenney, L. Dorf, K.S. Collins,* Applied Materials, Inc. **INVITED**

Sub-nm precision is increasingly being required of many critical plasma etching processes in the semiconductor industry. As such, atomic layer etching (ALE) has become a potential candidate for accurate control of a variety of critical etching processes. In ALE, the target substrate is first exposed to a reactive gas that passivates the surface followed by ion bombardment with energy below the sputtering threshold. It is essential to precisely control the ion/radical energy and flux during the etching process to remove the topmost passivated surface without damaging the underlying substrate. Once the passivation layer is removed, the etch process stops. The passivation and etching steps repeat until one has etched to the desired thickness. In contrast to conventional radio-frequency (RF) plasma etching processes, microfabrication using ALE promises high selectivity and low damage to the substrate. In this talk, we discuss the properties of ALE on a patterned surface using results from molecular dynamics (MD) simulations. A chlorinated Si/SiO2 surface was bombarded by Ar^+ or Cl^+ ions to remove the modified surface layers. With Ar^+ energy below the sputtering threshold, etch process stops after the Si surface becomes deficient in Cl atoms; while at high bombarding energy, Si removal continuous with lower rate partly due to physical sputtering. For Cl^+ ion bombardments, the Si surface is continuously etched at a constant rate, and the etch rate increases with Cl^+ ion energy. Results for different aspect ratios will also be discussed. These fundamental studies are used to interpret our layer-by-layer ALE experiments.

11:00am **PS+TF-WeM10 Isotropic Atomic Layer Etching of Titanium Nitride Using Formation and Desorption of Ammonium Salt*, Kazunori Shinoda,*** *N. Miyoshi, H. Kobayashi, M. Kurihara,* Hitachi, Japan*; S. Sakai, M. Izawa,* Hitachi High-Technologies, Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

There is growing interest in atomic layer etching (ALEt) as 3D devices become widely used and feature sizes continue to scale down. The development of isotropic ALEt for various materials will be important for existing and future 3D devices such as a 3D NAND, Fin FET, and GAA FET. Recently, the authors developed an isotropic ALEt for SiN using formation and desorption of an ammonium hexafluorosilicate-based modified layer [1]. High-throughput high-selectivity ALEt of SiN using IR irradiation was also demonstrated by the authors [2]. In this work, isotropic ALEt of TiN using formation and desorption of an ammonium salt-based modified layer is developed.

The experimental apparatus used in this study is composed of a reaction chamber and an x-ray photoelectron spectroscopy (XPS). TiN deposited by atomic layer deposition was used as the sample material. Several samples were exposed to radicals that were generated in fluorocarbon-based gas mixtures. The samples were then annealed by using circulating fluid. The surface of the samples was analyzed by XPS. Photoemission spectra obtained after radical exposure and after thermal annealing of the TiN samples are compared. The etching depth was evaluated by ellipsometry.

A nitrogen 1s peak (402 eV), which has been assigned as ammonium salt, was observed after radical exposure. Titanium 2p peaks (462 and 467 eV), which originate from a Ti-F bond, were observed simultaneously. These results imply that the surface of the radical exposed TiN consists mainly of ammonium salt such as ammonium fluorotitanate. After the samples were annealed on the wafer stage heated at 210°C, the nitrogen 1s peak at 402 eV, which is assigned as ammonium salt, disappeared. A nitrogen 1s peak at 396 eV, which is attributed to TiN, appeared after the ammonium salt-related peak disappeared. This phenomenon implies that the film of ammonium salt decomposed and desorbed from the TiN surfaces at elevated temperatures.

The preliminary tests of cyclic etching are carried out by repeating radical exposure and thermal annealing. For one cycle of etching, the etching depth increases with increasing radical exposure time and saturates at 0.7 nm. For multiple cycle etching, the etching depth increases with an increasing number of repetitions of the cycle. Tuning of the etched amount per cycle (EPC) in the range from 0.3 to 0.7 nm was demonstrated by changing the composition of gas mixtures. From these results, it is concluded that the ALEt of TiN was successfully demonstrated.

[1] K. Shinoda et al., Atomic Layer Etching Workshop 2015, July 1–2, p. 572 (2015).

[2] N. Miyoshi et al., AVS 62nd International Symposium & Exhibition, PS+SS+TF-WeM5 (2015).

11:20am **PS+TF-WeM11 Organic Etchants Toward Atomic Layer Etching of Magnetic Metals***, **Nicholas Altieri**, L. Minardi, E.L. Chen, J.P. Chang,* University of California Los Angeles

The continued advancement in logic and memory devices relies heavily on the introduction of new materials. Of specific interest in the field of memory application is the utilization of magnetic metals and alloys such as Co, Fe, and CoFe as well as additional doped alloys such as CoFeB. Contemporary techniques for patterning these materials rely on noble ion beam milling which, although effective, leaves much to be desired in achieving selectivity and retaining pattern transfer fidelity for high aspect ratio features. One solution is the pursuit of atomic layer etching through reversal of the atomic layer deposition scheme and generation of volatile metal-organic species reminiscent of ALD precursors. Due to the etch-resistant nature of the materials studied, removal at an atomic level is enabled by chemical modification of the surface through plasma exposure and subsequent introduction of organic ligands.

Selected single element Co and Fe films as well as the magnetic metal alloy CoFeB (30nm) were studied using this scheme. Organic chemistries, such as acetylacetone (acac) and hexafluoroacetylacetone (hfac) were first investigated to determine the feasibility of metal-organic formation through direct exposure. The efficacy of acetylacetone and hexafluoroacetylacetone etching chemistries were confirmed through previous solution-based studies on Co and Fe, respectively, via formation of $Co(acac)_2$ (257 amu) and $Fe(hfac)_3$ (680 amu) as confirmed through mass spectrometry. Use of these organics was extended to the boron-doped alloy in the form mixtures with volumetric ratios of 1:3, 1:1, and 3:1 (acac:hfac). $Co_{30}Fe_{45}B_{25}$ was shown to etch at rates up to 15 nm/min in the 1:1 solution and ~1 nm/min at an organic mixture partial pressure of 60 Torr. The composition of the film as well as its metallic nature were preserved as seen by x-ray photoelectron spectroscopy (XPS) through the detection of Co and Fe metallic peaks present at 778.2 and 706.7 eV, respectively.

Chemical modification of the surface was then investigated as a means of controlling the amount of material removed and determining effects on material properties under various process conditions. XPS analysis of Co and Fe films processed under O_2 plasma show increasing thickness of CoO and Fe_2O_3 up to 3.7nm and 4.6nm, respectively after 5 min exposure. Magnetic properties of both single element and alloyed films were characterized using superconducting quantum interference device magnetometry (SQUID) and displayed degraded magnetic properties through increasing coercivity with increasing oxidation time.

11:40am **PS+TF-WeM12 Conformality of Thermal Al_2O_3 Atomic Layer Etching in High Aspect Ratio Structures***, **Amy Marquardt**, H. Sun,* University of Colorado Boulder*; S.M. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) is the reverse of atomic layer deposition (ALD). Conformal deposition in high aspect ratio structures is one of the key features of ALD. The conformality of etching in high aspect ratio structures will also be important for thermal ALE. In this study, the conformality of thermal Al_2O_3 ALE was investigated in channels with high aspect ratios ranging from 60 to 200. Al_2O_3 ALD was used to deposit the initial Al_2O_3 films in the channels. The Al_2O_3 ALE was performed at 300°C using HF and $Al(CH_3)_3$ as the reactants. HF is known to fluorinate Al_2O_3 and form an AlF_3 layer on the Al_2O_3 surface. The $Al(CH_3)_3$ then undergoes a ligand-exchange transmetalation reaction with the AlF_3 layer. $Al(CH_3)_3$ accepts fluorine and donates methyl ligands to the surface. This ligand-exchange allows the Al in the AlF_3 layer to leave as a volatile reaction product such as $AlF(CH_3)_2$ or $Al(CH_3)_3$. The conformality of Al_2O_3 etching was examined in high aspect ratio channels defined by stainless steel foil spacers between silicon substrates. Spectroscopic ellipsometry was used to measure the Al_2O_3 film thickness in the channels. Increasing the aspect ratio increased the reactant exposure and purge times necessary to maintain conformal etching. Longer times were required to allow the reactants and products to diffuse in and out of the high aspect ratio channels. Increasing the reactant pressures also lowered the required reactant exposure times. However, increasing the reactant pressures from 0.1 to 9 Torr also increased the Al_2O_3 etching rate. The higher etching rates were attributed to a thicker AlF_3 layer formed at higher reactant partial pressures. Using longer reactant exposure or purge times or higher reactant pressures, conformal Al_2O_3 etching was obtained in the high aspect ratio channels.

12:00pm **PS+TF-WeM13 Thermal Atomic Layer Etching of Crystalline Aluminum Nitride Using Sequential, Self-Limiting HF and $Sn(acac)_2$ Reactions and Enhancement by H_2 and Ar Plasmas***, **Nicholas Johnon**, H. Sun, K. Sharma, S.M. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) has been recently demonstrated for a variety of oxides such as Al_2O_3, HfO_2 and ZrO_2 using sequential, self-limiting fluorination and ligand-exchange reactions. In this work, the thermal ALE of aluminum nitride, a III-V metal nitride, was performed for the first time. Crystalline aluminum nitride (AlN) films were etched using hydrogen fluoride (HF) and tin(II) acetylacetonate ($Sn(acac)_2$) as the reactants. The AlN films were in the crystalline wurtzite phase with the (0001) plane parallel to the surface. Film thicknesses were monitored versus number of ALE reaction cycles at 275°C using in situ spectroscopic ellipsometry (SE). A low etch rate of 0.07 Å/cycle was measured during etching of the first 40 Å of the film. These small etch rates corresponded with the AlO_xN_y layer on the AlN film. The etch rate then increased to 0.36 Å/cycle for the AlN films. In situ SE experiments established the HF and $Sn(acac)_2$ exposures that were necessary for self-limiting surface reactions. In the proposed reaction mechanism for thermal AlN ALE, HF fluorinates the AlN and produces an AlF_3 layer on the surface. The metal precursor, $Sn(acac)_2$, then accepts fluorine from the AlF_3 layer and transfers an acac ligand to the AlF_3 layer in a ligand-exchange reaction. The volatile etch products are SnF(acac) and either $Al(acac)_3$ or $AlF(acac)_2$. Adding a H_2 or Ar plasma exposure to the reaction sequence enhanced the etching rates. A H_2 or Ar plasma exposure after the $Sn(acac)_2$ exposure increased the AlN etch rate from 0.36 Å/cycle to 1.96 Å/cycle or 0.9 Å/cycle, respectively, at 275°C. The enhanced etch rates are believed to result from either H radicals or photons from the H_2 plasma or ions or photons from the Ar plasma. The H radicals may be able to remove acac surface species that may limit the etch rate. The photons or ions may also lead to the desorption of surface species or substrate excitation that enhances the etch rate.

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

Probing Electronic Properties

Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

To realize the selective growth and layered assembly of heterostructures at predefined location, here, we report on application of mask free, scanning probe based direct writing method. With the use of AFM cantilevers and developed water based “inks”, we demonstrate arrays of MoS_2 and WS_2 dots and ribbon arrays at predefined locations on variety of substrates. Employing this SPM based patterning method we have also fabricated MoS_2/WS_2 heterostructures of sub-micrometer scales in a controlled fashion. The quality of MoS_2/WS_2 heterostructures was confirmed by Raman spectroscopy, AFM characterization and electrical transport measurements. Our mask free nanolithography approach offers an alternative route for patterning and growth of TMDCs with added benefit of potential reduced contamination of the TMDCs surfaces and interfaces between materials and substrates. It demonstrates a promising unconventional technology for fabrication of high quality TMDCs heterostructures in convenient manner capable of nanoscale precision.

Acknowledgements

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

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

Thin Film
Room 105A - Session TF+MI+NS-WeM
ALD and Nanostructures

Moderators: Sean King, Intel Corporation, Mariadriana Creatore, Eindhoven University of Technology, Netherlands

8:00am **TF+MI+NS-WeM1 Scalable Manufacturing of Nanostructured Materials by Gas-Phase Deposition Techniques***, **Ruud van Ommen,*** Delft University of Technology, Netherlands **INVITED**

Core-shell nanoparticles and other nanostructured particles have high potential in applications such as catalysis, energy storage and pharma. However, a hurdle in their utilisation is that typically large amounts of such materials are required. Current liquid-phase and gas-phase synthesis methods often lack the high precision required or do not lend themselves to large-scale production. Gas-phase coating can be used to provide the surface of a particle with either a thin continuous coating or a decoration of nanoclusters. Coating techniques that can be used are chemical vapour deposition (CVD) [1], atomic layer deposition (ALD) [2], and molecular layer deposition (MLD) [3].

When carried out in a so-called fluidized bed, gas-phase coating is an attractive way of producing nanostructured particles with excellent scale-up potential. In such a system, the particles are suspended in an upward gas flow. We can do this both for nanoparticles and micron-sized particles. Nanoparticles – contrary to what is typically observed for larger particles – are fluidized as very dilute agglomerates with distinctive fluidization characteristics. I will discuss the challenges related to coating of nanoparticles using CVD, ALD, and MLD with such a system. Moreover, I will give a number of examples of the applications of nanostructured particles produced in this way.

[1] Valdesueiro, D., Meesters, G., Kreutzer, M., and van Ommen, J.R., 'Gas-phase deposition of ultrathin aluminium oxide films on nanoparticles at ambient conditions', Materials 8: 1249-1263 (2015).

[2] Goulas, A. and van Ommen, J.R., 'Atomic layer deposition of platinum clusters on titania nanoparticles at atmospheric pressure', Journal of Materials Chemistry A 1(15): p. 4647-4650 (2013).

[3] Vasudevan, S.A., Xu, Y., Karwal, S., van Ostaay, H.G.M.E., Meesters, G.M.H., Talebi, M., Sudhölter, E.J.R., and van Ommen, J.R., 'Controlled release from protein particles encapsulated by molecular layer deposition', Chemical Communications 51: 12540-12543 (2015).

8:40am **TF+MI+NS-WeM3 Surface Passivation of InP Nanowires by Atomic Layer Deposition***, **Lachlan Black**, Y. Cui, A. Cavalli, M.A. Verheijen, E.P.A.M. Bakkers, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands

III/V semiconductor nanowires offer a variety of novel properties that make them of interest for electronic and optoelectronic device applications, including enhanced light trapping/concentration, reduced material use, and relaxation of lattice-matching constraints, which enables novel heterostructures and growth on inexpensive substrates. However, the greatly increased surface-to-volume ratio of nanowires compared to planar devices significantly increases the importance of surface recombination and hence of effective passivation of the nanowire surface.

In this work, we focus on nanowires of InP, a material of particular interest for optoelectronic devices. In contrast to the situation for GaAs, the bare or natively oxidised surface of InP presents relatively few electronically active defect states to facilitate surface recombination. However, in order to form InP device structures it is necessary to deposit an insulating dielectric layer on part of the InP surface, and this tends to result in significant depassivation of the surface, to the extent that the performance of InP devices is commonly limited by surface recombination.

Atomic layer deposition (ALD), as a relatively “soft” deposition technique capable of forming well-controlled, high-quality dielectric layers, would seem to offer the best chance of successfully passivating InP nanowire surfaces. ALD can be performed at low substrate temperatures, which is important to avoid phosphorus out-diffusion and resulting damage of the InP surface, while its excellent conformality allows for uniform deposition on nanowire surfaces. Nevertheless, previous attempts to passivate InP surfaces by ALD have encountered similar difficulties to other techniques in achieving low surface recombination for deposited dielectric layers of appreciable thickness.

In this work, we demonstrate successful dielectric passivation of InP planar and nanowire surfaces in the presence of a relatively thick (>10 nm) ALD Al_2O_3 layer deposited from trimethylaluminium (TMA), through the use of a thin phosphate interlayer deposited at low temperature in the same system from trimethyl phosphate (TMP), in both cases using an O_2 plasma oxidant. Time-resolved photoluminescence measurements show that carrier lifetimes are increased relative to the native surface for both planar and nanowire InP samples (e.g. from 1.6 to 2.4 ns for one nanowire sample), in contrast to a strong depassivation observed following ALD of Al_2O_3 and other dielectrics on the bare InP surfaces. X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) are used to elucidate the composition and structure of the deposited phosphate layers.

9:00am **TF+MI+NS-WeM4 Selectivity and Nucleation Effects in Atomic Layer Deposition of Copper for Plasmonic Nanostructures***, **Jie Qi**, B.G. Willis,* University of Connecticut

Plasmonic nanostructures made of conducting metals such as copper, silver, and gold have been intensively investigated due to their capability for enabling optics beyond the diffraction limit and making it possible to manipulate visible and near-IR radiation at the nanometer scale. The interaction between metallic nanostructures and incident light induces large enhancements of the local electromagnetic fields via the excitation of localized surface plasmon resonances (LSPRs). These confined and enhanced fields have many exciting applications in optical detection, cancer therapeutics, biological and chemical sensors, spectroscopy, catalysis, and photovoltaics. A key feature of nanoscale plasmonic materials is a strong dependence of the plasmon resonance on size, shape, composition, and surroundings of the nanostructures. Selective area atomic layer deposition (SA-ALD) offers a promising nanofabrication technique to further tune the properties of plasmonic nanostructures with composition and thickness control at an atomic level. Successful application of SA-ALD requires good control of nucleation and surface morphology evolution, as well as good selectivity. Unfortunately, there are very few studies that report selectivity and/or nucleation characteristics, and their dependence on growth conditions.

In this work, we investigate the growth characteristics of Cu SA-ALD for tuning plasmonic nanostructures. Pd nanostructures are fabricated by electron-beam lithography and used as template layers. Samples are analyzed by AFM, high-resolution SEM, and image processing to investigate nuclei size and density, and morphology evolution. It has been found that nucleation is greatly affected by deposition temperature and co-reactant H_2 partial pressure. Poor nucleation leads to a rough surface with randomly distributed nanoparticles, while good nucleation leads to smooth, conformal growth over the entire feature. Sample surface pretreatments are found to be more critical for initiating growth on nanostructures compared to planar films, which might be related to residual impurities from photoresist layers or other contaminants from nanofabrication processing. Several preparation cleaning methods have been investigated for their effects on Cu film nucleation and growth selectivity including: UV-Ozone, O_2 plasma, annealing in H_2, annealing in He, boiling in water, and dipping in dilute HF.

9:20am **TF+MI+NS-WeM5 Metal Oxide Aerogel Patterning by CO_2 Laser Etching of ALD-coated Carbon Nanotube Macro-Structures***, C. Aksu, P.D. Bradford,* ***Jesse Jur,*** North Carolina State University

Patterning techniques of metal oxide foam architectures embedded within an ALD-coated carbon nanotube interconnected matrix are defined. Three dimensionally interconnected networks of carbon nanotube are produced from spinnable vertically aligned CNT arrays in which CNTs make. Atomic layer deposition is used to functionalize the surface of the CNTs in the array. Prior work has demonstrated that the CNT networks can be sacrificially removed to form aerogel architectures of the ALD material. In this study, we present a simple and scalable method to fabricate macro-sized structures of ALD alumina foams embedded in the carbon nanotube foam architecture via a CO2 continuous wave laser etching. Specifically, we have demonstrated the ability to ALD modify the CNT in large macro-structures (>1 cm2) and subsequently remove the CNT from specified areas, leading to the complex hybrid alumina-CNT periodic structures. The effects of ALD coating thickness are inspected by in-situ heating transmission electron microscopy methods and by high resolution scanning electron microscopy. Factors relating to manufacturability (i.e. etching speed and power) and dimension stability (i.e. laser etch size) are defined to identify scale-up opportunities.

9:40am **TF+MI+NS-WeM6 Tungsten ALD in Porous Carbon Nanotube Forests***, K. Hinton, N. Hollingworth, D.D. Allred,* ***Richard Vanfleet,*** Brigham Young University

We have deposited tungsten on carbon nanotube (CNT) forests by CVD (WF_6 & H_2) and ALD -the silane reduction of WF_6. Resulting structures are studied by scanning electron and transmission electron microscopy. We observed that the CNT forest provides a scaffolding for the nucleation and growth of the tungsten. Such structures may be a useful avenue for metal MEMS that does not require extensive etching. The present study may provide insight into the mechanisms of ALD in highly porous structures. In conventional ALD on surfaces which are largely planar, the amount of reactants needed to completely cover the surface does not change much from step-to-step. In contrast the surfaces of carbon nanotube forests consist of cylindrical tubes largely oriented perpendicular to the sample surface. Thus, the surface area increases with deposition. This is in addition to the changes in surface area associated with incubating early stage nucleation sites. When beginning with adequate tungsten or silane one might expect to move to starvation mode as the number of cycles increases if the amount of each reactant is kept constant. We see evidence for tungsten starvation in our research results. For low number of cycles the CNT fibers have a spatially uniform nucleation of tungsten. For low amounts of WF_6 or low “soak” times, as cycles increase, growth on the top surface and sidewalls of the carbon nanotube forest outpaces growth within the structure. Post deposition cross-sections show distinct bands witnessing the starvation of tungsten growth in the interior as more of the tungsten is deposited on regions that have direct access to the WF_6 gas. EDX analysis across such a cross-section shows distinct plateaus in the amount of tungsten present corresponding to the bands.

11:00am **TF+MI+NS-WeM10 Rational Design of Hyperbranched ZnO Nanowire Systems for Superomniphobic Surfaces Enabled by ALD***,* ***Ashley Bielinski****, M. Boban,* University of Michigan, Ann Arbor*; Y. He,* Pacific Northwest National Laboratory*; E. Kazyak,* University of Michigan, Ann Arbor*; C. Wang,* Pacific Northwest National Laboratory*; A. Tuteja, N.P. Dasgupta,* University of Michigan, Ann Arbor

Semiconductor nanowires (NWs) are powerful 1D building blocks for a range of technologies including electronics and optics, sensors, mechanical resonators, and energy conversion [1]. NW arrays are synthesized with careful control of morphology and composition using both top-down and bottom-up approaches. However, the hierarchical assembly of these NWs into heterogeneous systems remains challenging, largely due to lack of deterministic control of feature size, shape and position in 3D assemblies. Here we demonstrate that Atomic Layer Deposition (ALD) is a powerful tool for modifying interfaces to control the fabrication of ordered hyperbranched NW systems. Hierarchical branched NWs bridge the nano and micro length scales, while providing an exponential increase in surface area. Examples have been synthesized for a variety of applications, but the ability to tune the morphology along a spectrum in order to optimize the structure requires development.

Nanoscale patterning techniques for NW placement, while slow and costly on planar substrates, often become impossible on high aspect ratio structures. Solution-based techniques offer scalability and lower cost, but the results are often disordered and difficult to tune. Our approach uses ALD to catalyze the nucleation of NWs on the substrate during hydrothermal growth. ALD is essential for this approach because it deposits conformal films on ultra-high aspect ratio substrates, with atomic-scale control of film composition and structure. We’ve demonstrated that by varying the thickness of ALD ZnO films, their crystallographic orientation, roughness, and surface stress can be controlled [2]. These catalyst seed layers allow us to tune the NW array morphology, including density and orientation, over a range of substrate materials and geometries.

We further show that ALD can overcome challenges that arise when transitioning from simple NW arrays to complex branched structures [3]. First, amorphous ALD TiO_2 over-layers are used to reduce nanowire density creating space for subsequent levels of hierarchy. Next, ALD interlayers are used to block the crystallinity of the previous level of ZnO NWs to allow for non-epitaxial deposition of the subsequent ALD seed layer, forming core-shell NWs. These new techniques were used to grow hierarchical branched NW arrays, which were shown to be superomniphobic (repellent to high and low surface tension liquids) with tunable contact angles for different liquids using ALD to control the array properties.

[1] Dasgupta, N. P.; et al. *Adv. Mater.***2014**, *26* (14), 2137–2184.

[2] Bielinski, A. R.; et al. *Chem. Mater.***2015**, *27* (13), 4799–4807.

[3] Bielinski, A. R.; et al. *Submitted***2016**

11:20am **TF+MI+NS-WeM11 Bio-Templated *Morpho* Butterfly Wings by ALD for Photocatalysis***,* ***Robin E. Rodriguez****, D. Das, S.P. Agarwal,* University of Michigan, Ann Arbor*; W. Shang, T. Deng,* Shanghai Jiao Tong University, China*; N.P. Dasgupta,* University of Michigan, Ann Arbor

Hierarchical nanostructures found in biology have unique properties that inspire bio-mimetic engineering. These natural nanostructures present design principles of bottom-up nanomanufacturing for materials with tunable properties. For example, structural coloration is a phenomenon observed in a wide range of natural materials that take advantage of nanoscale hierarchical structures to tune their reflection and absorption properties through periodic diffraction and photonic resonances. Here we demonstrate *bio-templating* via Atomic Layer Deposition (ALD) as an approach to manufacture atomically-precise synthetic materials that manipulate the natural structural coloration found in *Morpho* butterfly wings for enhanced photocatalytic activity.

Until recently, conventional approaches to bio-templated nanomaterial synthesis have been limited in their ability to create highly conformal 3-D interfaces between temperature- and chemically-sensitive bio materials and functional thin films. ALD is uniquely suited for scalable and conformal bio-templating, which allows us to use the nanoscale structural complexity that nature provides to tune the interfacial properties of natural systems by coating them with functional materials. By varying the geometric and optical properties of the surface, ALD is able to tune structural coloration to manipulate the light absorbing and photocatalytic properties of natural materials with nanostructured surfaces.

Morpho butterflies are particularly interesting examples of structural coloration, which occurs due to hierarchical nanostructures on their wing surfaces. The combination of strong photonic resonances and high surface area in these wings represent an ideal template for photocatalysis. To demonstrate this, proof-of-concept tests were performed on *Morpho* wings coated by ALD of TiO_2 and ZnO. Electron microscopy images showed conformal coating of the wing geometries at the nanoscale. The structural coloration of the butterfly wings could be tuned using this approach, which was modeled using finite-difference time-domain simulations of the modified wing geometry. The viability of this approach was further demonstrated in the photocatalytic degradation of methylele blue dyes in water, which led to an increase in photocatalytic activity relative to planar thin film samples. The ALD deposited materials show superior photocatalytic activity which was attributed to enhanced light absorption and increased surface area from the butterfly's hierarchical structures.

Plasma Science and Technology
Room 104B - Session PS+TF-WeA

Plasma Deposition and Plasma Assisted ALD

Moderators: Noemi Leick, Colorado School of Mines, Adrie Mackus, Eindhoven University, Netherlands

2:20pm **PS+TF-WeA1 High Quality Film and Interface Formation using Appropriate Reaction Species*, Akinobu Teramoto,*** Tohoku University, Japan **INVITED**

The strong reactive species are required for the high quality film deposition by CVD or ALD. For oxides or nitrides formation, oxygen radicals or nitrogen radicals generated by the microwave exited plasma are very effective(1-3) because of high density and low plasma damages. The integrity of SiO_2 film formed by the microwave exited PECVD is the same as that formed by the thermal oxidation on Si(100) surface, and is superior than that formed by the thermal oxidation on any other surface of Si(100)(1, 2). The SiO_2 deposition rate of the microwave PECVD is sufficiently large for the practical use. For the SiNx film formation, the microwave PECVD is also effective. The quality of SiNx film formed by the PECVD at 400 °C is the same as that formed by thermal CVD(4, 5). However, the relatively long deposition time is required for high quality film deposition, and relatively low pressure is also required, as a result, the gap fill characteristics is weaker than the thermal CVD. The high quality SiNx film deposition at low temperature and relatively high pressure are required. The nitrogen radical generated by the atmospheric pressure discharge is attractive for these applications(6, 7).

We have to choose the reactive species more carefully when the depositing material is different from the substrate, such as Al_2O_3 on Si or GaN, SiO_2 on GaN. If the reactive species is excessively active, the species react not only the precursor but also the substrate, and the materials of the substrate and the film are mixed at the film/substrate interface, as a result, those mixed materials make defects and interface traps. Al_2O_3 can works as the gate insulator for the GaN-based MOSFET(8, 9) because of the large band gap and the high resistivity to Ga diffusion. The H_2O which has relatively lower oxidation ability than oxygen radical was used as the oxidant at the initial stage of Al_2O_3 ALD for suppressing the oxidation of GaN surface. Following radical oxygen treatment by microwave exited plasma is very effective for improving the film quality of Al_2O_3(9). It is noticed that the oxidation of GaN at the Al_2O_3/GaN interface must not occur during the oxygen treatment.

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3:00pm **PS+TF-WeA3 The Synergy of Diamond-like Carbon Film PECVD Systems: Plasma Diagnostics and Film Properties*, Tara Van Surksum,*** *E.R. Fisher,* Colorado State University

Diamond-like carbon (DLC) films have numerous potential applications because of their appealing mechanical and electronic properties (e.g., hardness, thermal conductivity, and high electrical resistance). Plasma enhanced chemical vapor deposition (PECVD) is a widely used technique in the production of DLC films, but to date, little is known about the underlying molecular-level chemistry involved in DLC plasma processing. In particular, energy partitioning within plasmas used to either produce or modify DLC films is not well understood. The present work focuses on investigating the fundamental chemistry of hydrocarbon plasmas used in DLC film processing as a means of understanding and ultimately controlling film fabrication. Here, we present a more holistic assessment of PECVD system used to create DLC films, including analysis of the gas-phase as well as the resulting materials. This comprehensive evaluation utilizing optical spectroscopy techniques and surface analysis tools (e.g., profilometry, contact angle goniometry, and Fourier transform infrared spectroscopy) is part of a larger effort to elucidate fundamental physical and chemical information on plasma processes that control deposition. For example, developing an understanding of energy partitioning within these plasma systems is a central component of this work as we have employed optical emission spectroscopy and broadband absorption spectroscopy to determine rotational and vibrational temperatures ($T_r$and T_v, respectively) of the CH radical in a variety of hydrocarbon precursor plasma systems. In CH_4 plasmas, T_v(CH) ranges from ~3000 to ~5000 K under most plasma conditions, whereas T_r generally reaches values ranging from 1000-2000 K. Both values appear to be correlated with system pressure and applied rf power. These results will also be presented in relationship to the properties of the deposited films. More importantly, data such as these provide valuable insight regarding possible mechanistic details in hydrocarbon plasmas linked to DLC film fabrication and help to unravel these complex systems with and without the presence of a substrate.

3:20pm **PS+TF-WeA4 ULK Film Dielectric Constant Restoration through Enhanced Organic Plasma Treatment*, Zhiguo Sun,*** *J. Shu, P. Mennell, Q. Yuan, A. Madan, S. Molis, J. Mody, Y. Zhang, J. Shepard Jr,* GLOBALFOUNDRIES

Ultra low k (ULK) films has been successfully integrated into Back End of Line(BEOL) interconnect to maintain a lower RC delay to take advantage of transistor continuous scaling, and to keep power consumption at a low level. However, due to its intrinsic composition and porosity, ULK films are susceptible to damage during the following process, especially patterning process and wet process such as wet clean and CMP. It is desirable to restore the dielectric constant to its original number to get full benefit if low k value. In this study, We will report a novel plasma treatment method being able to enhance the film resistance to plasma damage and repair the plasma damage. Through the detailed comparison between the pristine films,, damaged films and repaired films through analytical methods including Ellipsometry Porosimetry(EP) ,Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and Hg-probe, we find the organic plasma treatment capable of restoring the surface porosity, restore the lost methyl groups and restore the dielectric constant to its original value.

4:20pm **PS+TF-WeA7 Understanding of Low Temperature ALD of Silicon Nitride***, H.C.M. Knoops,* Oxford Instruments Plasma Technology, UK*; R.H.E.C. Bosch, T. Faraz, M. van Drunen, L.E. Cornelissen, M. Creatore,* ***Erwin Kessels,*** Eindhoven University of Technology, Netherlands

This contribution highlights insights into atomic layer deposition (ALD) of silicon nitride (SiN_x) and shows how considering these results in high material quality at low deposition temperatures. Thermal ALD processes generally require high temperatures for sufficient SiN_x quality and therefore plasma ALD has been studied extensively in the last few years. The model system discussed here consists of ALD processes using aminosilane precursors, such as $SiH_2(NH^tBu)_2$ (BTBAS) and $SiH_3N(^sBu)_2$ (DSBAS), and N_2 plasma as reactant.

Most plasma ALD processes for nitrides utilize NH_3 or H_2/N_2 plasmas, but for SiN_x it was found that the presence of H-containing species in the plasma strongly inhibits precursor adsorption.[1] DFT calculations demonstrated that groups with H on the surface have low reactivity with aminosilane precursors. Under-coordinated surfaces however, such as those obtained after N_2 plasma, have a much higher reactivity. To determine the nature of the surface, surface FT-IR studies were carried out. These indicated that the surface chemistry is rather complex as C and H species typically remain on the surface after the plasma step. Mass spectrometry showed that this can be related to reaction products that are created by the plasma step but which dissociate in the plasma and subsequently redeposit.[2] Shorter gas residence times reduce this redeposition effect and provide improved film properties (e.g., wet-etch rate, impurity content, and refractive index). The surface chemistry during the precursor step is relatively straightforward as gas-phase IR measurements and mass spectrometry measurements reveal that amino-groups from the precursor are released from the surface (e.g., in the form of H_2N^tBu). Note that not all the groups are released during the precursor step, as evidenced by the aforementioned redeposition effect.

Taking these aspects into account, high quality SiN_x layers were prepared by ALD at low temperatures. One particular example is that films prepared at 120 °C using BTBAS precursor and Ar/N_2 plasma were found to have excellent barrier properties against moisture.[3] Intrinsic water-vapor transmission rates in the range of 10^{-6} g/m^2/day were obtained for films as thin as 10 nm.[3] When DSBAS is used as precursor the redeposition effect appears to be reduced further, likely due to the fact this is a mono-aminosilane precursor. Precursor saturation, material quality and conformality vary with precursor and plasma employed and these aspects will be discussed in the contribution .

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4:40pm **PS+TF-WeA8 Plasma Assisted Atomic Layer Deposition of SiC_xN_y Films with Methylamine as the Carbon Source***, **Rafaiel Ovanesyan,** N. Leick, R.J. Gasvoda,* Colorado School of Mines*; K.M. Kelchner, D.M. Hausmann,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

The introduction of 3-D device architectures in integrated circuits has created a need for atomic layer deposition (ALD) of highly conformal ultra-thin films. In particular, ALD of low-dielectric-constant, carbon-containing silicon nitride (SiC_xN_y) films at temperatures ≤400 °C is required. However, controlled incorporation of C atoms into SiN_x during ALD remains challenging.

In this work, we report the C incorporation mechanism during two plasma-enhanced SiC_xN_y ALD processes. The first ALD process consisted of three steps, Si_2Cl_6/thermal CH_3NH_2/N_2 plasma, while the second process consists of two steps, Si_2Cl_6/CH_3NH_2 plasma. In both ALD processes, we have determined the film composition, reactive sites, and adsorbed surface species using in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. In addition, the growth per cycle (GPC) and refractive index were determined using in situ four-wavelength ellipsometry.

Our IR spectra show that in the first ALD process, the CH_3NH_2 thermally reacts with –$SiCl_x$ surface species created after the Si_2Cl_6 half-cycle to form -CH_x terminated surface amides. During the subsequent N_2 plasma half-cycle, in addition to nitridation of Si, a fraction of the surface CH_x groups were incorporated into the SiC_xN_y film as -N=C=N- species, which appear as a strong vibrational mode at ~2170 cm^{-1}. The composition of the SiN_x films in the two-step ALD process was very similar, with C incorporated primarily as -N=C=N- groups created during the CH_3NH_2 plasma half-cycle. We find that during the exposure of the film to Si_2Cl_6 following an CH_3NH_2 plasma half-cycle, surface carbodiimides (-N=C=NH) rearrange to nitriles (-NH-C≡N), while most of the surface is terminated with –$SiCl_x$ species. The subsequent CH_3NH_2 plasma half-cycle, shows that the-NH-C≡N species formed during the Si_2Cl_6 half-cycle are removed, and the N=C=NH surface species are restored along with –NH_x groups. For the Si_2Cl_6/CH_3NH_2 plasma ALD process, SiN_x films grown at 400 °C show a carbon content of ~4 at.% as measured through Rutherford backscattering spectroscopy combined with hydrogen forward scattering. Transmission electron microscopy shows a conformality of >95% for the SiC_xN_y films. The GPC for both processes was ~0.9 Å, with a refractive index of 1.95 and 1.86 for the N_2 plasma and CH_3NH_2 plasma ALD processes, respectively.

5:00pm **PS+TF-WeA9 Plasma Enhanced Atomic Layer Deposition in the Semiconductor Industry***, **Adrien LaVoie,*** Lam Research Corporation **INVITED**

Atomic layer deposition (ALD) has emerged as a key and enabling technology for <2X node fabrication methods in the modern semiconductor manufacturing toolbox. Today's applications range from front-end-of-line (FEOL) spacers and liners, isolation gapfill, FinFet conformal doping, multi-patterning layers, and through-Si-via (TSV) 3D liners. When considering ALD for HVM applications, the appropriate selection of platform and tool architecture is imperative with the goal of optimizing performance, reliability, cost, and throughput. In the first section, platform architecture features and requirements will be correlated to ALD market applications. In the second section, we focus on increasing throughput. Throughput demands have led to several hardware and process innovations including driving ALD towards operation in sub-saturation regimes. The greatest advantage of ALD is the self-limiting nature of the two half reactions which provides precise thickness control, extremely high film uniformity and conformality. However, the first half reaction of precursor adsorption requires saturation at longer times with diminishing growth per unit time when considering the dose saturation curve. The self-limiting nature is achieved at the expense of lower throughput and higher chemical consumption. An alternative is to perform "sub-saturated" processing in the sub-saturated regime. This presents a paradigm shift for ALD that permits conformal film deposition without satisfying saturated half reactions. Herein we demonstrate the modulation of dosing uniformity and conversion uniformity using various process parameters to achieve excellent wafer-to-wafer thickness control, within wafer non-uniformity and compositional uniformity. The utilization of the sub-saturation processing regime provides advantages in terms of throughput and chemical usage and has driven novel hardware designs.

5:40pm **PS+TF-WeA11 Substrate Biasing during Remote Plasma-ALD On Planar and 3D Substrates***, **Tahsin Faraz,*** Eindhoven University of Technology, The Netherlands*; H.C.M. Knoops,* Oxford Instruments Plasma Technology, UK*; D.M. Hausmann, J. Henri,* Lam Research Corporation*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Ion-surface interactions during plasma-enhanced atomic layer deposition (PEALD) can influence the physical and chemical properties of the growing material. The limit to which ion-surface interactions can influence the deposition process depends on the energy and flux of the ions which are governed, in principle, by various process parameters. In a low pressure, remote inductively-coupled-plasma (ICP) reactor (e.g., Oxford Instruments FlexAL) capable of producing a wide range of ion fluxes, the ion energy can be controlled independently of the ion flux if equipped with substrate biasing. Previously, our group demonstrated that the material properties of thin films deposited on planar substrates using remote plasma-ALD can be tailored by controlling the energy of the impinging ions through substrate biasing.[1]

In this contribution, we will investigate the role of the ion energy via substrate biasing during remote plasma-ALD on both planar and 3D topologies. An upgrade to enable substrate biasing (up to 100 W, 13.56 MHz RF power, -500 V resulting DC bias) has been implemented in the FlexAL system in our laboratory. PEALD processes for SiN_x, a material used as gate spacers and hard masks during CMOS fabrication, were developed using aminosilane precursors and N_2 plasma.[2] The processes were modified by incorporating a tunable RF bias signal on the substrate table during the N_2 plasma exposure step which enabled control over the energy of the nitrogen ions impinging on the growing film. SiN_x films were simultaneously deposited on planar Si wafers and 3D trench nanostructures (AR ~ 4.5 : 1) using bias powers upto 10 W (~ -65 V resulting DC bias). The planar films deposited with biasing typically exhibited lower refractive indices and densities (~ 1.71 and 2.75 g/cm^3 respectively for -65V) compared to those deposited without biasing (~ 1.93, 3.13 g/cm^3). A 30s dilute HF etch treatment was performed on the films deposited on 3D trench nanostructures. Horizontal SiN_x film regions located at the top and bottom surfaces of the trench exhibited very high wet etch rates (WER) and were completely removed after the etch. However, vertical SiN_x film regions exhibited very low WERs (~ 3 nm/min) and remained selectively at the trench sidewalls post-etch. It will be discussed that the results observed could hold potential applications in multiple patterning and area-selective processing techniques, relevant for the fabrication of state-of-the-art FinFETs and next-generation "gate-all-around" FETs.

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6:00pm **PS+TF-WeA12 A Novel ABC-type ALD Process for Cobalt using $CoCp_2$ and N_2 and H_2 Plasmas***, **Martijn Vos,** N.F.W. Thissen, A.J. Mackus, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands

Cobalt is a transition metal which is receiving much interest, among others due to its ferromagnetic properties. One of the promising applications is in multilayers and alloys of Co/Pt, which are used in nonvolatile memory devices such as magnetic random-access memory (MRAM). For many of the applications of Co the key strengths of atomic layer deposition (ALD), i.e. conformality and ultimate thickness control, can be very beneficial. In previous work, the ALD processes using cobaltocene ($CoCp_2$) and NH_3 or N_2/H_2 plasma showed a decent growth-per-cycle (GPC) and good material properties, including a low resistivity.[1,2] It was found that the best material properties were obtained for a N_2/H_2 mixing ratio of ~0.33, corresponding to the highest production of NH_3 in the plasma. This result suggests that NH_3 is necessary for obtaining high purity Co films.

In this contribution we address ALD of Co films using $CoCp_2$ and subsequent N_2 and $HH_2HHfdfd$ H_2 plasmas. By comparing this ABC process to the AB process with a combined N_2/H_2 plasma the role of NH_3 can be further investigated. Moreover the ABC process offers additional flexibility over the AB process, such as different powers and pressures during the subsequent plasma steps. Films were deposited on different substrates, including Si, SiO_2 and Pt, at temperatures from 100 to 300°C yielding a GPC between 0.2 and 0.4 Å. It will be shown that despite the absence of NH_3 in the plasma, the ABC process can be used to deposit high-purity films of Co on ALD Pt films, with contamination levels as low as 1 at.%, as measured by X-ray photoelectron spectroscopy (XPS). On the other hand, considerable amounts of C, O and N contamination (2-10 at.%) in Co films deposited on Si and SiO_2 suggest that NH_3 is a prerequisite for high purity films on these substrates. This difference between deposition on Pt and Si/SiO_2 is likely due to the catalytic activity of the Pt, causing the reduction or 'cleaning' of the deposited Co. In addition the fabrication of Co/Pt multilayers using ALD will be discussed.

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Thin Film

Room 105A - Session TF+EM+MI-WeA

Thin Films for Microelectronics

Moderators: Paul Poodt, Holst Centre / TNO, Netherlands, Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France

2:20pm **TF+EM+MI-WeA1 Impact of ALD VO_2 Film Thickness on the Electrical and Optical Properties of the Metal-Insulator Phase Transition***, **Virginia Wheeler**, B.P. Downey, J. Roussos, M. Currie, A. Giles, C. Ellis, J. Tischler, J. Caldwell, D.J. Meyer, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory

VO_2 films are known to undergo a metal-insulator phase transition (MIT) at a critical temperature (T_c = 68°C) near room temperature which results in significant changes in thermal emittance, optical transmittance and reflectance, and intrinsic electrical properties; thus attracting interest in a variety of new electronic, optoelectronic, and photonic applications. Atomic layer deposition (ALD) provides a way to obtain large area film uniformity, abrupt interfaces and angstrom-scale control of thickness conformally across planar, as well as three-dimensional, high surface area nanostructures, which could be used to integrate VO_2 films into complex electronic and optical devices for additional functionality. In this work, VO_2 electrical devices and VO_2 coated SiC-based nanoresonantors are used to investigate the impact of film thickness on electrical and optical properties.

The influence of VO_2 thickness on electrical performance was investigated using a simple two-terminal device structure. Sheet resistance measurements as a function of temperature revealed that the R_{off}/R_{on} ratio increased with increasing VO_2 thickness, up to R_{off}/R_{on} of ~7000 for a 92 nm film. Similarly, the T_c increased slightly with increasing thickness (T_c = 66^{o}C for 35nm, 73^{o}C for 92nm), while all films show relatively low hysteresis (ΔT<8^{o}C). Initial small-signal rf measurements using the 92 nm ALD VO_2 film demonstrated a cut-off frequency of greater than 1 THz, indicating the potential for rf-switch applications into millimeter wavelength frequencies using these ultra-thin ALD films, and the potential of these films to be conformally integrated into complex circuits with an ALD process.

For applications in the infrared, surface phonon-polariton-based SiC nanoresonators exhibiting strong, narrowband absorption features within the 10-12.5 µm range were coated with different thickness ALD VO_2 films. Since these films are transparent to infrared light below the Tc and reflective above the Tc, conformally coating these SiC nanostructures provides a way to add functionality to these structures by modulating the amplitude of the resonances with temperature. Initial results show that the magnitude of the resonance suppression increases with increasing VO_2 thickness and a VO_2 film thickness greater than 16nm is required to fully inhibit the signal. It was also determined that the SiC resonances become increasingly shifted and broadened with increasing thickness of the VO_2 coating. These results suggest that VO_2 can add active tunability and integrated switching to optical structures.

2:40pm **TF+EM+MI-WeA2 Study of Ru Silicidation with and without Sub-nm ALD TiN and TaN Barrier/nucleation Layers for Ru Interconnect Applications***, **Sonal Dey**,* SUNY College of Nanoscale Science and Engineering*; K.-H. Yu, S. Consiglio, K. Tapily, C.S. Wajda, G.J. Leusink,* TEL Technology Center, America, LLC*; J. Jordan-Sweet, C. Lavoie,* IBM T.J. Watson Research Center*; A.C. Diebold,* SUNY College of Nanoscale Science and Engineering

With continual shrinkage of the feature size in devices, contribution of the Cu interconnects, liners, and barrier layers to the RC time-delay is becoming a significant obstacle at the 10 nm technology node and below. Ru is a potential candidate to replace Cu as an interconnect material for ultra-scaled line widths where scaling effects on Cu line resistance become increasingly problematic. Ru has already been demonstrated to be useful as the seed layer for Cu electroplating but has been shown to be an inadequate barrier to prevent Cu diffusion into surrounding BEOL dielectrics and requires the use of an additional barrier layer such as a Ta-based nitride. In addition, TaN deposited by PVD is reaching a limit in its ability to conformally coat aggressively scaled structures in the sub 10 nm node. Accordingly, in this study we evaluated the thermal stability of thin Ru films (3 nm) with and without ultra-thin (~0.5 nm) highly conformal ALD TiN and TaN films as nucleation and/or barrier layers for Ru interconnect applications in advanced technology nodes. Si (100) substrates were chemically cleaned to remove the native oxides followed by deposition of ultra-thin ALD TiN and TaN barrier films. $TiCl_4$ and $Ta(NCMe_3)(NEtMe)_3$ precursors, along with NH_3, were used for deposition of the TiN and TaN layers, respectively. Using $Ru_3(CO)_{12}$, 3 nm of Ru was deposited by CVD on top of these refractory metal nitride films and also directly on Si. We also used PVD Cu (25nm)/Si as a control stack for our experiments. The diffusion kinetics of metal-silicide formation was evaluated using in-situ rapid thermal anneal (RTA) synchrotron x-ray diffraction (XRD) measurements and a Kissinger-like analysis to determine the transition temperatures of the metal-silicidation in these stacks and the effective activation energy (E_a) using three different ramp rates (0.3, 3, and 10 °C/s). The Ru/Si stack showed higher E_a = 2.48 eV as compared to the Cu/Si stack (E_a = 1.88 eV). A 0.5 nm thick TaN (E_a = 2.88 eV) was found to act as a more effective barrier as compared to 0.5 nm thick TiN (E_a = 2.64 eV). Scanning electron microscopy (SEM) data shows that both TaN and TiN act as nucleation layers for the growth of Ru microstructure on top. A fewer number of pin holes was observed for Ru films deposited on TaN although there was not significant change on the wettability properties of the Ru film with either TiN and TaN nucleation layers underneath. Additional physical and chemical characterization with XPS and TOF SIMS were also performed to gain understanding of the film stack properties before and after silicide formation.

3:00pm **TF+EM+MI-WeA3 2D - Material and Process Challenges of the Ultimate Thin Films in Nanoelectronics***, **Stefan de Gendt**,* KU Leuven, IMEC, Belgium*; S. Brems, D. Chiape,* IMEC, Belgium*; M. Heyne, K. Verguts,* KU Leuven, IMEC, Belgium*; R. Philipson,* KU Leuven, Belgium*; C. Lockhart de la Rosa, A. Delabie,* KU Leuven, IMEC, Belgium*; S. De Feyter,* KU Leuven, Belgium*; C. Huyghebaert,* IMEC, Belgium **INVITED**

Graphene has emerged as one of the promising candidates for post-Si electronics, both for channel (Logic, RF, sensors) and interconnect applications. Further, other two-dimensional (2D) materials such as transition metal dichalcogenides (MX2, with M a transition metal of group 4–7 and X a chalcogen) have versatile properties that complement or even supersede those of graphene. Both categories however share similar problems, related to the absence of good quality synthesis processes, subsequent layer transfer processes and doping and contacting challenges. To tackle the **first challenge** – growth – chemical vapor deposition (CVD) is widely considered to be the most economically viable method to produce both graphene and MX2 materials for high-end applications. However, in most cases, this deposition technique typically yields undesired grain boundaries in the 2D crystals, which drastically increases the sheet resistance of the layer. Strategies w.r.t. template and process development will be presented. Further, given growth temperature and template, direct growth on devices is often unfeasible, thus a **second challenge** relates to the requirement for a transfer process. For graphene, several transfer process possibilities have been evaluated, but up to now, the graphene transfer suffers from contamination often coming from the temporary support layer and/or etching products, wrinkle formation during bonding, crack formation during graphene handling, ... Moreover, with improvement in 2D quality the release from the growth template is hindered due to increased adhesion forces. At least for MX2 materials, the transfer challenge can be avoided through area selective growth. A process based on a reductive two step CVD process will be presented, whereby in a first step the metal precursor (WF6) is reduced to a lower oxidation state through sacrificial reaction with Si. Subsequently, the metallic film is allowed to react with a sulphur precursor (H2S). Challenges are again related to the (poly)crystallinity of the films and the control of lateral 2D versus crystal 3D growth. Last but not least, a **third challenge** related to 2D materials resides in the contacting and doping of these materials. Different strategies have been proposed to achieve doping, but in this presentation we will demonstrate the self-assembly of organic molecules physisorbed on top bulk and thin 2D layers as a means to achieve controlled doping.

4:40pm **TF+EM+MI-WeA8 Atomic Layer Deposition of Stoichiometric $TaSi_2$ on Si(001)**, ***JongYoun Choi**, S.W. Park,* University of California San Diego*; R. Hung,* Applied Materials Inc.

Transition metal disilicides are of great interest in Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs) due to their ability to tune the work function at the metal contact in the source/drain regions. Various kinds of transition metal silicides such as $TiSi_2$, $NiSi_2$ and WSi_2 have been studied in previous decades, however, nanoscale studies of $TaSi_2$ are relatively scarce. Previously, Lemonds *et al.* successfully demonstrated atomic layer deposition (ALD) of tantalum silicide ($TaSi_x$) on SiO_2 using TaF_5 and Si_2H_6. In this work, it is demonstrated that using similar reaction conditions $TaSi_2$ can be grown by ALD process on oxide-free clean Si(001). The growth rate of $TaSi_2$ on Si(001) was monitored *in-situ* using a Quartz Crystal Microbalance (QCM) during the deposition. This enabled optimization of the TaF_5 and Si_2H_6 dosing to avoid chemical vapor deposition (CVD) components. Scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), scanning tunneling spectroscopy (STS) and atomic force microscopy (AFM) have been used to investigate the atomic and electronic structure of Si(001) surface after $TaSi_2$ thin film deposition. HF cleaned Si(001) was used for the substrate. The chemical composition was determined by XPS after ALD to be that of a stoichiometric $TaSi_2$ film formed on the Si substrate. The key variables in forming stoichiometric $TaSi_2$ are the ratio of the precursors and the surface temperatures. In the ALD process, a 100x fold excess of Si_2H_6 is required to prevent formation of TaOx; in addition, the surface temperature must be above 240C. These requirements for excess Si_2H_6 and a high surface temperature are likely due to high activation barrier to break the residual Ta-F bonds on the surface after the TaF_4 half pulse since the Ta-F bonds are stronger than the Si-H bonds.

5:00pm **TF+EM+MI-WeA9 Different Approaches for Enhancing the Thermal Stability of $Ge_2Sb_2Te_5$ Thin Films by Carbon Addition***, **David Adams**, K. Childs, T. Gurrieri, W. Rice,* Sandia National Laboratories

Different forms of carbon-doped $Ge_2Sb_2Te_5$ chalcogenide thin films have been evaluated for potential use in phase change memory and thermal sensor applications. This includes films sputter deposited from single, carbon-doped targets and refined multilayers made by sequential deposition of chalcogenideand C layers. In both forms, the crystallization temperature (T_{cryt}) and the resistance change through crystallization vary with carbon content. Doped chalcogenide films sputter deposited from single targets exhibit increased T_{cryt} as the concentration of C is made larger. For example, films having ~7 at.% C exhibit a T_{cryt} that is approximately one hundred and fifteen degrees above that of undoped $Ge_2Sb_2Te_5$. Films with reduced C content, in the range 1-6 at.%, show intermediate crystallization temperatures. Multilayers fabricated by the sequential deposition of thin chalcogenideand C layers behave much like films grown from single targets, provided that multilayer periodicity is made small, < 3 nm. The crystallization temperature of multilayers also increases with C concentration and a prompt transition to a crystalline phase is observed when the carbon content is low. Interestingly, multilayers made with $\geq$ 9 at.% C do not transition abruptly to a crystalline state. Instead, a transformation occurs over a broad range of elevated temperature. Each form of chalcogenide thin film exhibits a decreased resistivity upon crystallization. In most cases, resistivity is reduced by 5 decades upon transforming to a face centered cubic structure or a subsequent hexagonal close packed lattice at higher temperature. The changes to microstructure and thickness associated with phase change will also be described. These film properties are investigated by cross-section and plan view electron microscopy.

This work was supported by Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.

5:20pm **TF+EM+MI-WeA10 Comparison of Electromigration and Resistivity in On-chip Co and Cu Damascene Nanowires***, **C.-K. Hu**, J. Kelly, J.H-C. Chen, H. Huang, Y. Ostrovski, R. Patlolla, B. Peethala, P. Adusumilli, T. Spooner,* IBM Research Division, Albany*; L. Gignac, S. Cohen,* IBM Research Division, T.J. Watson Research Center*; R. Long, G. Hornicek, T. Kane, G. Lian, M. Ali,* IBM Systems*; V.M. Kamineni, F. Mont, S. Siddiqui,* GLOBALFOUNDRIES

Cu metallization has been used for back end of the line (BEOL) on-chip interconnections since 1997. However, scaling Cu BEOL dimensions has increased Cu resistivity and degraded electromigration (EM) reliability. The Cu effective resistance has increased rapidly as the interconnect size has reduced and the ratio of liner area to total interconnect cross sectional area has increased. This size effect was caused primarily by increasing the probability of electron scattering with interfaces and grain boundaries. The EM lifetime degradation was caused by an increase in the volume fractions of diffusing atoms at interfaces and grain boundaries and a decrease in the void volume required to cause EM failure. It is estimated that ~ 70% of interconnect metal area could be occupied by the liner in the 5 nm technology node for reliable Cu metallization. To this end, an alternate metal, Co, was investigated. Multi-level Co BEOL was fabricated using typical 10 nm node technology wafer processing steps. A Co dual damascene process was used to fill the interconnect trenches and holes. The present Co resistivity study showed a similar size effect in Co as in Cu. This can be explained by the fact that the slope of resistivity vs. interconnect size is proportional to the product of the electron mean free path and resistivity, with the two slopes being about the same for Cu and Co. The effective resistivity difference between Co and Cu becomes small when no liner is used in Co lines. EM in 22 nm to 88 nm wide Co lines was tested using sample temperatures from 376^{o}C to 425^{o}C. Two–level EM structures consisted of either Co M1 to Co V1 to Co M2 or W CA to Co V0 to Co M1. The EM stress conditions for Co were far more severe than those for Cu. For comparison, EM in 24 nm wide Cu lines with a Co cap was also included. These data showed that both Co and Cu BEOL were highly reliable EM.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities

5:40pm **TF+EM+MI-WeA11 UV/VUV Curing Process for Low-k Organosilicate Dielectrics***, **Huifeng Zheng**, X. Guo, D. Pei, W. Li, J. Blatz, K. Hsu, D. Benjamin,* University of Wisconsin-Madison*; Y. Lin, H. Fung, C. Chen,* National Synchrotron Radiation Research Center, Taiwan, Republic of China*; Y. Nishi,* Stanford University*; J.L. Shohet,* University of Wisconsin-Madison

Porous SiCOH films are of great interest in semiconductor fabrication due to their low-k properties. Post-deposition treatments of SiCOH thin films are required to decompose labile pore generators (porogens) and to ensure optimum network formation to improve the electrical and mechanical properties of low-k dielectrics. The goal of this work is to optimize the vacuum-ultraviolet spectrum to identify those wavelengths that will have the most beneficial effect on improving dielectric properties and minimizing damage without the need for thermal heating of the dielectric. Vacuum ultraviolet (VUV) irradiation between 8.3-8.9 eV was found to increase the hardness and elastic modulus of low-k dielectrics at room temperature. Combined with UV exposure of 6.2 eV, it was found that this UV/VUV curing process compares favorably with current UV curing. The results also show that UV/VUV curing can overcome many of the drawbacks of UV curing and improve properties of dielectrics more efficiently without the need for high-temperature heating of the dielectric.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359

6:00pm **TF+EM+MI-WeA12 Effects of Cesium Ion Implantation on the Mechanical and Electrical Properties of Organosilicate Low-k Films***, **Weiyi Li**, D. Pei, X. Guo, M.-K. Cheng, S. Lee,* University of Wisconsin-Madison*; Q. Lin,* IBM Research Division, T.J. Watson Research Center*; S.W. King,* Intel Corporation*; J.L. Shohet,* University of Wisconsin-Madison

The effects of cesium (Cs) ion-implantation on uncured plasm a-enhanced chemical-vapor-deposited (PECVD) organosilicate low dielectric constant (low-k) (SiCOH) films have been investigated and compared with the effects of ultraviolet (UV) curing. The mechanical properties, including the elastic modulus and hardness, of the films were improved by up to 30% with Cs implantation, and further up to 52% after annealing at 400°C in a N2 ambient for one hour. These improvements in mechanical properties are either comparable with or better than the effects of UV-curing. These improvements are attributed to an enhancement of the Si-O-Si network structure. The k-value of the SiCOH films increased slightly after Cs implantation, and increased further after annealing. These increases are attributed to two carbon-loss mechanisms, i.e. the carbon loss due to Si-CH3 bond breakage from implanted Cs ions, and the carbon loss due to oxidation during the annealing. The time-zero dielectric breakdown strength was improved after the Cs implantation and the subsequent annealing, and were shown to be better compared with the UV-cured SiCOH films. Within the investigated range of implantation dose, an optimal dose can be found to achieve the best effects. These results indicate that Cs ion implantation has the potential to be a supplement to or a substitution for the incumbent UV curing method for processing SiCOH low-k films.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359.

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Thin Film
Room 104E - Session TF+MI-WeA
Thin Films for Magnetic and Optical Applications

Moderator: Subhadra Gupta, University of Alabama

2:20pm **TF+MI-WeA1 Tuning Static and Dynamic Magnetic Properties of FeGa/NiFe Multilayer Heterostructures via Magnetic anisotropy Dispersion***, **Colin Rementer**, Q. Xu, P. Nordeen, G.P. Carman, Y. Wang, J.P. Chang,* University of California Los Angeles

Iron-gallium (FeGa) is one of the most promising magnetic materials for use in composite multiferroics due to its high piezomagnetic coefficient (3 ppm/Oe) and high stiffness (70 GPa). It has been integrated into several multiferroic systems, but generally in MHz range or below.[1] In order to make it suitable for high frequency (GHz) applications, metalloid dopants have been used to soften magnetic materials and enhance their frequency dependent properties, but at the cost of the saturation magnetization as well as magnetoelastic properties.[2] A viable approach to circumvent this trade-off problem is to integrate a magnetic material with complementary properties into magnetic heterostructures. In this work, multilayer laminates were fabricated with FeGa and NiFe, a material with excellent properties in high frequency regimes.

FeGa (hard) and NiFe (soft) were sputtered via alloy targets with compositions $Fe_{85}Ga_{15}$ and $Ni_{81}Fe_{19}$ (at%) into multilayers with layer thicknesses ranging from 3-50 nm, with FeGa being used as the first and last layer in the stack. XPS confirmed the composition and showed there was no intermixing of the layers. Static magnetic properties were evaluated via SQUID magnetometry, and it was found that the incorporation of NiFe layers reduced the coercivity by up to 85%, from 30 Oe to 4 Oe. FMR studies showed a reduction of the linewidth of up to 50%, from 70 Oe to 38 Oe. It is believed that this effect is largely due to the decrease of magnetic anisotropy dispersion in the multilayers.[3] The multilayer films maintained a high magnetostriction of up to 190 ppm, on the same order of magnitude as giant magnetostrictive materials such as thin film Terfenol-D.[4] FeGa/NiFe heterostructures have been shown to be an excellent candidate for strain-coupled microwave multiferroics.

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2:40pm **TF+MI-WeA2 Magnetic Anisotropy of $CoFe_2O_4$ Nanotubes Synthesized by Radical-Enhanced ALD***, **Puilam(Cyrus) Cheung**, J. Chang,* University of California Los Angeles

Multiferroic materials, exhibiting ferroelectricity and ferromagnetism simultaneously, have attracted interests for energy efficient multifunctional applications at nanoscale such as memories, antennas and actuators. While room temperature single-phase multiferroic materials such as bismuth ferrite provide insufficient magnetoelectric effect, composite systems have enhanced magnetoelectric properties by combining piezoelectric materials and magnetostrictive materials through strain. However, such strain-mediated approach in thin film composites is limited by interfacial area and substrate clamping. Ferromagnetic nanowires, on the other hand, provides a new degree of freedom in manipulating magnetic properties through shape anisotropy.

In this work, cobalt ferrite ($CoFe\text{-}_2O_4$) nanotubes were grown on anodic aluminum oxide membranes using radical enhanced atomic layer deposition (RE-ALD) to study magnetic shape anisotropy. The deposition was achieved using metal tmhd precursors (tmhd = 2,2,6,6,tetramethyl-3,5-heptanedionato) and oxygen radicals at 200˚C. The ALD growth rate of cobalt ferrite was 0.18nm/cycle. Nanotubes array were formed inside the cylindrical pores of the membrane with diameter of 18nm, 35nm and 80nm. The morphology and magnetic properties of the nanotubes were studied using scanning electron microscopy, SQUID and energy dispersive X-ray spectroscopy. It was observed that as the wall thickness of the nanotube increases from 16nm to 32nm, the magnetic easy axis was switched from perpendicular to parallel to the nanowires axis, with a doubled saturation magnetization of $5.12x10^5$ emu. The out-of-plane anisotropy field was observed to be 18.7% higher than that from in-plane axis, indicating the out-of-plane axis was magnetically more favorable. As cobalt ferrite nanowires were formed, the preferential easy axis was reversed, which could potentially be implemented in manipulating of magnetization orientation if coupled to a piezoelectric material for device applications.

3:00pm **TF+MI-WeA3 Magnetic Anisotropy and Relaxation in Spintronic Materials***, **Claudia Mewes**, T. Mewes, J. Beik Mohammadi, A. Farrar, K. Cole,* The University of Alabama **INVITED**

Functional materials with optimized properties, such as the magnetic anisotropy and magnetic relaxation rate, are crucial for the next generation of spintronic devices. Therefore technological progress in this area depends heavily on the successful search for new materials as well as on a deeper understanding of the fundamental mechanisms of the magnetic relaxation and the magnetic anisotropy. This talk will focus on different aspects which can influence the magnetic relaxation as well as the magnetic anisotropy within a confined device setting.

For many spintronic applications the use of thin films with perpendicular anisotropy is often essential for the functionality of the device. For example the use of thin films with perpendicular anisotropy in spin transfer torque magnetic random access memories (STT MRAMs) leads to a reduction of the current density needed to switch the device state. In addition to the perpendicular anisotropy it is often crucial to have materials with a low magnetization relaxation rate. Therefore many spintronic applications rely on ultra-thin magnetic films with a low magnetization relaxation in which the perpendicular anisotropy is created through surface anisotropy. This approach is very sensitive to the interface morphology and chemical environment. In this talk I will discuss the effect of spatial fluctuations of the first order perpendicular anisotropy in thin films and its influence on the effective anisotropy for these materials.

Similar to the magnetic anisotropy the magnetic relaxation in thin ferromagnetic films can be affected by neighboring layers. Spin pumping is a well-known contribution that has to be taken into account for practical applications using multilayer structures. More recently a strong unidirectional contribution to the relaxation in exchange bias systems has been observed experimentally. To describe this phenomenon theoretically we use the formalism of an anisotropic Gilbert damping tensor that takes the place of the (scalar) Gilbert damping parameter in the Landau-Lifshitz-Gilbert equation of motion. In this talk I will discuss this approach to study the modified magnetization dynamics under the influence of unidirectional damping.

ACKNOWLEDGMENTS

C.K.A. Mewes acknowledges support by the NSF-CAREER Award No. 1452670, T. Mewes acknowledges support by the NSF-CAREER Award No. 0952929.

4:20pm **TF+MI-WeA7 Vacuum Furnace Annealing Block Copolymers for Bit Patterned Advanced Media***, **Allen Owen**, S. Gupta,* University of Alabama

Hard disk drive storage media is trending towards both smaller physical size and greater storage capacity, there by increasing the areal density of the magnetic storage media. Bit patterning shows potential as a method for increasing this areal density. A block copolymer template can be used to provide an etch mask for bit patterning a magnetic thin film. A statistical design of experiments was carried out to optimize the effect of nanopatterning via ion milling Co/Pd multilayers for PS-PFS block copolymers. The design of experiments varied the etch angle and etch time during ion milling. Samples that were sputter-deposited with Co/Pd multilayered thin films were spin-coated with PFS block copolymer and vacuum furnace annealed at 140 °C for 48 hours at a pressure of ~5 x 10^{-5} Torr. After vacuum furnace annealing, the films were ashed in oxygen plasma to remove the PS, leaving the PFS spheres as masks for the subsequent ion milling. The stack used was Pd5/$[Co0.3Pd1.0]_{14}$ /Pd 5 nm sputter deposited onto a Si substrate. The as deposited coercivity was ~1.3 kOe. After ion milling for 2 min at an angle of 45°, the coercivity was found to be ~0.6 kOe. Ion milling at 45° for 4 min resulted in a coercivity of ~0.07 kOe. This is in comparison with previous experiments using thermal annealing in atmosphere and solvothermal annealing with heptane, where the coercivity increased at ~4 min at the same 45° ion milling angle. The difference can be explained by the fact that for the previous experiments, the stack used was Ta5/[Co0.3Pd1.0]$_{14}$/Ta5 nm. The Ta capping layer must be more resistant to ion milling than Pd, which means the ion milling times must be adjusted to transfer the bit pattern to the media.

4:40pm **TF+MI-WeA8 Atomic Layer Deposition Enabled Synthesis of Miltiferroic Composite Nanostructures***, **Jeffrey Chang**, A. Buditama,* University of California at Los Angeles*; A. Rosenberg,* Stanford University*; L. Kornblum,* Yale University*; S.H. Tolbert,* University of California at Los Angeles*; K.A. Moler,* Stanford University*; C.H. Ahn,* Yale University*; J.P. Chang,* University of California at Los Angeles

Multiferroic materials, which exhibit controllable ferromagnetic (ferroelectric) properties via electric (magnetic) field, are of great interest due to their potential in enabling new device applications. Due to the scarcity of single-phase multiferroics in nature and their weak responses at room temperature, composite multiferroics are proposed to realize robust multiferroic behaviors by coupling the functional properties from the constituent phases. A strain-mediated coupling strategy is achieved by interfacing magnetostrictive ferromagnets with piezoelectric materials, where the interfacial area per volume, as well as the material crystallinity, play important roles in the attainable functional properties. With the aim of enhancing the composite magnetoelectric behavior by nanostructuring, atomic layer deposition (ALD), with its high quality and conformal film growth, shows considerable potential in achieving high quality multiferroic composites with industrial scalability.

In this work, lead-free ferroelectric/antiferromagnetic $BiFeO_3$ (BFO) and ferrimagnetic $CoFe_2O_4$ (CFO) thin films were grown on $SrTiO_3$ (001) substrates by ALD using tmhd-based metalorganic precursors(tmhd =2,2,6,6-tetramethylheptane-3,5 dione). The use of oxygen radicals as the oxidant provides a low temperature process capability at ~200°C. The growth rates for BFO and CFO are ~3.3Å/cycle and ~2.4Å/cycle, respectively. The BFO films showed epitaxial single crystalline growth in (001) pseudocubic orientation after being annealed under 650°C, while the CFO films are oriented polycrystalline due to the lattice mismatch between the film and substrate. The BFO piezoelectric properties were confirmed using piezo force microscopy, while tunable CFO magnetic properties were demonstrated by thickness-related strain relaxation measurements.

Multiferroic composite nanostructures were synthesized by implementing ALD processes with different substrates. Room-temperature magnetoelectric behaviors ($\alpha \approx 64\times10^{-3}$ Oe cm/V) and tunable magnetic anisotropies were observed in the BFO/CFO system with 2-2 and 1-3 orientations, respectively. The microscopic magnetic domain structures were characterized by the scanning SQUID systems. 0-3 CFO/PZT composites were enabled by using mesoporous PZT structures. The change in lattice parameters after poling was observed by high-resolution XRD measurements, showing that the strain interactions lead to the magnetoelectric behavior in the composite. Besides, the integration of the BFO/CFO system onto Si platforms demonstrated the versatility of the ALD processes, illustrating a path for integrating novel multiferroic materials into current industrial processes by ALD.

5:00pm **TF+MI-WeA9 Thin Film Challenges for High Performance Ir Plasmon Enhanced Photodiodes: from Simulation to Focal Plane Array Integration and Characterization***, **François Boulard**,* Univ. Grenoble Alpes, France*; O. Gravrand,* Univ. Grenoble Alpes,France*; D. Fowler,* Univ. Grenoble Alpes, France*; G. Badano,* Univ. Grenoble Alpes, France*; P. Ballet,* Univ. Grenoble Alpes, France*; M. Duperron,* Univ. Grenoble Alpes, France*; L. Adelmini, R. Espiau de Lamaestre,* Univ. Grenoble Alpes, France **INVITED**

For several decades now, Surface Plasmons (SP) have been increasingly studied for applications in many fields from chemistry, biology, to materials science. In the IR sensor community, the use of SPs to concentrate and channel light offers new possibilities to increase sensitivity or modify spectral response. However, the incorporation of metallic nanostructures in technologically mature components is challenging. This paper deals with the design and integration of a sub-wavelength photonic structure to add spectral functionalities to mid wave and longwave IR HgCdTe photodiodes. Based on simulation and experimental results, tradeoffs to reach the full potential of SP enhancement are discussed. The relationship between the metallic grating geometry and the excited optical mode is illustrated using numerical simulations. The agreement between the simulated and measured spectral response and dispersion relation on a test photodiode array is shown. The influence of the absorber, passivation, and adhesion layer properties and thicknesses on the resonance intensity and photodiode noise is experimentally illustrated. Finally, results of multicolor midwave IR focal plane arrays with shot noise limited operation and less than 0.3% defective pixels are presented.

6:00pm **TF+MI-WeA12 Watching Thin-film Aluminum Oxidize***, **David Allred**, M. Miles, S. Thomas, S. Willett, M.J. Greenburg, A. Vance, R.S. Turley,* Brigham Young University

In three years NASA will be in the midst of its decadal review, establishing priorities for the 2020s. Very likely one of the chief astrophysical missions will contain a LUVOIR (large, UV-optical-IR) telescope. This space-based observatory will likely contain the largest mirrors ever flown and will probe the cosmos seeking to address key questions of the origin, current status and evolution of our universe. These investigations will profit from a truly broad-band mirrors. Thus, the reflective coating will almost certainly be aluminum. To be viable, the top surface of such a space mirror needs to be bare without the tarnish layers that naturally form in air. This could open up the 11-15eV band for space-based astrophysics without sacrificing IR, visible and UV reflectance. We report on two techniques aimed at clarifying the oxidation mechanism for Al. First, we have used VUV (>10 eV) reflectometry of bare, freshly deposited aluminum mirrors as they age in controlled atmospheres, and second, variable-angle, spectroscopic ellipsometry is shown to be capable of measuring changes at the angstrom level in multilayers consisting of aluminum, protected by various vacuum-applied barrier layers. These ultrathin barrier layers included polymers such as parylene and inorganic films, such as MgF_2 and AlF_3. For example, we saw that the growth in oxidation thickness of aluminum protected by a 7nm MgF_2 film is logarithmic over a period of time of more than 1000 hrs.

Electronic Materials and Photonics
Room 102A - Session EM+AC+SS+TF-ThM

Radiation Detection Materials and Devices

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

8:00am **EM+AC+SS+TF-ThM1 Novel High Energy Resolution Scintillator Detectors*, Arnold Burger*,** *E. Rowe, L. Matei, P. Bhattacharya, M. Groza,* Fisk University*; K. Stassun,* Vanderbilt University*; A. Stowe,* Consolidated Nuclear Security Y-12*; N. Cherepy, S. Payne,* Lawrence Livermore National Laboratory **INVITED**

This presentation will review the status of bright scintillators for gamma and thermal neutrons applications. The scintillators are based on single crystals of halides or selenides that are activated by rare earth ions or are self activated. The main features that make them attractive for biological, medical, space and national security applications are: (i) high stopping power of radiation, (ii) high energy resolution, (iii) fast decay time, (iv) crystal growability at low cost, (v) good gamma/neutron discrimination via pulse shape analysis, and (vi) good spectral matching with silicon photodetectors for compact and low power devices and instrumentation.

8:40am **EM+AC+SS+TF-ThM3 Improved p–n Heterojunction Device Performance Induced by Irradiation in Amorphous Boron Carbide Films*, George Peterson*,** *Q. Su,* University of Nebraska - Lincoln*; Y. Wang,* Los Alamos National Laboratory*; P.A. Dowben, M. Nastasi,* University of Nebraska - Lincoln

Amorphous hydrogenated boron carbide films (a-B$_{10}$C$_{2+x}$:H$_y$) on Si p–n heterojunctions were fabricated utilizing plasma enhanced chemical vapor deposition (PECVD). These devices were found to be robust when irradiated with 200 keV He$^+$ ions. For low doses of irradiation, contrary to most other electrical devices, the electrical performance improved. On the heterojunction I(V) curve, reverse bias leakage current decreased by 3 orders of magnitude, series resistance across the device decreased by 64%, and saturation current due to generation of electron–hole pairs in the depletion region also decreased by an order of magnitude. It is believed that the improvements in the electrical properties of the devices are due to an initial passivation of defects in the a-B$_{10}$C$_{2+x}$:H$_y$ film resulting from electronic energy deposition, breaking bonds and allowing them to reform in a lower energy state, or resolving distorted icosahedron anion states.

9:00am **EM+AC+SS+TF-ThM4 Amorphous Hydrogenated Boron Carbide for Direct-Conversion Solid-State Neutron Detection*, Gyanendra Bhattarai*,** *T.D. Nguyen, S. Dhungana, A.N. Caruso, M.M. Paquette,* University of Missouri-Kansas City

The trade-off between conversion layer thickness and penetration depth of primary reaction products inherently limits the efficiency of conversion-layer solid-state neutron detectors, motivating the need for direct-conversion solutions. Direct-conversion devices, in principle, offer nearly unity detection efficiency, a minimum of fabrication steps, large-area scalability, and high efficiency density, all of which are essential for small-sized neutron spectrometers as well as for large-area detectors. However, to date, there is a lack of well-developed semiconductor materials with high thermal neutron absorption that also lead to energetic reaction products amenable to detection. Amorphous hydrogenated boron carbide (a-B$_x$C:H$_y$), a complex disordered semi-insulating material, is a promising candidate because of its high neutron absorption and high resistivity. Additionally, excellent mechanical, chemical, and thermal stability make it suitable for harsh detection environments. The main challenges, however, in the study of a-B$_x$C:H$_y$ are its low charge carrier mobility, the difficulties associated with making proper electrical contacts for accurate charge transport measurements, and the inefficacy of traditional experimental techniques and interpretations to address the complex nature of the material (i.e., it is a high-resistivity, disordered, molecular solid). This contribution will present an overview of how a-B$_x$C:H$_y$ may lead to high-efficiency neutron detectors based on theoretical simulations, the study of its charge transport metrics focusing mainly on charge carrier mobility and lifetime, and the development of proper electrical contacts on PECVD grown thin films of this material.

9:20am **EM+AC+SS+TF-ThM5 Radiation Damage of Low-κ Interlayer Dielectrics Studied with Electrically Detected Magnetic Resonance*, Michael Mutch*,** *P.M. Lenahan,* Pennsylvania State University*; S.W. King,* Intel Corporation

Radiation effects of MOS devices have been extensively studied due to the demand for electronic devices in space applications.[1] The scaling of these MOS devices will lead to an eventual need for low-dielectric constant (i.e., low-κ) dielectrics to reduce parasitic capacitances associated with scaling of back-end-of-line interlayer dielectrics (ILDs). However, little is known about radiation effects of low-κ ILDs. We utilize electrically detected magnetic resonance (EDMR) via spin-dependent trap-assisted tunneling (SDTAT) to study point defects in porous low-κ a-SiOC:H systems before and after exposing samples to radiation damage. SDTAT/EDMR has the sensitivity and analytical power to specifically identify only those defects which are involved in electronic transport. Due to the inherent complexity of the a-SiOC:H systems, multiple frequency EDMR is utilized to better understand defect structure when featureless spectra are present.

The a-SiOC:H films are grown via PECVD, and exhibit carbon dangling bonds prior to porogen removal via UV-annealing.[2] After porogen removal via UV treatment, it has been shown, via multiple frequency EDMR, that silicon dangling bonds are the dominating defect center responsible for SDTAT in these films.[2] The porous a-SiOC:H systems were subjected to a 15 Mrad total dose via a cobalt-60 dry cell gamma-ray source while simultaneously applying either positive, negative, or no bias. We find that the post-radiation IV curves are a strong function of the biasing conditions which were applied during radiation. This likely indicates that electron and hole traps will both play a role in radiation damage effects in these systems. We find that the EDMR response amplitude is greatly increased (by a factor of 4 or greater) after irradiation for all biasing conditions. This result indicates a substantial increase in the density of defects involved in electronic transport. Multiple frequency EDMR measurements suggest that the generated defects are primarily silicon dangling bonds.

[1] J. R. Schwank et al., IEEE Trans. Nuc. Sci. **55**, 1833 (2008).

[2] M. J. Mutch et al., J. Appl. Phys. **119**, 094102 (2016).

9:40am **EM+AC+SS+TF-ThM6 Modeling Unit Displacement Damage in Amorphous Silicon Oxycarbides*, Hepeng Ding*,** *M. Demkowicz,* MIT

Amorphous silicon oxycarbide (SiOC) is of great technological interest. To study its potential application as a radiation-resistant material, we present *ab initio* modeling investigations of unit displacement damage processes in it using density functional theory. We model 0.1 keV primary knock-on atoms (PKA) in SiO$_2$, SiOC, and hydrogenated SiOC (SiOCH) with different hydrogen levels. We find that PKAs affect the carbon-clustering tendency in both SiOC and SiOCH. Our results also suggest that SiOCH is irradiation indifferent, i.e., upon PKA, the potential energy does not increase and there is no major structural change.

This work was funded by the DOE Office of Nuclear Energy, Nuclear Energy Enabling Technologies, Reactor Materials program, under contract No. DE-NE0000533. Computational support was provided by DOE-NERSC and DOE-OLCF.

11:00am **EM+AC+SS+TF-ThM10 Position-Sensitive 3D CZT Gamma-Ray Detectors with Thickness Up to 50 mm*, Ralph James*,** *A.E. Bolotnikov, G.S. Camarda, Y. Cui, G. De Geronimo, J. Fried, A. Hossain, G. Mahler, U. Roy, E. Vernon, G. Yang,* Brookhaven National Laboratory **INVITED**

High-granularity position-sensitive detectors allow for accurate charge-signal corrections to overcome non-uniformities in the devices' responses caused by crystal defects. The operational principle of position-sensitive detectors is analogous to the well-known drift ionization chambers used for tracking charged particles and detecting the interaction events generated by gamma rays. Advantages of the position-sensitive designs were realized in a number CZT detectors, including CAPture™, hemispherical, Frisch-ring, capacitive Frisch-grid and even pixel detectors in which pixel contacts act like shielding electrodes. In our virtual Frisch-grid (VFG) devices, the sensing strips are separated from the crystal surfaces by a thin insulating layer, as it was originally done in other Frisch-grid designs. The amplitudes of the signals readout from the strips are used to measure the coordinates of the interaction points and correct the response non-uniformities. The drift time and the cathode-to-anode ratio were used to independently evaluate the location of the interaction points in Z directions, correct for electron loss, and identify and reject the events for which the charge losses caused by defects are so great that they cannot be corrected accurately. Combining these two techniques allows us to significantly enhance the spectral responses of position-sensitive VFG detectors, and to significantly improve their performance. Such high-granularity position-sensitive detectors open up the opportunity for using thicker, less expensive crystals. We demonstrated that today's CZT material is suitable for detectors with up to 40-50-mm drift distances, provided that the detectors have the ability to correct their response non-uniformities on a scale comparable to the sizes of electron clouds, which is ~100 m m. We employed an ASIC and data-acquisition system developed by BNL's Instrumentation Division for arrays of VFG detectors. For each detector we used 6 ASIC channels to read the negative signals from the cathode and from four position-sensing pads, and the positive signals from the anode. For each interaction event, the anode signal correlates with the *X* and *Y* values converted from the 4 strip signals and Z coordinate evaluated from the cathode signal. This relationship allows us to correct each anode signal in accordance with the location of the interaction point. We selected the voxel sizes to achieve the best performance, typically ~30x30 pixels in *XY*-space and ~100 segments in the Z-direction. The performance of thick position-sensitive VFG detectors fabricated from CZT crystals will be reported for a variety of radioactive sources and testing conditions.

11:40am **EM+AC+SS+TF-ThM12 Understanding the Electrical Properties of U_3O_8 for Direct Conversion Neutron Detectors**, ***Brandon Shaver**, S. Lawson, B. Musicó,* The University of Tennessee Knoxville*; S. Dhungana, G. Bhattarai, M.M. Paquette, A.N. Caruso,* University of Missouri-Kansas City*; T. Meek,* The University of Tennessee Knoxville

With a high neutron fission cross section for ^{238}U, U_3O_8 is one of a series of uranium oxide semiconductors that may be suitable for direct-conversion neutron detectors. However, the electrical transport properties of U_3O_8 are not well-characterized: the literature that does exist reports largely inconsistent resistivity values, and similarly contradictory values for work function. One of the reasons for these wide ranges is that slight changes in stoichiometry in urania-based systems, UO_2 for example, can have a tremendous influence on electrical properties; however, the details of these effects are not well-understood. We seek to rigorously characterize the electrical transport properties in U_3O_8 to understand the range of values that can be achieved and—importantly—their relationship to fabrication method as well as composition/microstructure. Samples of U_3O_8 pellets have been made by uniaxial pressing of U_3O_8 powder and subsequent sintering under various conditions. These samples have then been characterized to determined their microstructure, exact stoichiometric composition, and electrical properties. By carefully studying the relationship between sample preparation and electrical properties, we aim to establish the ability to control and optimize the electrical transport metrics of U_3O_8 critical for detection applications.

12:00pm **EM+AC+SS+TF-ThM13 Radiation Damage in 4H SiC nMOSFETs Detected by Electrically Detected Magnetic Resonance**, ***Ryan Waskiewicz**, M.A. Anders, P.M. Lenahan,* Pennsylvania State University*; A.J. Lelis,* U.S. Army Research Laboratory

Metal oxide semiconductor field effect transistors (MOSFETs) based upon 4H-SiC have great promise in high power and high temperature applications. An area of substantial interest is in outer space, where the devices will be subjected to ionizing radiation. The effects of ionizing radiation have been well studied in Si-based MOS devices, where E' and Pb centers play dominating roles as oxide and interface traps respectively. Very little is known about the types of defects created in radiation damage in SiC MOSFETs. In order to develop a fundamental understanding of ionizing radiation effects, we have performed a study utilizing electrically detected magnetic resonance (EDMR) via the bipolar amplification effect (BAE) [1]. We observe several changes between the pre- and post-irradiation EDMR results, which strongly indicate change in the structure of the SiC/SiO_2 interface region but relatively little change in the number of observed interface defects.

The devices used in this study had 50 nm thick thermally grown gate oxides in N_2O. After oxidation, the devices were subjected to the standard post-oxidation NO anneal at 1175°C. The n-channel 4H-SiC MOSFETs have been subjected to 6MRads of gamma radiation from a 60Co gamma source while a 10V bias applied to the gates. Standard transistor characteristic measurements made on the devices before and after irradiation indicate a threshold voltage shift of approximately -4V. We observed several significant changes in the EDMR response, the most obvious EDMR differences are in the amplitude of the BAE EDMR measurements as a function of applied gate voltage. The maximum EDMR amplitude increased by a factor of 7 as a result of the irradiation, and the gate bias at which the peak occurred shifted by approximately -4V, consistent with the approximate -4V shift in threshold voltage. BAE measurements measure spin dependent recombination due to deep level defects at and very close to the SiC/SiO_2 interface. We find significant change in the EDMR line shapes, observing significant post-irradiation broadening of the spectra. Surprisingly, we are unable to observe either silicon or carbon dangling bond defects in these preliminary measurements. It is clear from the measurements that both the pre-irradiation and post-irradiation measurements are dominated by silicon vacancies on the SiC side of the interface. EDMR measurements as a function of microwave power show quite significant changes in the saturation behavior of the magnetic resonance. These results suggest significant structural changes in the interface region.

[1] Thomas Aichinger and Patrick M. Lenahan, Appl. Phys. Lett. **101**, (2012)

Thin Film
Room 104E - Session TF1-ThM
Control and Modeling of Thin Film Growth and Film Characterization

Moderators: Berc Kalanyan, National Institute of Standards and Technology (NIST), Richard Vanfleet, Brigham Young University

8:00am **TF1-ThM1 Adventures in Group IV Ordering: Super-periodicities at the Atomic/Nano/Meso/scale**, ***Jerrold Floro**, J. Amatya, C. Duska, C.W. Petz,* University of Virginia*; D. Yang, J. Levy,* University of Pittsburgh **INVITED**

This talk will examine the perils, pitfalls, and possibilities for creating order across different lengthscales and dimensionalities in heteroepitaxial Group IV thin films and nanostructures. I will review our results in three projects: (i) Direct writing of ordered arrays of 3C-SiC quantum dots on Si (001); (ii) Directed self-assembly of 2D and 3D ordered arrays of Ge quantum dots on Si (001); and (iii) chemical ordering in $Si_{1-x}Ge_x$ alloys on Si (001). Herein, all the materials are grown by molecular beam epitaxy. Even though Group IV materials are amongst the most heavily studied epitaxial growth systems, in all three cases discussed here there were significant surprises, some "good" and some "bad". First I will briefly review our goal of using carbonaceous bumps, written on Si (001) by fine-spot electron-beam cracking of hydrocarbons, to direct the self-assembly of Ge quantum dots. We did not observe the latter to occur, but the formation of epitaxial 3C-SiC was itself interesting, and the carbide dots were successfully encapsulated in a Si matrix under optimized overgrowth conditions. We then used Ga focused ion beams (FIB) to create surface morphology that directs the self-assembly of Ge quantum dots. Atomic force microscopy (AFM) showed beautiful long-range order, both in single layers of dots, and in multiple layers of dots. However, cross-section transmission electron microscopy told a rather different story to the AFM, and this ultimately led us to abandon FIB as our patterning method of choice, in favor of electron beam lithography (ongoing). Finally, we recently revisited *chemical* ordering in $Si_{1-x}Ge_x$ alloys, which was intensively studied in the 1990's. Our work was driven by predictions that chemical ordering, with large order parameters, could produce observable effects on thermal transport, and likely on electrical transport as well. This could improve the thermoelectric figure of merit. However, despite an extensive survey of growth-parameter space, we never observed order parameters to exceed 0.24. We found it necessary to be very careful in our quantification of the order parameter. More interestingly, our results seem to suggest three mutually inconsistent results with regard to how ordering is affected by step density. Hence there is much more to be understood about the interactions of strain, steps, faceting, and dislocations on chemical ordering. We gratefully acknowledge the support of the Department of Energy Office of Basic Energy Sciences, the II-VI Foundation, and the National Science Foundation Division of Materials Research. Research was performed in part at the NIST Center for Nanoscale Science and Technology.

8:40am **TF1-ThM3 Combinatorial Fabrication of $Cu-Fe_2O_3$ Composite Nanostructures by Oblique Angle Co-Deposition**, *S. Larson, W.J. Huang,* ***Yiping Zhao**,* University of Georgia

Traditionally, new materials have been explored and discovered via the one by one trial-and-error method. This can require decades of research to identify and optimize a material system for technological application and commercialization. From an experimental point of view, to speed up materials discovery, a large amount of materials need to be synthesized/fabricated and characterized simultaneously. Such a parallel production and characterization process has been traditionally targeted by a so-called high throughput or combinatorial materials science. The adaptation of the combinatorial techniques to nanofabrication has been slow due to the complexity and variety of fabrication techniques. To-date, only few groups have realized combinatory nano-synthesis via multi-well hydrothermal and solvothermal methods. However, based on combinatory thin film deposition technique and shadowing growth mechanism, a new and versatile combinatory nanofabrication technique called the oblique angle co-deposition can be easily facilitated. It can be used to generate a library of nanomaterials with different morphology and structure. In this talk we demonstrate the feasibility of such a nanofabrication technique. Using the Cu-Fe_2O_3 system as an example, by carefully characterizing the vapor plumes of the source materials, a composition map can be generated, which is used to design the locations of all the substrate holders. The resulting nanostructures at different locations show different thickness, morphology, crystallinity, composition, as well as inhomogeneity in microstructures. In addition, material maps of all these structural parameters are established, which can be used to correlate their properties. By further oxidizing or reducing the composite nanostructures, the properties of the nanostructures such as band gap, photocatalytic performance, and magnetic properties can be easily linked to their composition and other structural parameters. Optimal materials for photocatalytic and magnetic applications are efficiently identified. It is expected that the oblique angle co-deposition and its variations could become the most powerful combinatory nanofabrication technique for nanomaterial survey.

9:00am **TF1-ThM4 Structural and Electronic Properties of Titanium Doped Ga_2O_3 Thin Films**, ***Sandeep Manandhar***, *E. Rubio, C.V. Ramana,* The University of Texas at El Paso

Gallium oxide (Ga_2O_3) has garnered significant interest due numerous applications of this material in gas sensing, optoelectronic devices, transparent electronic devices, and spintronics. From optical applications point of view, Ga_2O_3 finds attractive applications in luminescent phosphors, antireflection coatings, and solar cells. Ga_2O_3 has been recognized as a deep ultraviolet transparent conducting oxide (UV–TCO), which makes the material a potential candidate for transparent electrode applications in UV optoelectronics. However, while the large band gap makes it useful for far UV applications, it is possible to tune the properties and make it suitable for visible or low-UV applications if the band gap and electrical conductivity of Ga_2O_3 thin films are tuned. In this context, we propose and investigate to modify the properties of Ga_2O_3 by selectively doping with titanium (Ti). β-Ga_2O_3 thin films with variable Ti content were deposited by co-sputtering of the Ga-oxide ceramic and Ti metal by varying the sputtering power applied to these targets. The effect of Ti on the crystal structure and optical properties of β-Ga_2O_3 thin films is significant. For low Ti-content, films crystallize in β-phase of Ga_2O_3. However, increased Ti content induces amorphization of the Ga_2O_3 thin films. Band gap values showed a corresponding shift from ~5 eV to lower side indicating that the Ti incorporation induce changes in the electronic structure. A correlation between Ti-chemistry, structure and optical properties of Ga-Ti-O films will be discussed.

9:20am **TF1-ThM5 Characterizing Patterns and Order in Self-Assembled Langmuir Films of Quantum Dots**, ***Zachary Whitfield***, *J.J. Weimer,* University of Alabama in Huntsville

The goal of this analytical study is to establish methods to quantify the uniformity of self-assembled Langmuir monolayers of quantum dots (QDs) in an efficient and reliable manner. Gradient-core quantum dots (QDs) were selected for creating the thin films because of their growing popularity for use in industries. The QDs were cast as Langmuir films on a water subphase, and the Langmuir films were deposited onto substrates using the Langmuir-Schafer (LS) technique. Images were taken using an iSight digital camera of both the Langmuir and LS films with a black light source. Agglomerations, voids, islands, and ridges were some of the artifacts found when surveying the Langmuir films. These artifacts were seen to template directly to the LS films. Emission spectra of the LS films were mapped using fluorescence spectroscopy. Scanning probe microscopy was also performed to study surface morphology of samples. Image processing software was used to quantify the intensities of the variations at different spatial locations across the films. A direct correlation was made between the spatial variations in image brightness and the intensities of fluorescence spectra at the same given point on the LS films.

9:40am **TF1-ThM6 Radical-Based MBE Growth, Structure, Defects and Transport in High-Mobility Epitaxial La-doped $BaSnO_3$ Films**, *A. Prakash, P. Xu, J. Dewey,* ***Bharat Jalan***, University of Minnesota

We will present on the growth of phase-pure, epitaxial $BaSnO_3$ films using a novel radical-based molecular beam epitaxy (MBE) approach with scalable growth rates [1]. In this approach, we use a metal-organic precursor (hexamethylditin) as a tin source, a solid effusion cell for barium, and an rf plasma source for oxygn. $BaSnO_3$ films were grown on $SrTiO_3$ (001), $LaAlO_3$ (001) and LSAT (001) substrates. The substrate temperature and oxygen pressure were kept fixed at 900° C, and $5x10^{-6}$ Torr respectively whereas Ba/Sn beam equivalent pressure (BEP) ratio was varied to optimize cation stoichiometry. The unstrained lattice parameter determined using high-resolution X-ray diffraction, and the Rutherford backscattering spectroscopy (RBS) were used to optimize cation stoichiometry. Lanthanum was used as n-type dopants.

Stoichiometric composition yielded an unstrained lattice parameter value of 4.116±0.001Å, which is identical to that of bulk $BaSnO_3$. This value was found to increase for Ba-rich films whereas Sn-rich films resulted into secondary phase formation. A range of Ba/Sn flux ratio was identified where films cation stoichiometry was self-regulating indicating the presence of a "MBE growth window". Time-dependent reflection high-energy electron diffraction (RHEED) intensity oscillations were observed during film growth indicating films grew in a layer-by-layer fashion. Atomic force microscopy confirmed smooth surface morphology for stoichiometric films. Non-stoichiometry films showed surface nanocrystallites, which correlated with the film stoichiometry. Most remarkably, phase-pure $BaSnO_3$ could also be grown with the molecular oxygen (i.e. without any rf plasma) suggesting an important role of reactive radical chemistry during film growth. We will discuss these results in the context of highly reactive Sn radicals growth mechanism that assist with the reaction and compound formation.

Finally, we will present a comprehensive electrical characterization of La-doped $BaSnO_3$ and will discuss how electrical transport is influenced by the presence of structural defects such as dislocations, non-stoichiometry, and dopant concentration. We will also present different scattering mechanisms in La-doped $BaSnO_3$ that limits the room temperature electron mobility. We will present pathways to suppress these scattering rates - a step closer towards defect-managed high mobility oxide thin films and heterostructure.

Work supported by the NSF, and the AFOSR YIP Program.

[1] A. Prakash, J. Dewey, H. Yun, J.S. Jeong, K.A. Mkhoyan, and B. Jalan, “Hybrid molecular beam epitaxy for growth of stoichiometric $BaSnO_3$”, J. Vac. Sci. Technol. A, **33**, 060608 (2015).

11:00am **TF1-ThM10 Reduction of Extended Defects in SiC Epilayers Grown on 2° Offcut Substrates**, ***Rachael Myers-Ward***, *N. Mahadik, R. Stahlbush, P. Klein, K.M. Daniels, A. Boyd, K. Gaskill,* Naval Research Laboratory

Silicon carbide is a material of interest for high-voltage and high-power switching device applications. Basal plane dislocations (BPDs) are a major concern for SiC bipolar devices as they source Shockley-type stacking faults in the presence of an electron-hole plasma and reduce minority carrier lifetimes. Many researchers have investigated methods to reduce the BPD density by experimenting with pre-growth treatments, substrate orientation, growth parameters and growth interrupts. This work investigates extended defects, morphology and lifetime in 4H-SiC epilayers grown on substrates offcut 2° toward the [11-20].

Epilayers were grown on 2° offcut substrates in a horizontal hot-wall reactor using the standard chemistry of silane (2% in H_2) and propane. Epilayers were grown at various growth rates, C/Si ratios, and growth temperatures. The pressure was maintained at 100 mbar for all growths. Some samples were grown with a 5 µm highly doped n^+ buffer layer using ultra high purity nitrogen prior to the low doped epilayers. Ultraviolet photoluminescence (UVPL) imaging was used to identify BPDs in the low doped epilayers. Time resolved photoluminescence measurements were performed to determine the minority carrier lifetime of the layers and Raman spectroscopy was used to analyze polytype inclusions. Electron trap concentrations were determined using deep level transient spectroscopy (DLTS). Surface roughness was measured by atomic force microscopy and the morphology was also characterized using Nomarski microscopy.

When a 15 µm epilayer was grown without a buffer layer, step bunching was observed and the surface roughness was 6.0 nm RMS. For comparison, a standard 4° offcut sample typically has 3.0 nm RMS for a 20 µm epilayer. Using UVPL, it was found that after 4 µm of epi, 90% of the BPDs had converted in the low doped layer as compared to 70% in a 4° offcut sample, indicating the conversion is faster in the lower offcut material. 3C-SiC inclusions were present in the epilayers as verified using Raman spectroscopy for both unintentionally doped (UID) and N+ epilayers. These inclusions were reduced by increasing the growth temperature and lowering the C/Si ratio for N+ epilayers, but increasing C/Si ratios for UID films. Changing these growth parameters resulted in specular film morphology and resulted in minority carrier lifetimes on the order of 1 µs.

11:20am **TF1-ThM11 Modeling the Structure and Medium Range order of ALD Amorphous Oxide Thin Films**, ***Angel Yanguas-Gil***, *J.W. Elam,* Argonne National Laboratory

The evolution of microstructure during the early stages of growth is crucial for the chemical and electronic properties of oxide materials at the core of a wide range of applications, from gate dielectrics for conventional and power electronics to energy storage and catalysis. Through a combination of synchrotron studies and atomistic models we have studied the evolution of the structure for a variety of oxide materials including ZnO, In_2O_3, TiO_2, and HfO_2.

We have leveraged ALD's unique ability to grow conformally on high surface area materials to characterize the evolution of the coordination environment and medium range order using EXAFS, XANES, and PDF. We have compared these results with atomistic simulations, which have allowed us to calculate the pair correlation function and the EXAFS of the simulated material as a function of thickness and temperature.

We have combined these molecular dynamic calculations with simple Monte Carlo simulations to understand the evolution of microstructure during the early stages of growth. Our results are consistent with local structural relaxation mechanisms having a key role in allowing the transition from isolated cluster to bulk-like coordination and medium range. In particular, using the REAXFF potential we were able to look at the impact that hydroxyl groups have on delaying the formation of crystalline phases for low temperature ALD ZnO.

11:40am **TF1-ThM12 From Nano-porosity to Macro-scale Defects: Ellipsometric Porosimetry and Electrochemical Impedance Spectroscopy Characterization of Thin Inorganic Films**, ***Alberto Perrotta***[*], *W.M.M. Kessels, M. Creatore,* Eindhoven University of Technology, Netherlands

Nano-porosity is an intrinsic property of thin films, and it is identified in inorganic layers by the size of rings (e.g., -SiOSi-) and ring termination units (e.g., Si-OH). Porosity control is the key to several technological applications and selected examples are separation membranes, low-*k* dielectrics, and permeation barrier layers.

In moisture permeation barriers, H_2O permeation is known to occur through nano-porosity and the so-called macro-scale defects (from few nm to hundreds of µm). Therefore, the development of methodologies able to follow both permeation paths and predict the quality of a barrier layer are needed.

In this study, an in-depth analysis of nano-porosity in thin films and its impact on their moisture barrier performance are presented.[1] Several inorganic layers (SiO_2, Al_2O_3, SiN_x) deposited by plasma enhanced-chemical vapor deposition (PE-CVD) and (plasma assisted-) atomic layer deposition (ALD) have been considered. Ellipsometric porosimetry (EP) and electrochemical impedance spectroscopy (EIS) have been adopted as complementary techniques for the analysis of nano-porosity ranging from H_2O kinetic diameter (0.27 nm) up to 1 nm. The role of the specific nano-pore range in controlling the *intrinsic* barrier properties has been disclosed. In detail, absence of porosity with diameter above 0.27 nm led the transition from mediocre (10^{-4} $gm^{-1}day^{-2}$) to excellent (10^{-6} $gm^{-2}day^{-1}$) H_2O barrier properties. Moreover, PA-ALD Al_2O_3 and SiN_x (10-40 nm) layers showed no porosity in the 0.27-1 nm range, and therefore excellent *intrinsic* barrier properties.

Also, next to nano-porosity, macro-scale defect detection is shown possible by both EIS and EP. Specifically, EIS was shown able to directly detect such defects for barriers deposited on c-Si. With EP, the permeation of probe molecules through barriers deposited on polymers can be followed in time. It is thereby possible to discern diverse events, i.e., filling of nano-porosity in the barrier layer and swelling of the polymer.[2] The rate of permeation through the polymer and its swelling has been found to decrease of one order of magnitude upon deposition of porous barriers. The application of a denser layer, impermeable to the probe molecule, showed a further decrease in permeation rate and limited uptake in the polymer. This allowed the isolation of the permeation through macro-scale defects and, thus, their detection.

This research forms part of the research program of the Dutch Polymer Institute (DPI), project #752.

[1] Perrotta *et al., Microp. Mesop. Mat.* 188 (2014) 163; *Appl. Mater. Interfaces,* 7 (2015) 15968; *Plasma Processes Polym.* 12 (2015) 968.

[2] Perrotta *et al.,* to be submitted.

12:00pm **TF1-ThM13 Thermal Conductivity and Mechanical Properties of AlN-based Thin Films**, ***Vincent Moraes***, *H. Riedl,* Technische Universität Wien, Austria*; H. Bolvardi,* Oerlikon Balzers, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; M. Ikeda, L. Prochaska, S. Paschen, P.H. Mayrhofer,* Technische Universität Wien, Austria

While many research activities concentrate on mechanical properties and thermal stabilities of protective thin films, only little is known about their thermal properties being essential for the thermal management in various industrial applications. Based on the 3ω-method, we show the influence of Al and Cr on the temperature dependent thermal conductivity of single-phase cubic structured TiN and single-phase wurtzite structured AlN thin films, respectively, and compare them with the results obtained for CrN thin films.

The dc sputtered AlN thin films revealed a highly c-axis oriented growth for deposition temperatures of 250 to 700 °C. Their thermal conductivity was found to increase strongly with the film thickness, indicating progressing crystallization of the interface near amorphous regions during the sputtering process. For the 940 nm AlN film, we found a lower boundary for the thermal conductivity of 55.3 $W\cdot m^{-1}\cdot K^{-1}$. By the substitution of only 10 at.% Al with Cr, κ significantly reduces to ~ 5.0 $W\cdot m^{-1}\cdot K^{-1}$, although the single-phase wurtzite structure is maintained. The single-phase face centered cubic TiN and $Ti_{0.36}Al_{0.64}N$ thin films exhibit at room temperatures κ values of 3.1 $W\cdot m^{-1}\cdot K^{-1}$ and 2.5 $W\cdot m^{-1}\cdot K^{-1}$, respectively. Hence, also here, the substitutional alloying reduces the thermal conductivity, although at a significantly lower level. Single-phase face centered cubic CrN thin films show κ values of 3.6 $W\cdot m^{-1}\cdot K^{-1}$.

For all nitride based thin films investigated, the thermal conductivity slightly increases with increasing temperature between 200 and 330 K. This rather unusual behavior is based on the high defect density (especially point defects) within the films prepared by physical vapor deposition.

PACS numbers: 68.60.Dv; 68.55.J;

Keywords: Thermal conductivity; Nitride based thin films; Alloying effects; 3ω-method;

Thin Film
Room 105A - Session TF2-ThM
Area-selective Deposition and Sequential Infiltration Synthesis

Moderator: Giovanna Scarel, James Madison University

8:00am **TF2-ThM1 Area Selective Deposition from an Aqueous Fog**, *N. Murari, R.H. Mansergh, Y. Huang, D.A. Keszler,* ***John F. Conley, Jr.,*** Oregon State University

As ULSI technology continues to scale towards the sub-10 nm regime, lithographic patterning and registration to existing features have become increasingly difficult, expensive, and time consuming. Direct patterning or area selective deposition of materials only on desired areas of a substrate has been proposed as a way to overcome these lithographic challenges. Recently, several groups have demonstrated area selective atomic layer deposition (ALD) through approaches such as area deactivation - the use of polymers and self-assembled monolayers (SAMs) to inhibit ALD nucleation. While this work shows promise, alternatives to elevated temperature, vacuum based deposition techniques are desired by the microelectronics, photovoltaics, and display industries. Solution based deposition techniques offer a lower cost, more sustainable approach. Traditional spin-coating, however, is primarily limited to planar substrates and lacks the ability to form uniform films over large surface areas. A number of mist based deposition techniques have attempted to address the limitations of spin coating, but typically suffer from one or more disadvantages such as the requirement of high volatility precursors, uneven mist distribution, complex vapor transport, and/or poor control of film uniformity. A new aerosol based technique overcomes these problems by employing a novel atomizer consisting of two opposing jets located within the deposition

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

chamber. Head-on collision of the opposing jets shears the precursor droplets into a fine mist / fog, allowing the use of low volatility precursors. The uniform generation of mist is scalable for deposition on arbitrarily large substrate areas. In this work we use this method to demonstrate area selective deposition from an aqueous fog at room temperature and pressure.

Aerosol deposition was conducted on a BENEQ ACS 200-101at room temperature and pressure using precursor fog of aqueous based aluminum phosphate inorganic clusters. An octyltrichlorosilane (OTS-8) based SAM with a hydrophobic tail group is used as a growth inhibitor. OTS-8 is patterned on a hydrophilic Si wafer surface. Selective deposition of oxide thin films from an aqueous precursor aerosol fog is achieved with growth occurring only in the hydrophilic regions and not on the areas covered by OTS-8. Smooth films with sharp boundaries are deposited with average surface roughness of less than 1 nm RMS. Deposition selectivity is investigated as a function of pattern size, shape, and half pitch. Overall, room temperature area selective aerosol deposition is shown to be a potentially promising sustainable alternative to AS-ALD for large area electronics.

8:20am **TF2-ThM2 “Patterned-by-Printing” ZnO Vertical TFTs***, **Carolyn Ellinger**, S.F. Nelson,* Eastman Kodak Company

“Patterned-by-printing” uses selective area deposition (SAD) as an alternative approach to printed electronics: an inhibiting polymer ink is printed and the active materials are deposited via spatial atomic layer deposition (SALD). We have previously illustrated the use of this methodology to make planar ZnO thin-film transistors (TFTs) with equivalent device performance to TFTs fabricated from the same materials but patterned by conventional photolithographic means. We have further shown how patterned-by-printing enables freedom in circuit design due to the orthogonal nature of the patterning process, demonstrating facile fabrication of circuits with architectures that can be difficult to obtain using subtractive processing methods.

This talk will address fully patterned-by-printing vertical thin-film transistors (VTFTs), fabricated without any vacuum metallization steps. Using our standard toolset of SALD, inkjet printing and cleaning, we have explored the unique advantages offered by a patterned-by-printing approach for vertical TFT and circuit architectures. In addition to controlling the inhibitor pattern on the substrate by the print pattern, surface structures can be used to control the spatial location of the inhibitor ink via capillary forces. These vertical transistors have liberal design rules and low print resolution requirements as a result of self-aligned source and drain contacts. Starting with a gate structure having a re-entrant profile on the edge, conformal Al_2O_3 gate dielectric and ZnO semiconductor are patterned at low resolution using a printed inhibitor ink and SALD. The same inhibitor ink is printed at the same low resolution so that it is drawn into the reentrant profile, defining the semiconductor channel between SALD-deposited AZO source/drain contacts. The VTFTs have considerably shorter channel lengths than directly obtainable by the printed resolution, and correspondingly higher device performance from a simple additive patterning process. Furthermore, since each step is the same as used for our planar TFTs, circuits having mixed transistor architectures can be used to optimize performance. Individual device characteristics as well as circuit performance will be discussed.

8:40am **TF2-ThM3 Area-selective Atomic Layer Deposition of Metal and Magnetic Films***, **John Ekerdt**, H. Nallan, Z. Zhang, S. Chopra,* University of Texas at Austin **INVITED**

In this work, we demonstrate the selective atomic layer deposition of Co onto MgO/Si and HfO_2/Si substrates. Magnetic materials such as Ni and Co are used in a wide variety of devices ranging from microelectronics to RF technology to energy. Recently, Co films have been explored as the magnetic material for a magnetic tunnel junction structure of an STT-RAM heterostack. Previous efforts to deposit Co metals using ALD precursors bis(N-tert butyl, N’ethylpropionamidnato) cobalt (II) and H_2 have suffered from carbon and nitrogen incorporation into the film. Furthermore, etching ferromagnetic films typically relies on plasma processes that can generate side products and are detrimental to device performance.

Here we offer an alternative to this deposition and patterning approach through a sequence of area-selective atomic layer deposition (A-SALD) followed by an oxide reduction. A-SALD is a process by which the energy of a surface can be manipulated such that there is preferential wetting and nucleation of ALD precursors only in desired regions. It is shown that CoO ALD is successfully blocked on MgO or HfO_2 surfaces that have been treated with a self-assembled monolayer such as n-octadecyltrichlorosilane or a diblock polymer such as poly(trimethyl)silystyrene/polystyrene. Once patterned, these organic blocking layers are used to prevent CoO deposition in particular areas of the substrate. The CoO deposition is performed at a temperature of ~180^o using cobalt bis(diisopropylacetamidinate) and water as co-reactants. Following deposition, it is shown that the CoO can be reduced to form Co metal using a reducing gas such as H_2 or CO at elevated temperature and/or by capping the CoO film with an oxygen-scavening layer of Al that reacts to Al_2O_3. With this approach, we are able to deposit Co metal in only desired regions of the substrate. X-ray photoelectron spectroscopy is used to determine the oxidation state of cobalt and film stoichiometry. Film crystallinity and structure of the films are analyzed with X-ray diffraction and reflection high-energy electron diffraction. Using a scanning superconducting quantum interference device, we explore how the magnetic properties of the Co films can be manipulated using different CoO thickness and capping metals.

9:20am **TF2-ThM5 Selective Area Epitaxy of Magnesium Oxide Thin Films on Gallium Nitride Surfaces***, **Mark Losego**,* Georgia Institute of Technology*; J-P. Maria,* North Carolina State University*; E.A. Paisley,* Sandia National Laboratories

Selective area growth of thin films reduces the number of steps in microfabrication processing and enables novel device structures. Here we report for the first time selective area epitaxy of an oxide material on a GaN surface. Chlorination of the GaN surface via wet chemical processing is found effective to disrupt Mg adsorption and selectively prevent molecular beam epitaxy (MBE) growth of MgO. MgO films grown on neighboring, non-chlorinated surfaces are epitaxial with a (111) MgO || (0001) GaN crystallographic relationship. In-situ XPS studies reveal that a surface monolayer of adsorbed chlorine acts to prevent MgO deposition. Better than 3 micron lateral resolution for the selective area growth of MgO on GaN is demonstrated. This talk will present our current understanding of this selective growth process and detail our studies of the surface chemistry mechanisms.

9:40am **TF2-ThM6 Sequential Infiltration Synthesis (SIS) and its Applications in Nanofabrication***, **Qing Peng**,* University of Alabama

Chemical assembly of materials with atomic/molecular precision is the key to enable new generation technologies. Such sophisticated controllability relies on the understanding of fundamental mechanisms during atomic/molecular assembly processes. In this presentation, I will present the applications of sequential infiltration synthesis (SIS) in nano materials fabrication. The SIS method is based on the coupled diffusion and substrate site-limited reaction process. It shows great promise in the modification of the properties of polymers, and in the scalable and controllable manufacture of nanomaterials. The underlying mechanisms involved in the SIS process will be discussed along with its applications in the advanced lithography, nanostructure engineering and catalyst fabrication.

11:00am **TF2-ThM10 Understanding Growth of Infiltrated ZnO an Atomic Step at a Time***, **Leonidas Ocola**, D.J. Gosztola, A. Yanguas-Gil,* Argonne National Laboratory*; A. Connolly,* Vassar College

We have investigated a variation of atomic layer deposition (ALD), called sequential infiltration synthesis (SiS), as an alternate method to incorporate ZnO and other oxides inside polymethylmethacrylate (PMMA) and other polymers. The precursors used to synthesize ZnO in PMMA are water (H2O) and Diethylzinc (DEZ). SiS of ZnO in PMMA was accomplished by infiltrating (H2O:DEZ) cycles at 95 ^{o}C for periods of up to 4 min per cycle. Energy dispersive spectroscopy (EDS) results show that we synthesize ZnO up to 300 nm inside a PMMA film.

A key feature of an ALD process is the ability to add an atomic layer at a time. This characteristic allows for a detailed study of the formation of ZnO in the polymer matrix after each atomic step is formed. We followed each growth step of ZnO in PMMA using ex-situ photoluminescence (PL), Raman spectroscopy and x-ray photoemission spectroscopy (XPS). These studies show clear differences between mono, dimer and trimer Zn atom configurations. Mono Zn atoms (O-Zn and O-Zn-O) are formed with a single DEZ precursor pulse and one or two H2O pulses and exhibit pure UV emission with no evidence of oxygen vacancy states (V_O). Dimer Zn atoms (O-Zn-O-Zn and O-Zn-O-Zn-O) are formed with two pulses of DEZ and two or three pulses of H2O. They do not form yet a continuous film as shown with Raman spectroscopy. Dimers do show strong PL emission from V_O states In addition, XPS data show no evidence of ZnO wurtzite bonding. After 3 precursor cycles we observe first evidence of film formation inside the polymer matrix with Raman spectroscopy and wurtzite formation with XPS. The evolution of ZnO properties studied with PL, Raman and XPS from these initial stages up to 12 cycles of SiS ZnO will be presented. Such detailed study allows insight to growth mechanisms of ZnO in a non-traditional environment, which may lead to novel applications of ZnO as sensors or detectors.

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

11:20am **TF2-ThM11 Investigation of Vapor Phase Infiltration Kinetics: Infusing Metalorganic Vapors in Polymer Thin Films***, Collen Leng*[*]*, M.D. Losego,* Georgia Institute of Technology

Polymers can be chemically modified via infiltration and reaction with gaseous metalorganic precursors to create new hybrid organic-inorganic materials with novel electrical, chemical, and/or physical properties. These new materials can have applications as chemical barriers, filtration media, or photolithographic hard masks. Here, the focus is to have a better knowledge of the diffusion and reaction kinetics during this vapor phase infiltration process with the goal of understanding how both polymer structure and processing conditions can maximize the depth of inorganic infiltration. In this study, we use the model system of poly(methyl methacrylate) (PMMA) films exposed to trimethylaluminum (TMA) gaseous precursors. Spectroscopic ellipsometry is used to track infiltration by film swelling and changes in refractive index. At a process temperature of 60°C, films are found to initially swell in thickness with the square root of time, suggesting that kinetics are dominated by Fickian-like diffusion behavior. A maximum film swelling of 60% is measured at any exposure time exceeding 1000 minutes. Using these swelling curves as a proxy for infiltration amount, we calculate effective diffusion coefficients for TMA in PMMA at 60^o C to be on the order of 10^{-15} cm^2/s, with faster diffusion in PMMA films of lower molecular weight. At higher temperatures (160^o C), swelling is less significant, but refractive indices of infiltrated films increase by 2% to 3%. We interpret the decrease in swelling as a result of faster chain relaxation when processing above the glass transition temperature of the polymer. To determine whether polymer films infiltrated and swollen below T_g can also undergo similar polymer relaxation behaviors, a systematic study of post-annealing was carried out at 150^o C. In these instances, the amount of swelling decreases by approximately half and refractive index increases but to a lesser degree than those from the initial high process temperatures. The results of this study will be put in context with other ongoing research in the field to help build a phenomenological model that can be used to better design vapor phase processing schemes to form organic-inorganic hybrid materials.

11:40am **TF2-ThM12 Pyrolysis of Organic-Inorganic Hybrid Materials Formed by Sequential Organometallic Vapor Infiltration***, **Halil Akyildiz,*** Uludag University, Turkey*; P.D. Bradford, J.S. Jur,* North Carolina State University

Organic inorganic hybrid materials are of interest for wide variety of applications including flexible electronics and catalysis. This work explores the use of a sequential vapor infiltration (SVI) process by which organometallic ALD precursors are infiltrated into the bulk polymer materials and react with the available functional sites to form a network of organic-inorganic hybrid materials. In this study, thermal degradation characteristics of the SVI hybrid materials are studied with thermogravimetric analysis (TGA) under inert atmosphere. Higher thermal stability of the fibers of SVI hybrid materials is observed compared to the pristine PET fibers and different degradation steps in TGA are defined. Furthermore, increased thermal stability of hybrid materials is demonstrated by pyrolysis of SVI treated nylon-6 and polyester fiber mats at 900°C with high heating rates (up to 200°C/min). It is shown by SEM imaging that fabrics with SVI treatment retain their fibrous structure and high surface area, whereas pristine fabric samples are either completely degraded. Raman spectroscopy analysis of these carbon fibers confirms the graphitic and disordered carbon structures formation.

12:00pm **TF2-ThM13 Carbon Nanofibers Derived from a Cellulosic Polymer Enabled by Vapor Infiltration of Diethyl Zinc for Carbon Based Supercapacitors***, **Wenyi Xie,** O.J. Rojas, S. Khan, G.N. Parsons,* North Carolina State University

Common thermoplastic polymers, such as polyvinyl alcohol and cellulose derivatives are viable precursors to prepare carbon materials for supercapacitor electrodes. These polymers can be readily processed to prepare high external surface area nanofibers. However, thermoplastic polymers undergo melting transition upon heating, therefore result in loss of initial morphology and low carbon yield. In this study, vapor infiltration of diethyl zinc is applied to modify cellulose based nanofibers as the carbon precursor. Our goal is to investigate the effect of inorganic modification on the morphology, surface area and pore volume, as well as the supercapacitor performance of the carbon product from the modified cellulose based nanofibers.

Vapor infiltration of diethyl zinc (DEZ), was performed using a home-built viscous-flow hot-wall tube reactor. One cycle of the vapor infiltration chemistry consisted of a short dose of DEZ (1 s), followed by a DEZ-hold step (60 s) to enable the reactant to diffuse into the nanofibers, and then followed by a N_2 purge step (40 s) to remove excess reactant and byproducts. *Scanning electron microscopy* (SEM) revealed that the fiber structure of cellulose-based nanofibers could be preserved with at least ~ 8.0 wt % of Zn. Nitrogen sorption measurements at 77 K showed that the surface area and pore volume could be tuned by the DEZ infiltration process. Two-electrode symmetric capacitors were fabricated using the carbon materials from the DEZ modified cellulose based nanofibers. Cyclic voltammetry measurements were performed using 1 M KOH as the electrolyte to determine the specific capacitance. The carbon materials obtained from the DEZ modified cellulose based nanofibers showed a specific capacitance in range of ~25 to 50 F/g.

In this work, vapor infiltration of DEZ has enabled the preparation of carbon nanofibers from cellulose based nanofibers. By varying the loading of Zn, the surface area and pore volume of the resulting carbon nanofibers can be tuned to enhance the supercapacitor performance. Therefore, we believe that inorganic modification by vapor infiltration of DEZ is promising for modifying thermoplastic polymers to produce high performance nanostructured carbon materials for supercapacitors

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

Spectroscopic Ellipsometry Focus Topic
Room 104C - Session EL+AS+BI+EM+TF-ThA

Optical Characterization of Nanostructures and Metamaterials (2:20-3:40 pm)/Application of Spectroscopic Ellipsometry for the Characterization of Thin Films (4:00-6:00 pm) and Biological Materials Interfaces

Moderators: Tino Hofmann, University of North Carolina at Charlotte, Stefan Zollner, New Mexico State University, Heidemarie Schmidt, Technische Universität Chemnitz, Germany

2:20pm **EL+AS+BI+EM+TF-ThA1 Optical Properties of (Self-assembled) Nanostructured Surfaces Studied by Spectroscopic Mueller Matrix Ellipsometry and Local Direct Imaging Techniques*, Morten Kildemo,*** Norwegian University of Science and Technology, Norway **INVITED**

This paper covers several applications of ex-situ and in-situ Spectroscopic Mueller Matrix Ellipsometry (SMME) for the study of self-assembled nanostructured surfaces, with applications ranging from antireflection coatings, PV-absorbers, nanoimprinting masks, plasmonic polarizers, plasmonic meta-materials and in particular hyperbolic metamaterials and meta-surfaces. The optical analysis is systematically supported by AFM, SEM and TEM. As nanostructured surfaces are often inherently anisotropic, SMME with variable angle of incidence and full azimuthal rotation of the sample is shown to be a powerful optical technique to fully characterize such anisotropic and sometimes bi-anisotropic materials. The first part of the presentation briefly reviews an uniaxial effective medium approach to model the kinetics of the optical response of self-assembled straight and tilted GaSb nanopillars [Le Roy et al., Phys. Rev. B 2010, Nerbo et al. Appl. Phys. Lett. 2009], and SiO_2–nanopillars containing plasmonic Cu [Ghadyani et al., Opt. Exp. 2013]. The second part of the presentation discusses the experimentally extracted uniaxial and biaxial optical properties of self-assembled plasmonic hyperbolic meta-materials [X. Wang et al., *Block-copolymer based self-assembled hyperbolic metamaterials in the visible range.* (manuscript in preparation), 2016] and metasurfaces [Aas et al., Opt. Expr. 2013]. Hyperbolic metamaterials use the concept of controlling the propagative modes through the engineering of the dispersion relation, and are considered highly promising to reach different meta-properties. The presentation is closed by the discussion of the fascinating Mueller matrix response of a highly organized array of hemispherical Au nanoparticles produced by Focused-Ion-Beam milling, and the response is discussed in the context of highly organized meta-surfaces and plasmonic photonic crystals [Brakstad et al. Opt. Express 2015]

3:00pm **EL+AS+BI+EM+TF-ThA3 Optical Properties of Nanocrystalline Si_3N_4:TiN Thin Films*, Neil Murphy,*** Air Force Research Laboratory*; L. Sun,* General Dynamics Information Technology*; J.G. Jones,* Air Force Research Laboratory*; J.T. Grant,* Azimuth Corporation

Nanocomposite films comprised of mixed nitrides, especially Si-Me-N (Me=Ti, Zr, Hf), have generated significant attention due to their robust thermal and mechanical properties. In addition to their desirable structural characteristics, the mixing of dielectric Si_3N_4 with various metallic nitrides has the potential for the deposition of hybrid thin films with controllable optical absorption based on the fraction of metallic nitrides present within the Si_3N_4 matrix. In this work, nanocrystalline $Si_3N\text{-}_4$ thin films, doped with varying amounts of TiN (1-20 at.%), are deposited using reactive magnetron co-deposition. Note that the Berg model for reactive sputtering is utilized to select the initial conditions for the deposition of the films, which are sputtered from elemental targets within a mixed nitrogen-argon environment and characterized *in-situ* using spectroscopic ellipsometry. The TiN content is varied through systematic adjustment of the current applied to the Ti cathode concurrent with pulsed DC deposition of Si_3N_4 at a constant current of 0.4 A. The use of *-in-situ-* ellipsometry, interrogating wavelengths from 381-1700 nm, allows for the real-time measurement of the refractive index, extinction coefficient, and thickness of the growing films. Additionally, *in-situ* ellipsometry data is used to observe the behavior of the films at the onset of growth, indicating the onset of Volmer-weber type nucleation. All ellipsometric data are fit using a Bruggeman effective medium approximation, varying the amount of TiN present within the films. Optical characterization of the Si_3N_4:TiN thin films indicates that the refractive index at 550 nm decreases gradually from 2.05 to 1.99 as the TiN content is increased from 0-20 at%, while the extinction coefficient rises from 0 to 0.35. These films demonstrate strong absorption features starting from 550 nm out to 1500 nm, allowing for efficient absorption of visible and near-infrared wavelengths. Variation of the TiN content within Si_3N_4:TiN films allows for the user to select the magnitude of extinction coefficient and refractive index, leading to potential applications as mechanically robust layers in interference filters, or as alternatives to lossy metallic configurations in plasmonic devices.

3:20pm **EL+AS+BI+EM+TF-ThA4 The Effect of Aluminum Content on Properties of Al-doped Zinc Oxide Thin Films Grown at Room Temperature*, Lirong Sun,*** General Dynamics Information Technology*; N.R. Murphy,* Air Force Research Laboratory*; J.T. Grant,* Azimuth Corporation*; J.G. Jones,* Air Force Research Laboratory

Transparent conductive Al-doped zinc oxide (AZO) thin films have shown excellent structural, optical and electrical properties for applications in photovoltaic and optoelectronic devices, transparent conducting electrodes, solar cells, liquid crystal displays, touchscreens, energy efficient window coatings and heat reflective coatings. In this work, the AZO thin films were deposited at room temperature by multi-target reactive magnetron sputtering using metallic Zn and Al targets simultaneously. The Al doping content of the AZO films by x-ray photoelectron spectroscopy (XPS) had great impacts on optical properties in the near infrared (NIR) and in the UV regions and were strongly correlated to their electrical properties. The spectroscopic ellipsometry data in three incident angles and transmission intensity data were measured and fitted simultaneously with a Tauc-Lorentz oscillator and a Drude model in the wavelength of 270 -2500 nm. The transmittance and reflectance spectra, the derived refractive index and extinction coefficient, were tailored in the NIR region by Al content and correlated to the electrical resistivity. The blue shift of the absorption edge in the UV region and the widening of the optical band gap were associated with the increase of the Al content. Structural, optical and electrical properties were characterized using x-ray diffraction, scanning electronic microscopy, UV-Vis-NIR spectra and four-point probe methods.

4:00pm **EL+AS+BI+EM+TF-ThA6 Optical Monitoring of Growth (and Death) of Thin Film Materials for Solar Cells*, Nikolas Podraza,*** *K. Ghimire, M.M. Junda, A.A. Ibdah, P. Koirala,* University of Toledo*; S. Marsillac,* Old Dominion University*; R.W. Collins, Y. Yan,* University of Toledo **INVITED**

Performance of thin film solar cells depends on (i) electronic quality of the components (doped and undoped semiconductors, metallic and transparent conducting contact layers), (ii) component optical response, and (iii) full opto-electronic response of the photovoltaic (PV) device structure dictated by layer properties and thickness. Spectroscopic ellipsometry probes (ii) and (iii) through measurement of both thickness and optical response ($N = n + ik$, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, $\alpha = 4\pi k/\lambda$) of multiple layers in thin film device structures. Assessing (i) electronic quality of materials or devices optically relies on understanding other property information deduced from the optical response, such as connecting variations in film structure (crystallinity, degree of disorder) or growth evolution to device performance. In situ, real time spectroscopic ellipsometry (RTSE) monitors growth evolution and post-deposition processes to better understand property changes with thickness, phase transitions and separation, and process kinetics. RTSE of hydrogenated silicon (Si:H), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS) absorbers have been used to understand growth and its relationship to the respective device performance. All of these are relatively mature PV technologies, where knowledge gained from RTSE during growth can potentially improve metrology and manufacturing. The potential impact of RTSE is equally strong when applied to developing technologies. Organometal lead halide perovskite semiconductors ($CH_3NH_3PbI_3$) are used in >20% initial efficiency solar cells but suffer from degradation with temperature, bias, moisture, and ultraviolet light exposure. The time scale of device performance degradation is much shorter than that of other polycrystalline PV (CdTe, CIGS). RTSE has been applied during co-evaporation of CH_3NH_3I and PbI_2 to produce the perovskite, but also during decomposition of the perovskite. Significant fractions of CH_3NH_3I and PbI_2 at the substrate / perovskite and perovskite / ambient interfaces after deposition even under simple atmospheric exposure begin to appear in a matter of minutes. The ability to track the degradation – or death of this material – in addition to growth may be equally important to assessing the ultimate stability and manufacturability of these next generation PV materials.

4:40pm **EL+AS+BI+EM+TF-ThA8 Monitoring Nanometer-Thin Film Formation using Ellipsometry*, Bert Müller,*** *F.M. Weiss, T. Töpper, B. Osmani,* University of Basel, Switzerland

Elastomers can transform electrical energy into mechanical one. They have a wide variety of appli-cations including powering wipers, sound generation, and operating camera lenses. Sandwiched between electrodes the deformable but incompressible elastomer laterally expands when apply-ing a voltage. To provide the necessary strain of at least 10 %, micrometer-thick silicone mem-branes need an operation voltage of several hundred volts, which is inappropriate for the human body. Nanometer-thin membranes, however, require only a few volts. To generate forces as nec-essary for artificial sphincters, i.e. muscles to treat incontinence, several ten thousand membranes have to be sandwiched. Currently, the manufacturing methods such as organic molecular deposition only reach deposition rates of about one micrometer per hour, which does not allow fabricating the sandwiched nanostructures in an efficient way. We have developed an alternative deposition method to pre-pare extremely flat silicone membranes that are below one micrometer thick. The root-mean-square-roughness is smaller than one nanometer. For this purpose, silicone polymers in solution are sprayed by electrospray deposition [1,2]. Usually electrospraying is based on direct current mode. Here, we have employed, however, an alternating current to avoid charge accumulation on the substrate. Spectroscopic ellipsometry has been used to monitor the formation of confluent organic films and electrodes as well as the changes of the organic thin films during ultra-violet radiation treatments. This in situ technique enabled us to derive the refractive index, the porosity, the surface rough-ness, and the film thickness. The derived quantities on surface roughness and film thickness were validated using atomic force microscopy. The combination of electrospraying, ultra-violet light curing, and in situ ellipsometry has a huge potential to efficiently create and monitor nanometer-thin, ultra-flat elastomeric membranes, which may become part of artificial muscles for medical applications and beyond.

[1] F.M. Weiss, T. Töpper, B. Osmani, S. Peters, G. Kovacs, and B. Müller Electrospraying Nanometer-Thin Elastomer Films for Low-Voltage Dielectric Actuators Advanced Electronic Materials (2016) 1500476; DOI: 10.1002/aelm.201500476

[2] F.M. Weiss, T. Töpper, B. Osmani, H. Deyhle, G. Kovacs, and B. Müller Thin Film Formation and Morphology of Electro-sprayed Polydimethylsiloxane Langmuir 32 (2016) 3276-3283

5:00pm **EL+AS+BI+EM+TF-ThA9 Optical Determination of Electrical Response for Thin Film Transparent Conductors: Spectral Range Dependence***, **Prakash Uprety**, M.M. Junda, K. Lambright, R. Khanal, A. Phillips, M. Heben, D. Giolando, N.J. Podraza,* University of Toledo

Thin films with simultaneous high transparency and electrical conductivity have applications in photovoltaics, displays, and other opto-electronic devices. Accurate characterization of electrical transport properties along with optical properties in these transparent conductors, particularly when in the device structure, is of critical importance to their use. Spectroscopic ellipsometry (SE) provides a widely applicable method for determining such properties without many of the complications and limitations that accompany other methods that make use of physical contact to the film. As is described by the Drude model, free carrier optical absorption has increasing effect on the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) with decreasing photon energies. Thus, extracting ε from SE measurements spanning the visible to terahertz (THz) frequency ranges provides sensitivity to film thickness and morphology at higher energies and free carrier absorption dominating the optical response at low energies. In this work fluorine doped tin oxide (SnO_2:F), aluminum doped zinc oxide (ZnO:Al), and sprayed single walled carbon nanotube (CNT) thin films are measured with ex situ SE over a spectral range of 0.035 to 5.9 eV using a single rotating compensator multichannel ellipsometer (0.75 - 5.9 eV) and a single rotating compensator Fourier transform infrared ellipsometer (0.035 - 0.75 eV). Additionally, the ZnO:Al and CNT films are measured using a single rotating compensator THz ellipsometer (0.4 - 5.8 meV) to further extend the measured spectral range to lower energies. Due to the wide spectral range measured, a single model describing ε and layer thicknesses has sufficient sensitivity to simultaneously determine electronic transitions, vibrational phonon modes, and free carrier absorption. The electrical properties in the Drude model are described by the bulk material resistivity ρ and scattering time τ. Optically extracted ρ has increasing correspondence to ρ deduced from four point probe electrical measurements as increasing low photon energies are included in the fitting (< 5% variation in ρ for ZnO:Al analzying the full measured range); a behavior that demonstrates the benefit of extending the measurement spectrum to very low energies. The analyzed spectral range dependence of optically determined transport properties in these examples is considered to illustrate how narrower spectral range measurements impact deduced ρ and τ.

5:20pm **EL+AS+BI+EM+TF-ThA10 Spectroscopic Ellipsometry Studies of CdS-CdSe-CdTe Alloys: Applications in Thin Film Solar Cells***, **Maxwell Junda**, C.R. Grice, Y. Yan, N.J. Podraza,* University of Toledo

Recent studies have demonstrated that photovoltaic (PV) device performance of thin film cadmium telluride (CdTe) solar cells is improved when a thin cadmium selenide (CdSe) layer is added at the cadmium sulfide (CdS) / CdTe interface and when oxygen is added to the CdS window layer (CdS:O). Specifically, devices fabricated with this configuration show increased short circuit current density without a corresponding degradation in open circuit voltage. The high temperature close spaced sublimation (CSS) deposition of the CdTe layers in these devices effectively anneals the existing CdS:O / CdSe window layer creating alloyed regions between these three materials as opposed to distinct, separate layers at the front side of the device. To better understand the sources of performance gain, we begin by using ex situ spectroscopic ellipsometry (SE) from the near infrared to the ultraviolet (0.74 – 5.9 eV) to study the optical and structural properties of these alloys. Films of CdS:O, CdS_xSe_{1-x}, and $CdSe_yTe_{1-y}$ are fabricated on soda lime glass substrates by radio frequency sputtering a stack of layered combinations of CdS, CdSe, and/or CdTe followed either by annealing at the CdTe CSS deposition temperature or actual CSS of CdTe. A parameterized model describing the critical point transitions in the optical response ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) is developed, allowing for tracking of the changes in ε as a result of film composition and processing for each alloy. Additionally, structural and compositional variations introduced by the alloying of materials is considered and supported by complementary x-ray diffraction and energy dispersive x-ray spectroscopy measurements. The database of ε developed for these materials can be used to assess how the oxygen introduced in the CdS:O layer and diffusion of CdSe into both CdTe and CdS:O modify that interface and impact PV device performance.

5:40pm **EL+AS+BI+EM+TF-ThA11 Development of Growth Evolution Diagrams for RF Sputtered Nanocrystalline Hydrogenated Silicon Thin Films via Real Time Spectroscopic Ellipsometry***, **Dipendra Adhikari**, M. M. Junda, N. J. Podraza,* University of Toledo

As a result of its increased visible light absorption and increased stability in comparison to hydrogenated amorphous silicon (a-Si:H), hydrogenated nanocrystalline silicon (nc-Si:H) thin films are of considerable interest for a variety of opto-electronic applications, including photovoltaic (PV) devices. Radio frequency (RF) sputtering in an Ar + H_2 ambient provides a cost effective deposition technique for Si:H films and has advantages over conventional plasma enhanced chemical vapor deposition as a result of the potential to improve deposition rates and the elimination of hazardous precursor gasses. In this work we investigate how pressure, RF power, and Ar/H_2 ambient gas composition ratio influence film structure (thicknesses; amorphous, nanocrystalline, mixed phase composition) and optical response of Si:H films deposited by RF sputtering onto native oxide covered crystalline silicon wafer substrates using in situ real time spectroscopic ellipsometry (RTSE) over the near infrared to ultraviolet spectral range. Through analysis of RTSE measurements and application of virtual interface analysis where appropriate, the time evolution of bulk layer thickness, surface roughness, and complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra are extracted. Variations in nucleation and evolution of crystallites forming from the amorphous phase as a function of pressure, power, or Ar/H_2 ratio can be deduced from the growth evolution and used to create growth evolution diagrams. Overall film quality, crystallinity, and hydrogen incorporation (assessed using infrared extended measurements), are also determined from ε. X-ray diffraction measurements provide complementary information about how deposition conditions influence the density, size, and preferred orientation of crystallites. In addition to controlling film phase and structure, improvement of the deposition rate is also of practical interest and is explored here.

Electronic Materials and Photonics
Room 102A - Session EM+SS+TF-ThA

Materials and Interfaces for Energy Storage

Moderators: Michelle Paquette, University of Missouri-Kansas City, Lee Walsh, University of Texas at Dallas

2:20pm **EM+SS+TF-ThA1 Strain Engineering of Ultrathin Metal Oxide Coatings Deposited using Atomic Layer Deposition for Controlled Electrochemical Energy Storage**, ***Nitin Muralidharan***, *R.E. Carter, A.P. Cohn, L. Oakes, C.L. Pint,* Vanderbilt University

Strain engineering has transformed applications in the semiconductor electronics industry, but has not been widely explored as a tool for electrochemical applications. Here we study the role of strain on the electrochemistry of metal oxide coatings deposited using atomic layer deposition onto super-elastic NiTi alloy surfaces. Specifically, we focus on vanadium pentoxide (V_2O_5) due to its well-known capability to function as a cathode for the intercalation of lithium ions. Exploiting the capability of NiTi to "lock-in" strain in the elastic regime, which extends up to ~ 15% strain, we study the correlation between strain transferred to the V_2O_5 active material and the electrochemical performance during lithium intercalation. Overall, our results indicate that pre-straining the material changes both the kinetics and energetics for intercalation properties. Furthermore, the diffusion coefficient of lithium ions in the V_2O_5 lattice can be effectively doubled through the application of elastic strains as low as ~0.25%. These results provide a route to controllably engineer bulk materials using principles of mechanics to improve battery or other electrochemical application performance.

2:40pm **EM+SS+TF-ThA2 Probing Li-Ion Transport in All-Solid-State Batteries through Electron Transparent Electrodes**, ***Alexander Yulaev,*** Center for Nanoscale Science and Technology, NIST, Gaithersburg, MD, USA*; A.A. Talin,* Sandia National Laboratories*; M.S. Leite,* University of Maryland*; A. Kolmakov,* NIST/CNST

All-solid-state batteries demonstrate a high power-to-weight ratio and high energy density, offering prospective opportunities for miniaturized micro-electronics and medical devices. Moreover, solid state batteries reduce the safety risk of thermal runaway that may occur in electrochemical cells with liquid electrolytes. In spite of growing interests, the details of lithium transport in solid electrolytes and their interfaces are not yet well understood due to a scarcity of experimental methods to probe electrochemical processes at the nanoscale. For instance, the factors controlling the rate and reversibility of Li ion intercalation are still an active area of research. Here we apply a combination of optical and scanning electron microscopies to resolve spatially Li-ion transport across a thin LiPON electrolyte. Using lithographically patterned electrodes, we monitor Li-ion transport through optically and electron transparent ultrathin anodes made either of high capacity silicon or carbon. The variation of the probing depth is achieved by altering the energy of the primary electron beam from 1 keV to 15 keV. Analogous to SEM tomography, the sequence of depth dependent 2D images can be employed to reconstruct the 3D diffusion pathways of Li ions in the electrolyte. In addition, we investigate Li plating/intercalation reactions, which occur at the anode-electrolyte interface during charge/discharge cycles. We foresee that this approach will help elucidate the effects of chemical and ion transport inhomogeneity inside the electrolyte and electrodes on the overall performance of the battery.

3:00pm **EM+SS+TF-ThA3 Thin Film Battery Materials for Fundamental Studies and Applications**, ***Nancy Dudney***, *K. Kercher, M. Veith,* Oak Ridge National Laboratory **INVITED**

Although most commercial rechargeable batteries are prepared by bulk and powder processing methods, vapor deposition of materials has led to important advances for fundamental research, modification of battery materials and interfaces, and also for commercialization of thin film batteries. Each of these areas will be illustrated with our studies of thin film materials for electrolyte, anode, and cathode components of rechargeable lithium and lithium-ion batteries with both planar and 3-dimensional architectures.

Acknowledgement: This work was supported by the U. S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.

4:00pm **EM+SS+TF-ThA6 Silicon Compatible Pseudocapacitors Based on Nickel Hydroxide Functionalization of Carbonized Porous Silicon**, ***Joshua Fain***, *J.W. Mares, S.M. Weiss,* Vanderbilt University

We report on silicon (Si) compatible energy-storage supercapacitors (SCs) that incorporate pseudocapacitive nickel hydroxide [$Ni(OH)_2$] coupled with an electric double layer capacitance (EDLC) contributed by constituent $Ni(OH)_2$ and carbon layers. SCs can charge and discharge their energy much more rapidly than conventional batteries (within a few seconds to minutes), while possessing a higher energy storage capability than traditional capacitors (specific capacitances can reach thousands of F/g). Although SCs have made a commercial impact in regenerative breaking, there remains untapped potential for this technology in on-chip energy storage that could lead to reduced size and weight of microelectronic devices. However, advancements in Si-based on-chip energy storage has been hindered due to the rapid corrosion of Si by most electrolytes necessary for energy storage. Recently, it has been shown that conformal carbonization of high surface area porous silicon (PSi) electrodes protects the Si matrix from corrosion while also contributing to energy-storage EDLC behavior. Here, we show that functionalization of carbonized PSi with pseudocapacitive $Ni(OH)_2$ leads to significantly improved energy-storage capabilities of the SC electrode from a few to over 100F/g (with respect to the mass of the entire electrode), and up to 1400 F/g (with respect to the mass of only the $Ni(OH)_2$ - corrected for EDL contribution of the carbon). The electrodes were fabricated by electrochemical etching of PSi, followed by carbonization using chemical vapor deposition, and finally inclusion of $Ni(OH)_2$ into the matrix via a sol-gel process or electrochemical deposition. Cyclic voltammetry (CV) and charge/discharge experiments were carried out to investigate the energy storage capabilities of composite pseudocapacitive electrodes prepared with varying sol-gel concentrations and different electrochemical deposition parameters. Scan rates of 1-50 mV/s were used. Clear oxidation and reduction peaks were evident in the CV curves along with the EDLC contribution. We observed a tradeoff between specific surface area and $Ni(OH)_2$ quantity: the higher the $Ni(OH)_2$ coverage in the PSi matrix, the lower the accessible surface area. The highest specific capacitance of 1400 F/g was measured on an electrode with a modest concentration of $Ni(OH)_2$ (5 mg/mL nickel acetate tetrahydrate:2-methoxyethanol) at 50 mV/s. The results of these studies suggest that PSi is an excellent high surface area host template for $Ni(OH)_2$ that enables high specific capacitance to be achieved on a Si-compatible platform that could be directly integrated into microelectronic devices.

4:20pm **EM+SS+TF-ThA7 In-situ Raman of Sodium Ion Cointercalation into Highly Crystalline Few-Layered Graphene**, ***Adam Cohn***, *C.L. Pint,* Vanderbilt University

A maximum sodium capacity of ~ 35 mAh/g has restricted the use of crystalline carbon for sodium ion battery anodes. We demonstrate that a diglyme solvent shell encapsulating a sodium ion acts as a "non-stick" coating to facilitate rapid ion insertion into crystalline few-layer graphene and bypass slow desolvation kinetics. This yields storage capacities above 150 mAh/g, cycling performance with negligible capacity fade over 8000 cycles, and ~ 100 mAh/g capacities maintained at currents of 30 A/g (~ 12 second charge). Raman spectroscopy elucidates the ordered, but non-destructive cointercalation mechanism that differs from desolvated ion intercalation processes. In-situ Raman measurements identify the Na+ staging sequence and isolates Fermi energies for the first and second stage ternary intercalation compounds at ~ 0.8 eV and ~ 1.2 eV.

4:40pm **EM+SS+TF-ThA8 Using X-ray Reflectivity to Measure the Vacuum Ultraviolet Absorption Spectrum in Low-k Dielectrics**, ***Faraz Choudhury***, *H.M. Nguyen, W. Li,* University of Wisconsin-Madison*; Y. Nishi,* Stanford University*; J.L. Shohet,* University of Wisconsin-Madison

During plasma processing, low-k dielectrics are exposed to high levels of vacuum ultraviolet (VUV) radiation that can cause severe damage to the dielectric material. The degree and nature of VUV-induced damage depends on the VUV photon energies.[1] In this work, we determine the VUV absorption spectrum of low-k organosilicate glass (OSG) using specular X-ray reflectivity (XRR). Low-k SiCOH films were exposed to synchrotron VUV radiation with energies ranging from 7 to 25 eV and the electron density depth profile of the VUV irradiated films were extracted from the fitting of the XRR experimental data using the Parratt method. The results show that the depth of the VUV induced damage layer is sensitive to the photon energy. Between 7 to 11 eV, the depth of the damaged layer decreases sharply from 110 nm to 60 nm and then gradually increases to 85 nm at 21 eV. The maximum VUV absorption in low-k films occurs between 11 and 15 eV. This method is also utilized to investigate the penetration depth of 5 to 25 eV photons in porous SiCOH films with porosities ranging from 15 to 50%. It is seen that the penetration depth of photons increases with porosity. This work shows that XRR electron density depth profiling can be a very effective, non-destructive tool to determine the penetration depth and absorption coefficients of photons and other reactive species from a plasma in various kinds of dielectric films.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359

[1] T. V. Rakhimova et al, J. Phys. D: Appl. Phys. 47 (2014) 025102

5:00pm **EM+SS+TF-ThA9 On-chip [^{18}F]fluoride Concentration for Microfluidic PET Tracer Synthesis***, **Xin Zhang**, J. Buck, M. Nickels, C. Manning, L. Bellan,* Vanderbilt University

Positron emission tomography (PET) is a valuable medical imaging method that relies on radioactive tracers that target specific sites in the body. Development of these tracers is currently hindered by the enormous infrastructure requirements to perform the necessary radioisotope production and subsequent reactions. To overcome this hurdle and facilitate PET tracer development, we are designing simple, modular microfluidic systems that support on-chip radiosynthesis reactions with small volumes of reagents. In this work, [^{18}F]fluoride (a positron emitter widely used in PET imaging due to its convenient half-life of 110 minutes) is concentrated with a miniaturized anion exchange column located in a microfluidic device fabricated in polydimethylsiloxane (PDMS). By employing a microfluidic device, we aim to achieve more controlled diffusion and reactive kinetics. Instead of relying on complicated flow control elements (e.g. valves), in this microfluidic system, a channel containing pillars with a spacing less than the average diameter of the anion exchange beads is used to trap relatively monodispersed, rigid polystyrene/divinyl benzene beads. We characterized the ability of this miniaturized on-chip exchange column to capture and release quantities of [^{18}F]fluoride appropriate for human imaging (a typical dose is 10 mCi).

Our device is composed of a main chamber with larger microchannels (9 mm long) connected to an inlet and outlet. A laser writer (Heidelberg µPG 101) was used to create patterns on a silicon wafer using a 60 µm thick layerof mr-DWL resist; this template was subsequently used to pattern a microfluidic structure in PDMS. The desired quantity (2.9 mL) of anion exchange beads was trapped by a double row of square pillars near the outlet of the chamber, and the beads subsequently activated with 1.0 M of $KHCO_3$. Diluted [^{18}F]fluoride (100 mCi/mL) sourced from a nearby cyclotron was introduced into the system using a syringe pump, flowing at 0.05 mL/min for 10 minutes.

By quantifying the radioactivity of the [^{18}F]fluoride introduced, the radioactivity of the chip, and the radioactivity of the outflow, we could determine trapping and release efficiency. We observed near complete capture of [^{18}F]fluoride (50 mCi)on our chips in a relatively short time. Moreover, elution with a small volume (less than 200 mL) of Kryptofix (K_{222})/K_2CO_3 was able to release nearly all the [^{18}F]fluoride (49 mCi). Thus, this device is capable of simply and efficiently trapping [^{18}F]fluoride and controllably releasing the concentrated radiolabel in small volumes for downstream reaction with desired molecules.

5:40pm **EM+SS+TF-ThA11 The Role of Electron-Beam Deposition Rate in Controlling Properties of the Titanium/Semiconductor Interface***, **Keren Freedy**, A. Giri, B.M. Foley,* University of Virginia*; J. Bogan, R. O'Conner,* Dublin City University, Ireland*; P.E. Hopkins, S. McDonnell,* University of Virginia

Electron beam evaporation under high vacuum is very widely used for contact deposition in electronic device fabrication. Ti has a low work function and is commonly deposited as a contact or adhesion layer for other metals in silicon-based devices and more recently in 2D semiconductors. Previous work on Ti/MoS_2 contacts suggests that electron beam evaporation of Ti under high vacuum results in the formation of TiO_2 at the interface while UHV deposition results in unintentional reactions between metallic Ti and the MoS_2 substrate (McDonnell et al., 10.1021/acsami.6b00275). Since the majority of reports using Ti as a contact metal utilize HV rather than UHV e-beam processes, understanding the role of process conditions on the properties of this contact/semiconductor interface is of the utmost importance. To avoid the large variability observed in metal/MoS_2 contacts, we focus on Si as a case study to investigate the thermal and electronic properties of the Ti/semiconductor interface. The present study examines the effect of deposition rate on the properties of the Ti/Si interface. Electron beam evaporation of Ti onto both hydrogen-terminated and native oxide (001) Si surfaces is performed at varied deposition rates ranging from 0.1 to 5 A/s at pressures of ~10^{-6} Torr. Prior to ex-situ characterization, the samples are capped with Au in the evaporator to prevent further oxidation in air. Photoelectron spectroscopy measurements reveal that oxide composition is inversely proportional to the deposition rate. X-ray diffraction data shows no evidence of metallic Ti at slower deposition rates. Due to an appreciable partial pressure of O_2 at high vacuum, the composition of the deposited material is sensitive to the impingement rate of Ti on the surface. It follows that higher deposition rates should result in a smaller fraction of oxide phases. Electron and phonon transport across the interface will be studied as a function of deposition rate.

6:00pm **EM+SS+TF-ThA12 Single Crystal Study of Layered U_nRhIn_{3n+2} Materials: Case of the Novel U_2RhIn_8 Compound***, **Attila Bartha**, M. Kratochvílová,* Charles University, Czech Republic*; M. Dušek,* Institute of Physics ASCR, Czech Republic*; M. Diviš, J. Custers, V. Sechovský,* Charles University, Czech Republic

Materials of reduced dimensionality appear in many contemporary fields of research and technology, because they encompass a wide variety of interesting electronic phenomena. For instance carbon can be prepared in 3D (diamond), quasi-2D (graphite), 2D (graphene) or 1D (carbon nanotubes). All of these structures have distinct electronics. Diamond is an insulator. Graphene is semimetal. However, when the dimensionality is increased by putting several graphene layers together (eventually making graphite), the resulting band structure moves to that of a more trivial metal. Another example is high temperature superconductors being quasi-2D materials as well.

The role of dimensionality in *f*-electron systems has been mainly discussed in the context of quantum phase transitions and related phenomena. The series $Ce_nT_mIn_{3n+2m}$ (n = 1, 2; m = 0, 1, 2; T = transition metal) of layered compounds has been extensively investigated. $CeIn_3$ is cubic (3D) and orders antiferromagnetically (AFM) at T_N = 10.2 K. Under hydrostatic pressure superconductivity appears with highest T_c = 0.3 K at p = 2.5 GPa. In $CeRhIn_5$, the anisotropic crystal structure leads to a quasi-2D electronic and magnetic structure. The AFM order is reduced (T_N = 3.8 K) while superconductivity is supported, T_c increases to 1.9 K at p = 1.77 GPa.

We report on the properties of the novel U_2RhIn_8 compound studied the single crystal form in the context of parent $URhIn_5$ and UIn_3 systems [1]. The compounds were prepared by In self-flux method. U_2RhIn_8 adopts the Ho_2CoGa_8-type structure with lattice parameters a = 4.6056(6) Å and c = 11.9911(15) Å. The behavior of U_2RhIn_8 strongly resembles features of related $URhIn_5$ and UIn_3 with respect to magnetization, specific heat, and resistivity, except for magnetocrystalline anisotropy developing with lowering dimensionality in the series UIn_3 vs. U_2RhIn_8 and $URhIn_5$. U_2RhIn_8 orders AFM below T_N = 117 K and exhibits slightly enhanced Sommerfeld coefficient γ = 47 $mJ.mol^{-1}.K^{-2}$. Magnetic field leaves the value of Néel temperature for both $URhIn_5$ and U_2RhIn_8 unaffected up to 9 T. On the other hand, T_N increases with applying hydrostatic pressure up to 3.2 GPa. Results of thermal expansion measurement will be discussed in the framework of Ehrenfest relations. The character of uranium 5*f* electron states of U_2RhIn_8 was studied by first principles calculations based on the density functional theory combined with the Hubbard model. The overall phase diagram of U_2RhIn_8 is discussed in the context of magnetism in related UTX_5 and UX_3 (T = transition metal, X = In, Ga) compounds.

[1] A. Bartha *et al.*, J. Magn. Magn. Mater. 381 (2015) 310-315

Thin Film

Room 104E - Session TF+BI-ThA

Thin Films for Bio-related Applications

Moderator: Angel Yanguas-Gil, Argonne National Lab

2:20pm **TF+BI-ThA1 Self-healing Antifouling Fluorinated Monolayers and Polymer Brushes: One Fluorine Goes a Long Way!***, **Zhanhua Wang**, H. Zuilhof,* Wageningen University, Netherlands

Organic monolayers or polymer brushes, often in combination with surface structuring, are widely used to prevent nonspecific adsorption of polymeric or biological material on sensor and microfluidic surfaces. Here we show how robust, covalently attached alkyne– derived monolayers or ATRP-produced polymer brushes, with a varying numbers of fluorine atoms, on atomically flat Si(111), effectively repel a wide range of apolar polymers without the need for micro– or nanostructuring of the surface. We have studied the antifouling property of fluoro-hydro monolayers and of fluorine-containing polymer brushes towards a range of commonly used polymers/plastics with comparable molecular weight in non– aqueous solvent, and have investigated the effect of polymer molecular weight on the fouling behavior. In addition, we show how for fluorinated polymer brushes this property can be self-repaired upon damage. These studies relied on a range of characterization methods: wettability studies, ellipsometry, X– ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). We developed a novel surface morphology survey by AFM characterization that can accurately quantify the degree of fouling.

These findings and analysis offer significant potential for antifouling applications of ultrathin and covalently bound fluorine– containing coatings for a range of micro– and nanotechnological applications.

Lit:

J. Mater. Chem. A, 2016, 4, 2408–2412

Adv. Mater. Interfaces **2016**, *3*, 1500514

2:40pm **TF+BI-ThA2 Sensitivity Enhancement in Grating Coupled Bloch Surface Wave Resonance by Azimuthal Control***, **Vijay Koju**, W.M. Robertson,* Middle Tennessee State University

Bloch surface waves (BSWs) are electromagnetic excitation modes that exist at the interface of truncated dielectric multilayer structures and a homogeneous medium. Although BSWs are intrinsically present at such interfaces, they cannot be directly excited by light incident from the homogeneous medium due to their non-radiative and evanescent nature. The use of a grating coupler or a prism mitigates this inability by providing an additional momentum to the free-space wave vector required to satisfy the phase matching condition with the BSW wave vector. Since Grating-coupled Bloch surface wave resonance (GCBSWR) bio-sensors do not require a bulky prism to couple light into BSWs, they are strong candidates for nanoscale bio-sensors. But GCBSWR bio-sensors, based on either wavelength or angular interrogation, are observed to be less sensitive compared to prism-coupled Bloch surface wave resonance (PCBSWR) bio-sensors. However, due to their inhomogeneous surface architecture, GCBSWR bio-sensors can be interrogated by rotating the grating platform azimuthally. Exploiting this ability, here we present a new method for improving sensing capability of GCBSWR bio-sensors. We demonstrate computationally, using a three-dimensional scattering matrix based rigorous coupled wave analysis method, that the proposed azimuthal angle interrogation technique highly enhances the sensitivity of GCBSWR bio-sensors. For our study we use a sixteen layered TiO_2-SiO_2 multilayer with SiO_2 gratings on the top sensing platform. We fix the wavelength and incident angle of the incoming light, and sweep over the azimuthal angle to simulate the sensitivity as a function of changing refractive index of the sensing layer. Furthermore, we show that contrary to conventional GCBSWR bio-sensors that only work for transverse electric mode, azimuthal angle based GCBSWR bio-sensors work for both transverse electric and transverse magnetic modes.

4:00pm **TF+BI-ThA6 Thin Film Technologies for Biomedical Devices-Current State of Art and Future Opportunities***, **Mallika Kamarajugadda**,* Medtronic plc **INVITED**

Thin film coatings are becoming ubiquitous in the medical device industry. Capabilities of medical devices and implants are greatly enhanced by thin films, which impart different properties such as adhesion, wear resistance, corrosion resistance, lubricity, radiopacity, electrical insulation, and bio response. Thin film deposition processes for medical devices are often challenging due to the complex substrate geometry of the components and the requirement for biocompatibility. In biomedical thin film coatings, the shape of a surface controls its interaction with biological components. Optimizing the interactions that occur at the surface of implanted biomaterials will be the key to further advances in this field. Furthermore, as treatment options shift towards non-invasive methods, and device size is reduced, researchers will need to work towards overcoming technological challenges to leverage thin film technology in medical devices. This talk will provide current examples of thin film coating applications in the medical device industry along with the future opportunties.

4:40pm **TF+BI-ThA8 Preparation and Characterization of Amino Coatings for Peptide Arrays***, **Gaurav Saini**, L. Howell, M. Greving, P. Walsh, D. Smith,* HealthTell Inc. **INVITED**

Amine-functionalized substrates are among the most commonly used materials in solid-phase peptide synthesis. Chemical stability and amine loading of the amino coating are two important properties that determine silane selection as a building layer in peptide synthesis. We synthesized three different amino coatings *i.e.*, APTES (3-aminopropyltriethoxysilane), APDEMS (3-aminopropyldiethoxymethylsilane) and APDIPES (3-aminopropyldiisopropylethoxysilane), and determined their strengths and limitations as a building layer in peptide array synthesis. Here, amino coatings were synthesized via gas-phase deposition of the corresponding silanes on thermal oxide-terminated silicon substrates in a commercial chemical vapor deposition system. A 16-mer peptide coating was then synthesized on the amino surfaces and the chemical stability of the surface to highly acidic side chain deprotection (SCD) treatments was determined. After SCD, the coating thicknesses decrease to different degrees on the surfaces: it is greatest for the APDIPES surface, lowest for the APTES surface and intermediate for the APDEMS surface, which indicates that peptide-functionalized APTES and APDIPES surfaces are chemically most and least stable to SCD treatment, respectively. The effect of amine loading on peptide density and purity was also determined for the three amino surfaces. Four different trimers were synthesized on the amino surfaces, and the density and purity of these trimers for the three surfaces was determined. A positive correlation between the amine loadings and peptide densities was observed; peptide density was highest for the APTES surface and lowest for the APDIPES surface. However, high amine loading is found to have a negative impact on peptide purity; peptide purity is highest for the APDIPES surface and lowest for APTES surface. Coated surfaces were characterized by spectroscopic ellipsometry, contact angle goniometry, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), spectrophotometry, and MALDI-MS.

5:20pm **TF+BI-ThA10 Electronic Characterization of SWCNT/Block Copolymer-based Nanofiber for Biosensor Application***, **Amrit Sharma**,* Clark Atlanta University

The aim of this research is to fabricate an electrically conducting, smooth, continuous and sensitive nanofiber using polystyrene (PS), triblock copolymer (PS-b-PDMS-b-PS) and single-walled carbon nanotubes (SWCNTs) by electrospinning. The electronic nanofibers may be utilized for effective bio-sensing applications. The SWCNTs have been of great interest to researchers because of their exceptional electrical, mechanical, and thermal properties. The nanoscale diameter, high aspect ratio, and low density make them an ideal reinforcing candidate for novel nano composite material.

Electrically conducting nanofibers have been prepared by electrospinning a solution of PS, PS-b-PDMS-b-PS and functionalized SWCNTs in the ratio 5:1:0.05 using solvent DMF. The nanofibers formed had an average diameter of 5 µm and height 4 µm. These nanofibers were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), optical microscopy and electrical characterization.

The electrical characterization of a single fiber shows an almost linear graph of current vs voltage using four-point probe (also known as Kelvin sensing) method. This linear graph exemplifies the conducting nature of the nanofiber. From the graph, a resistance, resistivity and conductivity of the single were measured. The study suggests that the SWCNT/block copolymer nanofibers have superior performance in the development of ultra-high sensitive sensor for the detection of single molecule relative to conventional materials due to significantly larger surface-to-volume ratio. Future work includes preparing nanofibers decorated with functional groups and binding with specific type of enzyme or protein to study their I-V behavior. This approach or method can be utilized for bio-sensing activities, especially for the detection of various antibodies and protein molecules.

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Faculty Advisor/ Mentor: Dr. Michael D. Williams, mdwms@cau.edu

Thin Film
Room 105A - Session TF-ThA

Self-assembled Monolayers and Organic/Inorganic Interface Engineering

Moderators: Matthew Linford, Brigham Young University, Adrienne Stiff-Roberts, Duke University

2:20pm **TF-ThA1 Surface Affinity Control by Polymer Brushes for Direct Self-Assembly***, R. Tiron, A. Gharbi,* ***M. Argoud****, F. Delachat, P. Pimenta Barros,* CEA-LETI, MINATEC, France*; X. Chevalier,* ARKEMA FRANCE*; S. Bouanani,* STMicroelectronics, France*; G. Claveau, C. Lapeyre,* CEA-LETI, MINATEC*; G. Chamiot-Maitrala,* CEA-LETI, France*; C. Monget, V. Farys,* STMicroelectronics, France*; C. Nicolet, C. Navarro,* ARKEMA FRANCE **INVITED**

The ongoing progress in nanoscience and nanotechnology leads to a continual device miniaturization. Until now, lithography has been the main driving force of this process. Block copolymers have become of great interest for high-resolution patterning due to their low fabrication cost, ease of use and high throughput potential. Self-assembling materials used in conjunction with the most advanced exposure tools may extend the current manufacturing practices to dimensions of 10nm and beyond. Density multiplication of patterned templates by DSA of block copolymers stands out as a promising alternative to overcome the limitation of conventional lithography.

In this paper, we investigate the potential of DSA to address both contact via level patterning as well as line and space application. Using the 300mm pilot line available in LETI and Arkema materials, our approach is based on the graphoepitaxy of PS-b-PMMA block copolymers. Our integration scheme is based on BCP self-assembly inside organic hard mask guiding patterns obtained using 193i nm lithography. The process is monitored at different steps: the generation of guiding patterns, the directed self-assembly of block copolymers and PMMA removal, and finally the transfer of PS patterns into the metallic under layer by plasma etching.

Furthermore, several process flows are investigated, either by tuning different material related parameters such as the block copolymer intrinsic period or the interaction with the guiding pattern surface (sidewall and bottom-side affinity). The final lithographic performances are finely optimized as a function of the self-assembly process parameters such as the film thickness and bake (temperature and time).

Finally, DSA performances as a function of guiding patterns density are investigated. Thus, for the best integration approach, defect-free isolated and dense patterns for both contact shrink and multiplication (doubling and more) have been achieved on the same processed wafer.

These results show that contact hole shrink and multiplication approach using DSA is well compatible with the conventional integration used for CMOS technology.

3:00pm **TF-ThA3 Measuring the Rate of Organic Reactions on Surfaces***,* ***Rickdeb Sen****, J. Escorihuela, M.M.J. Smulders, H. Zuilhof,* Wageningen University, Netherlands

Ultrathin coatings like self-assembled monolayers and polymer brushes have been used for a wide variety of studies and applications. Reactions within such monolayers or brushes are often difficult to follow, and their rates are typically not measurable: apart from a handful of cases in which electrochemical methods have been used, no rigorously measured kinetics on reactions within e.g. self-assembled monolayers are available.

The current presentation will outline a generic approach, combining ambient mass spectrometry and XPS, to fill this gap, and provide a novel method to measure the rate of intramonolayer or intrapolymer organic reactions. Examples will include a variety of so-called click reactions, as these display a very high potential in materials science.

Reference: Langmuir 2016, 32, 3412−3419

4:00pm **TF-ThA6** ***Operando*** **Investigation of Chemical Bonding at Hybrid Interfaces: the Effect of Humidity on Polymer/metal Oxide Bonds***,* ***Sven Pletincx****,* Vrije Universiteit Brussel, Belgium*; L. Trotochaud, A.R. Head, O. Karslıoğlu,* Lawrence Berkeley Lab, University of California, Berkeley*; L.I. Fockaert, J.M.C. Mol,* TU Delft, Netherlands*; H. Bluhm,* Lawrence Berkeley Lab, University of California, Berkeley*; H. Terryn, T. Hauffman,* Vrije Universiteit Brussel, Belgium

Stability in aqueous and corrosive environments of formed bonds between carboxylic acid functional groups of a polymer and a hydroxylated surface of aluminium oxide has a great relevance to a broad range of applications. One of the most important industrial problems of adhesion phenomena includes the loss of desired chemical interactions at the interface as a result of humidity and ionic compounds present in the atmosphere. Conventional vacuum techniques do not permit analysis under atmospheric conditions or can nullify the influence of ex-situ atmospheric modifications upon exposure of the sample to an ultra-high vacuum environment. Also, because of the relatively thick polymer layer present in conventional hybrid systems, a buried interface exists, which is difficult to characterize with surface-sensitive analytical techniques. Recent developments in the field of ambient-pressure x-ray photoelectron spectroscopy (APXPS) enable a novel approach to probe these interfaces. A broad range of relative humidities can be reached in the analysis chamber, making it possible to unravel interfacial chemistry changes *operando*.

The amount of bonds formed at the hybrid interface and their binding mechanism (monodentate, bidentate, Brønsted interactions, Lewis interactions) are largely determined by oxide properties such as surface hydroxyl content, acid/base character, and dielectric properties. In this work, aluminium oxide is synthesized by electropolishing and anodizing pretreatment steps to carefully control oxide properties on the nanoscale and fully characterized by different analysis techniques. Polyacrylic acid coatings are made sufficiently thin to access the interface with surface analysis techniques with probing depths between 5-10 nm.

Complementary to APXPS, a vibrational spectroscopy technique using the so-called Kretschmann configuration is used to characterize the formed bonds at the metal oxide/polymer interface. An Al layer is sputtered on an IR transparent crystal, with the Al thickness selected such that the FTIR signal from the oxide/polymer interface is amplified as a result of the Kretschmann effect, and thus an interface-specific spectrum of the oxide/polymer surface is attained. 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. Preliminary results show an increase in the amount of bonds at the oxide/polymer interface, together with an increase in water content directly at this interface. It seems that water, at least during the first 24 hours of interaction, triggers an increased wet adhesion.

4:20pm **TF-ThA7 Integration of Redox-Active Diruthenium-based Molecular Layer onto Electrodes for Memory Device Applications***,* ***Sujitra Pookpanratana****,* National Institute of Standards and Technology (NIST)*; H. Zhu,* George Mason University*; J.W.F. Robertson,* NIST*; S.N. Natoli,* Purdue University*; E.G. Bittle, C.A. Richter,* NIST*; T. Ren,* Purdue University*; Q. Li,* George Mason University*; C.A. Hacker,* NIST

Attaching and integrating electrochemically-active molecules to a variety of different surfaces is of importance for applications in catalysis, memory devices, and molecular electronics. With the increasing demand for personal electronics, growth in Flash-based memory has increased dramatically. However, the dimensional scaling of memory components faces many critical material limitations. A critical component to the memory device is the floating gate or charge trapping layer. To scale the charge trapping layer to nanometer dimensions, one approach is to use a discrete charge storage layer that is based on organic molecules.[1,2,3] Reduction-oxidation (redox) active organic molecules hold potential for memory devices due to their nanoscale dimensions, potential for high charge density, and synthetic flexibility that could be tailor-made for specific electronic functionality.

Here, we investigated the potential of diruthenium-bearing organometallic molecules as the charge trapping layer for memory devices. Diruthenium-bearing organometallic molecules display multiple redox states,[4] which makes them ideal to incorporate within non-volatile memory devices. Monolayer assembly is performed in a stepwise fashion by first forming azide-terminated monolayer on SiO_2 by using azidoundecyl trimethoxysilane followed by a Cu-catalyzed azide-alkyne cycloaddition click reaction to attach diruthenium (Ru_2) compounds (note: SiO_2 serves as the tunneling layer).[5] Infrared spectroscopy and X-ray photoelectron spectroscopy confirmed the Ru_2 attachment. Ultraviolet photoelectron spectroscopy identified the occupied electronic levels of the hybrid organic-inorganic surfaces before and after click reaction. Voltammetric measurements on Ru_2-terminated SiO_2/Si and Au electrodes confirm that the Ru_2 is still electrochemically-active with accessible electronic states integrated on both surfaces.

To complete the memory capacitor device, an Al_2O_3 layer (serving as a charge blocking layer) was deposited by atomic layer deposition over the molecular layer followed by a metal Pd gate. The impact of different Ru_2 compounds on the electronic structure and electrochemical properties of the electrodes and properties of the memory devices will be compared.

Our results will provide future design considerations and limitations for molecular-integrated memory devices.

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4:40pm **TF-ThA8 Fabrication Methods of Organic-Inorganic Hybrids Based on Atomic Layer Deposition***, **Myung Mo Sung**,* Hanyang University, Korea **INVITED**

Organic-inorganic hybrid materials are particularly attractive because they can provide means for not only combining the distinct properties of organic and inorganic components, but outperforming their constituents. The incorporation of inorganic layers into organic layers, therefore, provides the opportunity for developing new hybrid materials with synergic behavior, leading to improved performance. In this presentation, we report three fabrication methods of organic-inorganic hybrid materials using atomic layer deposition (ALD). (1) Molecular layer deposition (MLD) is a gas phase process analogous to ALD and also relies on sequential saturated surface reactions which result in the formation of a self-assembled organic monolayer in each sequence. The MLD method can be combined with ALD to take advantages of the possibility of obtaining organic–inorganic hybrid thin films. The advantages of the MLD technique combined with ALD include accurate control of film thickness, large-scale uniformity, excellent conformality, good reproducibility, multilayer processing capability, sharp interfaces, and excellent film qualities at relatively low temperatures. (2) Large-area graphene films produced by means of chemical vapor deposition (CVD) are polycrystalline and thus contain numerous grain boundaries that can greatly degrade their performance and produce inhomogeneous properties. A better grain boundary engineering in CVD graphene is essential to realize the full potential of graphene in large-scale applications. Here, we report a defect-selective atomic layer deposition (ALD) for stitching grain boundaries of CVD graphene with ZnO so as to increase the connectivity between grains. In the present ALD process, ZnO with hexagonal wurtzite structure was selectively grown mainly on the defect-rich grain boundaries to produce ZnO-stitched CVD graphene with well-connected grains. (3) ALD under high pressure showed that precursors often diffuse sub-surface into polymers. This subsurface diffusion and reaction cold result in the change of the chemical composition and the physical properties of the bulk polymers. Atomic layer infiltration provides a new approach for preparation of organic-inorganic hybrid materials from polymers.

Tribology Focus Topic
Room 101A - Session TR+BI+SE+TF-ThA
Materials Tribology

Moderator: Michael Chandross, Sandia National Laboratories

2:20pm **TR+BI+SE+TF-ThA1 Reaction Pathways and Tribofilm Formation Kinetics at a Solid-Solid Interface***, H.L. Adams,* University of Wisconsin-Milwaukee*; A. Martini,* University of California Merced*; **Wilfred Tysoe**,* University of Wisconsin-Milwaukee **INVITED**

Perhaps the most difficult surface-science challenge is to monitor reaction pathways and kinetics at sliding solid-solid interfaces, in particular for opaque contacting materials [1]. Optical techniques can be used to interrogate the interface when one of the contacting surfaces is transparent, but they are often not sensitive to the first monolayer. Strategies for measuring reaction pathways and their kinetics for well-defined surfaces in ultrahigh vacuum (UHV) are described using the example of sliding-induced decomposition of adsorbed methyl thiolate species, formed by exposure to dimethyl disulfide, on copper. Surface science experiments show that methyl thiolates are stable up to ~425 K on copper, but decompose during rubbing; the effect of the external force is to lower the reaction activation barrier so that it proceeds at room temperature. The surface reaction products can be monitored immediately after sliding in UHV using surface spectroscopies (for example, Auger spectroscopy). However, the reaction kinetics can also be monitored in situ first, by measuring the gas-phase species evolved as a function of the number of times the surface is rubbed, where methane and ethane are detected and second, by measuring the change in friction force due to the evolution of the nature of the species present on the surface. This allows the elementary steps in the tribofilm formation pathway to be identified and their rates measured.

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3:00pm **TR+BI+SE+TF-ThA3 Nanotribology of Graphene Revisited: The Influence of Contact Size and Substrate Topography***, A. Balkanci,* Bilkent University, Turkey*; Z. Ye, A. Martini,* University of California Merced*; **Mehmet Z. Baykara**,* Bilkent University, Turkey

Two-dimensional (2D) materials have been the focus of intense research in recent years thanks to their outstanding electronic and mechanical attributes. In particular, graphene exhibits exceptional potential as a solid lubricant appropriate for use in nano-/micro-scale mechanical systems. As such, a comprehensive evaluation of its frictional properties on such small length scales is of crucial concern. While pioneering studies toward this purpose have revealed strongly layer-dependent frictional behavior [1], the precise roles that contact size and substrate topography (important design parameters for mobile components in nano-/micro-scale devices) play in the lubricative nature of graphene have not been explored yet in detail.

In this contribution, we present a combined experimental and numerical study aimed at evaluating the influence of contact size and substrate topography on the nanotribological characteristics of graphene. In particular, atomic force microscopy (AFM) is employed under ambient conditions to measure friction forces on mechanically-exfoliated graphene as a function of applied load, number of graphene layers, and contact size. To study the influence of contact size on measured frictional properties, AFM probes with different tip apex sizes are obtained by thermal evaporation of gold and platinum onto the probes. In conjunction with the experiments, molecular dynamics (MD) simulations are performed that involve the calculation of friction forces experienced by model tip apexes of varying size on single- and few-layer graphene. Moreover, substrates with various RMS roughness and correlation length values are employed in the MD simulations to investigate the effect of substrate topography on frictional behavior. Results reveal that a subtle interplay between contact size and substrate topography determines the layer-dependent frictional behavior of graphene, providing a new perspective to the nanotribology of this remarkable material.

[1]: C. Lee *et al.*, Science **328**, 76 (2010)

3:20pm **TR+BI+SE+TF-ThA4 Iron-Doped Diamond-Like Carbon Coatings (Fe-DLCs): Synthesis, Characterization, and Tribology--Seminal Results***, **Parag Gupta**,* Northwestern University/Argonne National Lab.*; M.E. Graham,* Northwestern University

Iron-doped diamond-like carbon coatings (Fe-DLCs) of ≈ 0.1 to 35 at.% Fe content have been synthesized, characterized, and tribologically tested. Coatings were deposited on Si(111), 52100 steel ball, and H-13 steel flat substrates using a closed-field unbalanced magnetron sputter deposition process with unmodified and modified graphite target states, the latter with press-fit cast gray iron slugs. Process parameters of target modification, target power, acetylene flowrate, and substrate bias were varied and used in establishing a process-conditioning window to create predictable coatings.

Mechanical characterization was done to determine deposition rate, thickness, internal stress, and hardness. Cross-sectional characterization was done to determine coating uniformity, to understand coating adhesion and morphology, and to confirm interlayer presence and morphology (if deposited). Surface characterization was done to determine surface roughness and mechanical anisotropy. Chemical characterization was done to determine elemental concentration and chemical anisotropy. Finally, structural characterization was done to determine carbon bond order.

Using a ball-on-flat reciprocating tribometer, highly-doped Fe-DLCs were studied at either room temperature or ≈ 100 °C and with either coating / coating or steel / coating contact. Electrical contact resistance between interfaces was measured *in situ*. A contact pressure of ≈ 1 GPa was employed alongside an average sliding speed of 1.0 cm / s, except when non-monotonic sequential speed stepping was prescribed. The boundary-lubricated sliding tests were conducted in the presence of poly-alpha-olefin SAE grade 30 synthetic base stock oil (PAO10) with and without molybdenum dithiocarbamate (MoDTC) and zinc dialkyldithiophosphate (ZDDP) additives, both at 0.5 wt.%. Coatings were also tested in unlubricated conditions.

Friction responses were determined, and wear assessments were conducted. Tribofilm and debris analyses were done. The results were compared to those from DLC, CrN + DLC, Si-DLC, and W-DLC coatings obtained from Oerlikon Balzers. Results indicate that Fe-DLC samples containing between 12 and 35 at.% Fe exhibit negligible wear in the presence of PAO10 with MoDTC and ZDDP, affirming the influence of iron in catalyzing protective tribofilms. Additionally, wear on such samples in both lubricated and unlubricated conditions is far lower than that observed for other coatings, indicating that these Fe-DLCs are robust in any conditions.

4:00pm **TR+BI+SE+TF-ThA6 Tribo-Rheometry of Soft Matter***, J. Kim,* ***Alison Dunn,*** University of Illinois at Urbana-Champaign **INVITED**

Hydrogel surfaces are biomimics for sensing and mobility systems in the body such as the eyes and large joints due to their compliance, controllable chemistry, permeability, and integrated aqueous component. Recent studies have shown that polymer concentration gradients in the top microns of crosslinked hydrogel surfaces result in a less dense surface region. In addition, the lubrication of hydrogel interfaces is driven by the effective mesh size, a parameter which follows from the local density. Given the similarity of a dilute crosslinked hydrogel surface with a dilute polymer solution, we probe the surface of a polyacrylamide hydrogel using stepped-velocity tribo-rheometry over 5 decades of sliding speed, with an annular aluminum countersurface. Three distinct lubricating regimes emerge based on a) hysteretic torque response depending upon increasing or decreasing sliding speeds, and b) characteristic torque overshoot following velocity step changes. This evidence supports the analogy of a rheology-like lubrication response. We postulate that the mechanisms of hydrogel-against-hard material lubrication are due to distinct complex fluid behavior characterized by weakly or strongly time-dependent response. Tribo-rheometry is particularly suited to uncover the lubrication mechanisms of complex interfaces such as are formed with hydrated hydrogel surfaces and biological surfaces.

4:40pm **TR+BI+SE+TF-ThA8 Friction Coefficient Lowering in High-hardness Boron Nitride Films Under Ultra-high Vacuum***,* ***Masao Noma,*** Shinko Seiki Co., Ltd, Japan*; K. Eriguchi,* Kyoto University, Japan*; M. Yamashita,* Hyogo Prefectural Institute of Technology, Japan*; S. Hasegawa,* Osaka University, Japan

Solid lubricant material with low friction coefficient is of technological interest for its usage under harsh environments such as ultra-high vacuum. At present, MoSi -containing films [1] are the most widely employed for space applications because of their low friction coefficients (0.02–0.05) in vacuum [2]. However, the mechanical hardness and the oxidation resistance temperature are 10–20 GPa [3] and 360 °C [4], respectively, inapplicable to a long term operation in space. Boron nitride (BN) films have been considered an alternative material because of their superior high hardness and oxidation resistance temperature, 45 GPa and 1200 °C, respectively [5]. We have proposed a novel reactive plasma-assisted coating technique (RePAC) for forming 1-μm-thick high-hardness BN films (~50 GPa) [6][7]. In this study, we present "friction coefficient lowering" phenomena in the high-hardness BN films under ultra-high vacuum (~10^{-6} Pa), which is in sharp contrast to "friction coefficient increase" usually observed for other hard coating materials. The time-dependent high-vacuum friction measurement revealed that the friction coefficient decrease from 0.1 to 0.03 was found for the substrate bias voltage from −90 to −180 V in the RePAC. In this (incident ion energy) region, the cubic BN phase was formed in the turbostratic BN background, leading to the high-hardness of ~50 GPa at atmosphere [7]. Moreover, the obtained low friction coefficient was confirmed to be stable (<0.05) for long time exposures to the vacuum (~96 hrs). The friction coefficients of the present BN films are comparable to widely reported values of MoS_2 films. The BN film prepared by the RePAC is one of promising hard coating materials for harsh environment (e.g., space) applications.

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5:00pm **TR+BI+SE+TF-ThA9 Nanoscale Friction Properties of Water Intercalated Graphene on Mica and its Isotope Effects***,* ***Hyunsoo Lee,*** Institute for Basic Science (IBS) & Korea Advanced Institute of Science and Technology (KAIST)*; J.-H. Ko,* KAIST, Republic of Korea*; J.S. Choi,* Electronics and Telecommunications Research Institute, Republic of Korea*; J.H. Hwang,* IBS & KAIST, Republic of Korea*; Y.-H. Kim,* KAIST, Republic of Korea*; M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)*; J.Y. Park,* IBS & KAIST, Republic of Korea

We demonstrate that the frictional behavior of hydrophobic graphene on hydrophilic mica is affected by water intercalation after exposure to humid air using atomic force microscopy. The single- and multi-layer graphene were formed by mechanical exfoliation on freshly cleaved muscovite mica. The adsorption of the ice-like water layer between graphene and mica led to friction enhancement, as compared with a pristine graphene/mica sample, which is presumably due to additional frictional energy dissipation at the solid–liquid interface. Moreover, friction on the graphene increased as the number of stacking water layers increased. The magnitude of friction increase was, on the other hand, reduced as following increase of the number of covering graphene layer above intercalated water layer, and then the friction is eventually not distinguished from the multi-layer graphene stack excluded water adsorption. Using the first-principle density functional theory calculations we explain this unexpected behavior by the increased spectral range of vibration modes of graphene caused by water, particularly the low frequency flexural modes, and by the better overlap of the graphene vibration modes with the mica phonons, which favors a more efficient dissipation of the frictional energy. Additionally, we found that the intercalation of deuterium oxide (D_2O) leads to the lower friction, compared to H_2O intercalated graphene on mica. We attribute this isotope effect with to the low vibrational frequency of D_2O adsorbate, which results in the low rate of frictional energy dissipation at the interface.

5:20pm **TR+BI+SE+TF-ThA10 The Remarkable Friction Behavior of Copper at Cryogenic Temperatures***,* ***Andrew Kustas,*** Sandia National Laboratories*; J. Curry,* Lehigh University*; T. Babuska, M. Chandross, P. Lu, T.A. Furnish, N. Argibay,* Sandia National Laboratories

It is commonly accepted that unlubricated, self-mated pure metal contacts over the course of sliding invariably cold-weld and gall, leading to undesirably high friction and wear. Recent work with nanostructured pure metals has shown that in fact it is possible to obtain low friction ($\mu < 0.5$) with pure bare metals such as pure Cu and Au at room temperature. Here we discuss those findings, and more recent work that shows the impact of temperature, stress and microstructure evolution on friction of self-mated pure metals. Variable temperature friction experiments were used to show the existence of a temperature-dependent transition for Cu from high ($\mu > 1$) to low ($\mu = 0.25$) friction, achieved by sufficiently reducing temperature and promoting the development of nanocrystalline surface films that are unachievable at room temperature at the relatively high applied stresses imposed. In-situ electrical contact resistance (ECR) measurements were used to indirectly measure the evolution of the microstructure (grain size) at the interface throughout the experiment. Microscopy was then used to verify claims of nanocrystalline surface film formation at low temperatures. Lastly, an analytical model based exclusively on materials properties is presented that incorporates stress and temperature over time to predict grain size, connecting grain size to friction behavior, for pure FCC metals. While more work is needed to develop the proposed framework, a model that intrinsically connects grain size to friction behavior of metals based exclusively on materials properties is transformational to alloy design, and raises a number of compelling and highly fundamental questions for further research.

5:40pm **TR+BI+SE+TF-ThA11 Understanding Friction in MoS2, Part 1: Stress, Time and Temperature***,* ***Tomas Babuska,*** Sandia National Laboratories*; J. Curry,* Lehigh University*; M. Chandross, M.T. Dugger,* Sandia National Laboratories*; B. Krick,* Lehigh University*; N. Argibay,* Sandia National Laboratories

In the 90 years since the first patent was issued for molybdenum disulfide (MoS_2) as a friction and wear reducing additive, great strides have been made in understanding its remarkable lubricity. However, much remains to be understood about the mechanisms of friction at the molecular scale. Firstly, we present results of investigations into the origins of the well-known non-Amontonian behavior of MoS_2. We show that the apparent return to Amontonian behavior previously reported with steel is in fact associated with an elasto-plastic transition of the contact, and that the stress-dependent friction predictable varies as a function of substrate composition and microstructure (hardness). Time-dependent friction evolution (i.e. run-in behavior) was also found be strongly a function of substrate material composition and stress; these results imply a potentially useful connection between stress and microstructure evolution in both film and substrate that is discussed. We also report on investigations into the temperature-dependent friction and wear behavior of pure MoS_2. In the range -150 to 250°C, we report dramatic deviations from previous literature, as well as the existence of transitions between thermal and athermal behavior as a function of temperature. Evidence of deviations from classical Arrhenius behavior is presented, and the implications of these findings discussed in the context of thermally-activated friction models at the molecular scale. Finally, we end with a discussion of how these findings collectively advance our ability to develop a practical predictive friction model for MoS_2 that includes temperature, stress, substrate effects, defect density and commensurability as their foundation.

6:00pm **TR+BI+SE+TF-ThA12 Understanding Friction in MoS2, Part 2: Water, Oxidation and Run- in***, **John Curry**,* Lehigh University*; M. Chandross, T. Babuska,* Sandia National Laboratories*; N.C. Strandwitz, H. Luftman,* Lehigh University*; M.T. Dugger, N. Argibay,* Sandia National Laboratories*; B. Krick,* Lehigh University

Effects of water vapor and oxidation resistance for amorphous (sputtered) and highly ordered (N_2 sprayed) MoS_2 were investigated with a high-sensitivity, low energy ion scattering (HS-LEIS) spectrometer, molecular dynamics simulations and accompanying tribological testing in each environment of interest. Recent studies have shown that N_2 sprayed MoS_2 coatings possess a preferential surface parallel basal plane texture as deposited due to the kinetic energy imparted during spraying, effectively shearing MoS_2 particles onto the surface. As such, the highly ordered structure of the sprayed coatings both at the surface and throughout the bulk of the film are hypothesized to act as a diffusion barrier to environmental contaminants. Coatings were exposed to molecular oxygen at 250°C and atomic oxygen at 20°C for 30 minutes each and subsequently depth profiled in the HS-LEIS. Results show that N_2 sprayed coatings were successful in limiting the depth of oxidation for both types of exposure. The main contributor, however, to increased initial friction post exposure was the type of coating (amorphous vs highly oriented). Tribological experiments in dry and humid nitrogen showed the initial friction response to be unaffected for sprayed samples while greatly affected for sputtered. Spiral orbit tribological testing was utilized in dry and humid nitrogen environments to further assess the effect of prolonged sliding on purely amorphous MoS_2 with and without formation of a transfer film. It is hypothesized that water does not poison friction behavior of established films of highly oriented MoS_2, but it does poison the ability to form long range order and sintering of crystallites.

Spectroscopic Ellipsometry Focus Topic
Room Hall D - Session EL+AS+EM+TF-ThP
Spectroscopic Ellipsometry Poster Session

EL+AS+EM+TF-ThP1 FTIR Ellipsometry Studies of Thermally Grown GeO₂ on Ge*, **Jaime Moya**, T.N. Nunley, N.S. Fernando, N. Samarasingha, S. Zollner,* New Mexico State University

To study the vibrational modes of GeO_2, we produced a set of thermal GeO_2 oxides ranging from 45 to 136 nm in thickness. Receiving a set of Ge Bulk wafers, we cleaved and roughened the back sides via an aluminum abrasive to avoid backside reflections. To remove carbon-containing surface contaminants and leave a stable oxide on the wafer, we performed a hybrid dry/wet clean. The dry clean was done by subjecting the wafer to an ozone clean in an ultrapure oxygen environment while heating the sample to 150°C for 1 hour, followed by a 30 minute incubation period. The samples were then cleaned ultrasonically for 20 minutes in deionized water followed by 20 minutes in isopropanol. No harsh chemicals were used. The samples were then dried with nitrogen and annealed at 270 kPa and 550°C in ultrapure oxygen for a few hours to achieve different oxide thicknesses.

Using Fourier-transform infrared ellipsometry, the ellipsometric angles ψ and Δ were measured from 250 to 6000cm^{-1} at several angles of incidence (60° to 75°). The infrared lattice absorption peak of the amorphous GeO_2 was fit with a Lorentz oscillator.

When comparing our results to Lippincott's *et al.* [1] transmission measurements of vitreous GeO_2 formed by quenching hexagonal GeO_2, we see a negative shift in vibrational frequency. The difference can be attributed to the different Ge-O bond length comparing the vitreous GeO_2 and our amorphous thermal oxide. Our amorphous thermal oxide GeO_2 samples have a longer bond length, corresponding to a weaker bond and a lower vibrational frequency. This shift also shows a lower density of our samples compared to Lippincott *et al* [1].

References

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EL+AS+EM+TF-ThP2 Anisotropic Bruggeman Effective Medium Approach for Modeling Spectroscopic Ellipsometry Data of Porous Samples*, **Stefan Schöeche**, J. VanDerslice, J.A. Woollam,* J.A. Woollam Co., Inc.

Porous materials are widely used with applications including filtration devices, low-k dielectrics, catalysts, optical coatings, and more. The porous medium is described by its total porosity, pore diameter and specific surface area. The overall properties of the porous material are a result of the combined constituents and can often be approximated using effective medium theories. Due to complicated microstructure, these effective properties may vary along different directions or within the material resulting in anisotropic optical properties or gradients in pore size and total porosity.

Spectroscopic ellipsometry (SE) based porosimetry monitors the optical and structural changes of a porous sample during an adsorption and desorption cycle, i.e., insitu monitoring while the sample is exposed to an atmosphere with solvent partial pressure P varied between zero and the saturation vapor pressure of the solvent over flat surface P_0. Ellipsometric porosimetry based on the Lorentz-Lorenz equation is widely used to characterize thin porous films since it is simple (only requires refractive index at one wavelength) and the skeletal material refractive index is not needed for the calculation. However, the theory is based on invalid assumptions on the microscopic nature of the film, the choice of refractive index is random, it is applicable only to isotropic and homogeneous samples, makes assumptions on the filling of pores at relative pressures P/P_0=0 and P/P_0=1, ignores potential inaccessible pores, and does not provide access to the skeletal refractive index.

We present an alternative approach to analyze porous samples based on the anisotropic Bruggeman effective medium approximation (ABEMA). The model uses well established theory to best match the SE data over a wide spectral range, is easily extendable to more constituents, accounts for optical anisotropy due to the shape of the pores or the pore network, allows determination of the skeletal refractive index in unknown materials, is sensitive to inaccessible pores, and allows grading of relevant sample properties such as the total porosity. A comparison of the two model approaches for data obtained on a porous SiO_2 film on Si substrate will be shown.

EL+AS+EM+TF-ThP3 Optical Constants of M2-phase VO₂ Measured by Spectroscopic Ellipsometry*, **SamuelT. White**, R.F. Haglund, K. Hallman,* Vanderbilt University

Vanadium dioxide (VO_2) is a highly interesting material due to changes in its electronic and optical properties associated with the reversible phase transition from a monoclinic (M1) to a rutile (R) crystal structure. This transition makes VO_2 a promising candidate for many applications, including ultrafast electrical switching and optical modulation. There exists another, distinct monoclinic phase (M2) which also can undergo the transition to R, and which is structurally similar to a possible transient phase appearing in the M1-R phase transition. Thus, M2 is important to understanding the M1-R transition, besides being potentially useful for application in its own right; however, M2 and its phase transition are not as well-characterized as M1. Establishing the optical constants for M2-phase vanadium dioxide is an important step in characterizing this phase and will help provide understanding of its relationship to the other phases.

Here, variable-temperature spectroscopic ellipsometry is used to measure the optical constants of thin-film M2-phase VO_2 below and above the phase-transition temperature, for wavelengths ranging from 370 to 1690 nm. Samples were prepared by electron-beam deposition onto a silicon substrate, with Cr doping to prepare the M2-phase. Experiments were performed both at room temperature and at 95°C with a JA Woolam M-2000 Spectroscopic Ellipsometer equipped with a heated sample stage. VO_2 layer thickness was established by profilometry measurements, and the optical constants were extracted by fitting data to a sum of three Lorentz oscillators. The results are compared to those obtained for thin-film M1-phase VO_2.

The optical constants for M2 and M1 are found to have similar wavelength-dependence, and to agree generally with results obtained for M1 by other researchers. The extinction coefficient, k, is very close for both samples over all wavelengths measured. The index of refraction, n, on the other hand, is larger for M2 than for M1 by ~5-10% for almost all wavelengths measured, with the greatest difference occurring at wavelengths near the peak value, ~430 nm. At elevated temperatures, both samples show optical constants typical of R-phase VO_2, though the index of refraction again appears to be higher for the M2 sample than for the M1 sample. Repeating this experiment with samples prepared by another method may help to distinguish effects due to phase difference due to those due to other sample differences.

Thin Film
Room Hall D - Session TF-ThP
Thin Films Poster Session

TF-ThP2 Interfaces in Hybrid Structures: A 'non'-Destructive, In Situ Insight in Bonds and Failure*, **Tom Hauffman**, S. Pletincx, K. Marcoen,* Vrije Universiteit Brussel, Belgium*; P. Kerger,* Max Planck Institut fur Eisenforschung GmbH (Düsseldorf- Germany), Germany*; L.I. Fockaert,* Technical University of Delft, Netherlands*; M. Rohwerder,* Max Planck Institut fur Eisenforschung GmbH (Düsseldorf- Germany), Germany*; J.M.C. Mol,* Technical University of Delft, Netherlands*; H. Terryn,* Vrije Universiteit Brussel, Belgium

Polymer/(hydr)oxide/metal systems play an important role in engineering. In aerospace, microelectronics, automotive, packaging and even biomedical industry engineering metals are adhesively bonded by a polymer adhesive. Next to adhesive joints, organic coatings are used in these industries and in construction in order to protect the underlying substrate against atmospheric influences. The interface between the organic layer and the oxide of these hybrid systems is very important as it determines largely the performance of the entire system. However, in which sense this interface is of extreme importance is the topic of a large debate. Although mechanical interlocking has always been put forward as the main force holding hybrid structures, it becomes increasingly clear that interfacial chemical interactions are the key players in hybrid structure durability. Furthermore, the access to the interface of hybrid structures is challenging as it is mostly covered by µm range thick polymer overlayers. The so-called buried interface can only be accessed by using monomeric model compounds or by removing (e.g. by argon sputtering or stripping) the polymeric layer partially [1-5]. However, monomers do not fully represent the interphases to be expected in polymer – metal oxide structures and sputtering alters the interface itself. In this presentation, we will present an innovative approach to study interfacial interactions between metallic oxide layers and polymeric films in a non-destructive, in situ manner. This will be done using ultrathin polymeric films deposited on well-tuned oxides. The interactions will be probed using X-ray Photoelectron Spectroscopy, AFM-TOF-SIMS, Infrared Spectroscopy in a Kretchmann geometry and Near Ambient Pressure X-Ray Photoelectron Spectroscopy.

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TF-ThP5 Valence Band Investigation of Cu(In,Ga)Se$_2$ Semiconductor: Improvements by Ag Alloying, ***Kevin Jones**, R.L. Opila, F. Fang,* University of Delaware*; L. Chen, W. Shafaraman,* University of Delaware and Institute of Energy Conversion at University of Delaware

The surface valence band-edge energy lies below the Fermi level by about 1.1eV for CuInSe$_2$. This energy is larger than the bulk band gap energy of 1.04eV, therefore was indicated that the surface of CuInSe$_2$ has a wider bandgap than its bulk. It was later found that the surface band gap of polycrystalline CuInSe$_2$ is 1.4eV, more than 0.3eV larger than its bulk band gap. This led to many experimental observations of what may be the cause of this surface widening effect, in which most progress has been computational. Empirical data suggest that preferential formations of electrical neutral defect pairs are created naturally in Cu-chalcopyrites, in which forms a so called “surface defect layer” on the surface and between the interfaces of the buffer and back contact layer of Cu-based solar devices. The need for an efficient wide band gap absorber has been established for a monolithic tandem solar cell design of the Cu(In,Ga)Se-$_2$ thin-film system, therefore, understanding related surface electronic properties is a necessity for band gap tuning. This work investigates the surfaces of the proposed Ag-alloyed wide band gap system of Cu(In,Ga)Se$_2$, by way of ultra-violet photoemission spectroscopy. In these efforts, we relate the valence band spectra of certain Ag and Ga ratios of Cu-In-Se system to reported empirical data of CuInSe$_2$ and CuIn$_5$Se$_8$ (ODC) stoichiometry, and how these ratios effect surface electronic properties.

TF-ThP7 Internal Charge Transfer at the MBE-Grown Complex Oxide Interface, ***Peng Xu**,* University of Minnesota*; T.C. Droubay,* Pacific Northwest National Laboratory*; J.S. Jeong, K.A. Mkhoyan,* University of Minnesota*; P.V. Sushko, S.A. Chambers,* Pacific Northwest National Laboratory*; B. Jalan,* University of Minnesota

Two-dimensional (2D) ultra-high carrier densities are of significant interest for novel plasmonic and high charge-gain devices. The highest 2D electron density obtained is thus far limited to 3×10^{14} cm^{-2} (½ electron/unit cell/interface) at GdTiO$_3$/SrTiO$_3$ interfaces, and is typically an order of magnitude lower at LaAlO$_3$/SrTiO$_3$ interfaces. In this work, we will present detailed study from experiments and modeling to show that carrier densities much higher than 3×10^{14} cm^{-2}/interface can be achieved via band engineering at MBE-grown NdTiO$_3$/SrTiO$_3$ interfaces. The SrTiO$_3$ (8 u.c.)/ NdTiO$_3$ (2 u.c) /SrTiO$_3$ (8 u.c.) /LSAT(001) heterostructure shows the expected 0.5 electron/unit cell/interface starting at $t = 2$ u.c., but then exhibits a higher carrier density regime at $t \geq 6$ u.c. due to additional charge transfer from broken gap band alignment between NdTiO$_3$ and SrTiO$_3$. The thickness dependence of electronic transport behavior will also be discussed.

TF-ThP9 Preparation of a Transparent Conductive Multilayer Consists of MoO$_3$/Ag/MoO$_3$ and its Application in OLEDs, ***Midori Kawamura**, T. Chiba, T. Kiba, Y. Abe, K.H. Kim,* Kitami Institute of Technology, Japan

Transparent conductive films are widely used as electrodes in solar cells and display devices. As a material, indium tin oxide (ITO) has been most popular. However, development of indium-free or indium-saving materials is also demanded. As one of the solutions, a multilayer structure with oxide/metal/oxide layers has been developed. Previously, we have prepared indium zinc oxide (IZO)/Ag/IZO multilayer as an anode of an OLED, and obtained an excellent properties. In the present paper, we prepared an indium-free multilayer consists of molybdenum oxide (MoO$_3$) and Ag. We report a properties of the multilayer as a transparent conductive film and as an anode of OLED.

Film deposition was conducted on a glass substrate at room temperature by vacuum evaporation method. The thicknesses of the Ag layer and the MoO3 layer were varied from 10 to 14 nm and 5 to 30 nm, respectively. The figure of merit (FOM) was calculated based on the sheet resistance and transmittance at a wavelength of 550 nm to estimate the performance of the transparent conductive films. The OLEDs consists of anode/MoO$_3$(1nm)/α-NPD(60,70nm)/Alq$_3$(65, 75nm)/LiF(1nm)/Al(150nm) were fabricated and the current [http://ejje.weblio.jp/content/current+of+electricity] and the luminance of the devices as a function of applied voltage were measured.

Sheet resistance of the multilayer was mainly governed by thickness of the Ag layer, therefore multilayer where the thickness of Ag layer was 14 nm showed low values. However, optical transmittance at a wavelength of 550nm changed depending on the thickness of oxide layer, and the highest FOM value was obtained in a multilayer consists of MoO$_3$(30nm)/Ag(14nm)/MoO$_3$(30nm). By AFM observation, it was found that hillocks were formed on the multilayer surface and this caused a short-circuit of an OLED device. Finally, we obtained a good OLED properties by increasing thicknesses of organic layers. It is found that efforts to reduce surface roughness of the multilayer is needed to improve OLED properties further.

TF-ThP11 X-Ray Analysis of Metamorphic In$_x$Ga$_{1-x}$As/In$_y$Ga$_{1-y}$As Superlattices on GaAs (001) Substrates, ***Fahad Althowibi**, J.E. Ayers,* University of Connecticut

Strained-layer superlattices have been used in metamorphic device structures for the control of the threading dislocation density. If placed below a graded layer, the superlattice can modify the misfit dislocation length, and if placed above a metamorphic buffer, the superlattice can promote annihilation and coalescence reactions between threading dislocations. In either application, the superlattice is metamorphic, or partly lattice relaxed, and it is of interest to be able to determine the threading dislocation density within the superlattice by means of non-destructive characterization. In this paper we report a study of the dynamical x-ray diffraction from In$_x$Ga$_{1-x}$As/In$_y$Ga$_{1-y}$As superlattices grown epitaxially on GaAs (001) substrates. We show that the threading dislocation density in the superlattice may be estimated from non-destructive x-ray rocking curve measurements. This approach may also be extended to complex device structures containing metamorphic superlattices.

TF-ThP12 Synthesis of Novel Ta Precursor and its Application in Atomic Layer Deposition of TaN Film, *J.H. Han,* Korea Research Institute of Chemical Technology, Republic of Korea*; S.C. Lee, H.Y. Kim, T.M. Chung,* Korea Research Institute of Chemical Technology*;* ***ChangGyun Kim,*** Korea Research Institute of Chemical Technology, Republic of Korea

Tantalum nitride (TaN) film has received considerable attention for the application in the Cu diffusion barrier owing to its promising properties including high electrical conductivity, high chemical stability, and high resistivity against Cu diffusion [1,2]. Although physical vapor deposition method such as sputtering is being mainly used for TaN coating in semiconductor industry, the use of atomic layer deposition (ALD) is expected to be essential to fabricate highly scaled semiconductor devices. A variety of Ta precursors have been reported for TaN ALD films. Although tantalum halides such as TaCl$_5$, TaF$_5$ and TaI$_5$ were most widely performed with NH$_3$ and ^{t}BuNH$_2$, the halide precursors are solid with relatively low vapor pressure [3]. In addition, ALD with halide sources resulted in formation of corrosive by-products and required relatively high growth temperature to obtain pure TaN film.

We successfully synthesized novel Ta precursor which is thermally stable and volatile liquid at room temperature. Thermal decomposition test for novel Ta precursor revealed that it starts to decompose approximately at 350 °C. Self-limiting growth of TaN ALD film was observed with co-reactant either NH$_3$ or NH$_3$ plasma at the temperatures of 150-300 °C. Deposition rate of TaN using NH$_3$ plasma at 200 °C is 0.06 nm/cycle, and AES depth profile showed that PEALD TaN film contains carbon and oxygen levels below 5 %. In this presentation, chemical/physical characteristics and Cu diffusion barrier property of TaN film will be covered.

Figure. AES depth profile of PEALD TaN film grown at 200 °C

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TF-ThP13 Transmission of Plasma-Generated Free Radicals through Silicon Nitride Dielectric Films*, F.A. Choudhury,* ***G. Sabat****, M. Sussman,* University of Wisconsin-Madison*; Y. Nishi,* Stanford University*; J.L. Shohet,* University of Wisconsin-Madison

A high concentration of free-radicals is present in many processing plasmas, which affects the processing conditions and the properties of materials exposed to the plasma. Determining the types and concentrations of these free radicals is critical in order to determine their effects on the materials being processed. Previous work utilized simulations[1] to determine the free-radical density and doses from the processing plasma. Several techniques have been developed and tested over the years for radical measurements[2], but the methods do not provide a direct measurement of the free radical concentrations at the location of the sample during processing. A new technique, using fluorophore dyes, that can detect free radicals in a processing plasma and determine the their fluence at the surface of a sample during processing is investigated. The fluorophores used in this work is Alexa Fluor® 488. After reaction with reactive oxygen species (ROS), the bright green fluorescence (excitation/emission maxima ~490/515 nm) of the dye is significantly degraded. This degradation is measured using a fluorometer. The change in intensity of the fluorescence is used to measure the free radical fluence incident on the sample holder under various plasma conditions. This technique is also used to determine the number of free radicals that can penetrate through a layer of Silicon Nitride (SiN) film as follows. Alexa 488 is placed under free-standing SiN films of various thicknesses and exposed to oxygen plasma to determine the absorption coefficient and penetration depth of the free radicals. Using this method, the absorption length was found to be about 30 nm. Using X-ray Reflection (XRR) spectroscopy, it was found that the top 25 nm of the plasma-exposed film is modified which corresponds to the depth of free radical induced damage.

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TF-ThP16 PEALD BSG PSG Doping Diffusion Characterization*,* ***Jeff Shu****, Y. Zhang, H. Sheng, J. Liu,* GLOBALFOUNDRIES U.S. Inc.

Continuous CMOS scaling becomes more and more difficult due to the extreme process challenges. After FIN FET device architectures were introduced into the industry at end of 2011, they have been widely adopted by the industry to continue device scaling with improved short channel control and performance at lower supply voltages. Compared to SOI substrate, careful punch-through stopper junction design and STI are required for FINs formed on bulk substrate [1]. A novel subfin doping technique had been reported at the 14nm node, which is achieved through solid-source doping to enable better optimization of punch-through stopper dopants [2]. High dopant concentration below the channel to suppress leakage and low dopant concentration in the channel for high performance & less variability can be achieved by solid-source doping techniques while high impurity concentration in the channel and silicon damage could be caused if ion implantation is used for this subfin doping. In this paper, thorough diffusion characterizations were performed at both BSG (Boron Doped Silicate Glass) and PSG (Phosphorus Doped Silicate Glass) on silicon substrates with different drive-in anneal conditions and different insulator cap options. A novel solid-source doping scheme with BSG for NFET subfin doping and PSG for PFET subfin doping is proposed due to the fact that no enough space exists to continue the traditional dual doped liner (BSG/PSG) scheme on 7nm node and beyond.

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TF-ThP17 Low Temperature Deposition of nc-Silicon Thin Films using SiH_4/H_2 mixture*,* ***Moniruzzaman Syed****,* Lemoyne Owen College*; Tong. Goh,* University of Malaya, Malaysia*; N.F.F.B. Nazarudin,* University of Malaya, Kuala Lumpur*; A. Jahangir,* University of Memphis*; Y. Hamada,* Lemoyne Owen College*; A.M. Ali,* King Khalid University, Saudi Arabia

Nanocrystalline-silicon (nc-Si) films were simultaneously deposited on glass and single-crystal Si substrates that were exposed to H_2 plasma excited using RF $_{\text{power}}$ = 80 W prior to the film deposition, under 250ºC by plasma enhanced chemical vapor deposition using a SiH_4/H_2 mixture. Structural changes of the nc-Si films were investigated by X-ray diffraction, Raman spectroscopy, infrared absorption, UV-VIS and AFM measurements. All nc-Si films were deposited as a function of RF power conditions. <110> preferentially oriented nc-Si films were observed to grow suddenly with RF power of 80 W resulted in improved crystalline qualities. These results were examined on the basis of the effect of various mechanisms on the crystalline properties, although these mechanisms may jointly determine the properties.

KEYWORDS: polycrystalline Si, plasma-enhanced chemical vapor deposition, surface morphology of substrates, growth mechanism, crystalline qualities

TF-ThP19 Low Energy Ion Scattering (LEIS) Analysis of ALD Deposited GaSb Films on SiO_2*,* ***Thomas Grehl****, P. Brüner,* ION-TOF GmbH, Germany*; R. ter Veen, M. Fartmann,* Tascon GmbH, Germany*; T. Blomberg, M. Tuominen,* ASM Microchemistry Ltd., Finland

GaSb is a promising candidate as a III-V channel material for p-channel for future metal-oxide-semiconductor field-effect transistors (p-MOSFETs) due to its high hole mobility. Also other applications like thin film solar cells or other optoelectronic applications are being discussed. In many of these applications, a well-controlled deposition of GaSb thin films is required.

During deposition process development, characterization of the early stages of film growth is essential to optimize the deposition conditions and possible pre-treatments of the substrate. Low Energy Ion Scattering (LEIS) is a valuable tool for this: Its key feature is the ability to quantitatively determine the composition of the outermost atomic layer. In addition, it non-destructively obtains information about the composition of the first few nm of the sample. These features make it the ideal technique to follow the nucleation of the film and its development until the film is closed. This includes information about the initial growth per cycle as a function of the cycle number, the accurate determination of film closure, and monitoring of unexpected contamination.

The instrument in this study is equipped with a high-sensitivity and high-resolution energy analyzer to record the energy spectrum of noble gas ions scattered back from the sample surface. The 3 – 8 keV ions undergo binary collisions with surface atoms, leading to a characteristic energy loss depending on the mass of the scattering partner. The energy loss is used for identification, while the intensity is used for quantifying the surface coverage per element. Ions which were scattered at sub-surface atoms are detected with a lower probability due to specific neutralization and reionization effects. At the same time they exhibit a depth-dependent energy loss by traveling through the solid. This explains why on the one hand the surface composition can quantified with ultimate surface sensitivity of one atomic layer, and at the same time the composition of the first few nm can be determined without sputtering.

The GaSb films in this study were deposited on SiO_2, using a $GaCl_3$ + $Sb(SiMe_3)_3$ chemistry at 110 °C in a Pulsar 2000 reactor. Samples were taken out after 1 – 20 ALD cycles and analyzed using LEIS. As the analysis involved transport of the samples through air, an appropriate method to remove atmospheric hydrocarbons from the surface had to be applied. For this purpose, different treatments were tested for their ability to remove the adsorbents while minimizing the effect on the composition of the surface.

TF-ThP21 Characterization and Use of Porous Materials for Solid Phase Microextraction by Sputtering and CVD*,* ***Massoud Kaykhaii****, T. Roychowdhury, A. Diwan, B. Singh, M.R. Linford,* Brigham Young University

This presentation will focus on both the characterization of new materials for SPME and their use in extracting analytes of interest from complex matrices. Solid phase microextraction (SPME) is an important sampling tool. It consists of placing a coated fiber above a sample (headspace mode) or immersing it in a liquid such that molecules (analytes) of interest can be selectively extracted and concentrated. The captured species are then released by heating or dissolution into a chromatograph for separation and identification. It is a ‘green’ method because no additional solvent is used in this process. We have developed a new class of SPME fibers that offer extraordinary capacity and speed. They are prepared by sputtering a material under conditions that lead to a nanoporous coating on the fiber. When silicon is sputtered under these conditions, its outermost surface can be additionally oxidized, leading to a high density of silanol groups than can be subsequently silanized. For example, the fibers can be derivatized with octadecyldimethylmethoxysilane by chemical vapor deposition (CVD), which creates a hydrophobic extraction medium. The performance of our 2 micron sputtered coatings has been compared to that of thicker (7 micron) commercial coatings. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity for alcohols, amines, aldehydes, and esters. Real world samples, e.g., hops and PAH from water, have also been analyzed. Different coating thicknesses have been prepared and evaluated. Sputtered coatings have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and wetting.

TF-ThP22 Simulation and Characterization of Short Channel Organic Thin Film Transistors Fabricated Using Ink-jet Printing and Imprint Process*, Juhyun Bae,* Sungkyunkwan University, Republic of Korea*; K.H. Kim, N.Y. Kwon,* Samsung Electronics Co., LTD., South Korea*; I.S. Chung,* Sungkyunkwan University, Republic of Korea

Printable Organic Thin Film Transistors (OTFTs) are of increasing interest for low cost electronic applications. Among those, inkjet-printing has attracted attention in flexible and light-weight electronic products based on OTFTs due to its advantages like non-contact patterning and good local registration without wasting material. In addition, To use inkjet-printed TFTs for commercial productions, it is required to reduce channel length below 10µm because TFTs with channel lengths of 5 and 10 µm are typically used in active-matrix display applications.

In this work, We fabricated short channel OTFTs on a polyethersulphone substrate using inkjet printing combined with an imprint method. 6,13-bis(triisopropylsilylethynyl) TIPS pentacene and polyvinyl alcohol were used for an active material and a gate insulator, respectively. We utilized schematic of bottom contact OTFTs with silver electrode. Imprint method was attempted to precisely separate printing of S/D electrodes has difficulties in controlling the short channel lengths. Thereby we obtain the 2.5um, 3.8nm and 6.4um channel length. This confined structure could dominant big grains instead of dendrite grains. Because confined structure is to reduce the solvent evaporation at the edge of droplet since boundary is blocked. Physical analysis of confined structure was investigated using scanning probe microscopy(SPM). Furthermore, we clearly obtained big grains in SEM images. We found that crystallization of TIPS pentacene is confirmed from big grains and dendrite grains plays an important role in determining the electrical properties. To compare the electrical properties of the two types of grain, we measured the transfer and family curve from OTFTs having big grains and dendrite grains TIPS pentacene for three channel lengths by Keithley-4200.

The mobility and on/off ratio of case of big grains are better than case of dendrite grains. And as the channel length decrease, the on current slightly increases and the off current decreases. However, the threshold voltages and field-effect mobility of OTFTs appeared a small fluctuations in the different channel length.

The experimental I_{DS}-V_{DS} family curves and I_{DS}-V_{GS} transfer curves were numerically well simulated by SILVACO. The simulation is applied the same schematic structure of experiment. Simulation results also obtained that as the channel length decrease, the on current increases and the off current decreases. And threshold voltages and mobility were rarely fluctuations in the difference in the channel length. Therefore, we could admit the simulation results support for the experiment results.

TF-ThP24 Toward Reliable Production of Well-Structured, Self-Assembled Thin Films of Quantum Dots for Surface Coatings*, Cuong Nguyen,* *J.J. Weimer,* The University of Alabama in Huntsville

The goal of this study is to deposit Langmuir films of quantum dots (QDs) as reliably well-structured, self-assembled, monolayer films. Such films will be increasingly important as pre-cursors to coat thin-film light-emitting devices, solar cells, transistors, and diode lasers where the uniformity of the film plays a key role in the consistency of its properties. The structure of the Langmuir films is imaged at macroscopic to microscopic scales using optical and Brewster angle microscopy. Image processing and analysis are done to characterize the patterns. Corresponding image analysis is also done on Langmuir-Schaefer (LS) films that have been templated from the Langmuir films, and comparisons are made to the film quality in the two cases. The topography and thickness of the LS films are subsequently measured by scanning probe microscopy. The structure of the Langmuir films is controlled to first order by the concentration and volume used during deposition. Common patterns seen include agglomerates, sheets, and streaks. The structure can be refined by adding an organic co-additive at different molar concentration ratios. Above a certain ratio, the QDs and co-additive show phase separation. Systematic characterization of the relationships between deposition parameters and film structure will bring the Langmuir deposition process from being just a laboratory-scale experiment to being a reliable production-level tool to produce well-structured, self-assembled thin films of QDs for surface coatings.

TF-ThP25 *IN SITU* Spectroscopic Analysis of Perovskite/Graphene Hybrid Films for Graphene-Based Perovskite Solar Cells*, Seth B. Darling,* Argonne National Laboratory, University of Chicago*; M.A. Acik,* Argonne National Laboratory

Power conversion efficiency in perovskite-based solar cells has improved to ≥20%, however, there is insufficient understanding of the underlying optoelectronic device function. Organolead halide perovskites, $MAPbX_3$ (X=I, Br, Cl), have stood out with their long electron-hole diffusion length and high electron/hole mobility. Replacement of ETL/HTL with graphene-derived materials (graphene oxide, reduced graphene oxide, n/p-doped graphene, etc.) has emerged recently as a pathway to improved device performance. Nevertheless, graphene/perovskite structure-property relationships are not well understood due to unclear chemistry/poor characterization at the interfaces of ETL/perovskite/HTL hybrids (1). To explore interfacial working mechanisms and perovskite film formation, we performed variable temperature (≤600°C) *in situ* spectroscopy (infrared absorption, micro-Raman, UV-vis-NIR, x-ray photoelectron and luminescence). Our studies targeted perovskite/graphene interfaces and perovskite growth mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, weak cation-anion-solvent coordination. Effect of film thickness, lead content, stoichiometry control, underlayer/overlayer composition, and growth temperature were optimized for better film efficiency and charge transport (2). To address film scalability and stability, we studied opto-thermal changes in reduced graphene/graphite oxide (RGO) upon halide-based ($CH_3NH_3PbI_3$, $CH_3NH_3PbBr_3$, $CH_3NH_3PbCl_3$) perovskite deposition, and performed spectroscopic analysis derived from the intensity and peak areas of perovskite vibrational normal modes of C-H (~2800-3200 cm^{-1}) and N-H (~2000-2800 cm^{-1}) and their interfacial reactions with oxygen functional groups in RGO (3). Controlled perovskite formation was achieved at room temperature for bromide/chloride-based perovskites resulting improved chemical stability with heat (*vs.* iodide derivative) that were decomposed at ≥150°C. Poor perovskite formation was monitored on RGO resulting in film degradation in air (O_2, H_2O) by *in situ* characterization (4); additional insights were derived from defect analysis from I_D/I_G ratio variation at perovskite/RGO interfaces. Film morphology and composition was examined by *ex situ* XRD, SEM, TEM, and AFM.

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TF-ThP26 Synergetic Effect of Nitrogen and Fluorine on the Total Dose Radiation Hardness of the Buried Oxide Layer in SOI Wafers*, Zhongshan Zheng,* Institute of Microelectronics of Chinese Academy of Sciences, China

In order to improve the total dose radiation hardness of the buried oxide layer in silicon-on-insulator (SOI) wafers, the buried oxide was modified by a combined implantation of nitrogen and fluorine ions and subsequent anneal processing. The samples were irradiated using Co-60 gamma rays with various doses, and the radiation responses of the buried oxide layers were characterized using the capacitance-voltage (C-V) technique. The experimental results show the considerably increased radiation hardness of the modified buried oxide layers which received a proper post-implantation annealing with the nitrogen- and fluorine-related electron traps introduced. It is also found that the anneal time is a very important variable affecting the radiation hardness for the modified buried oxide layers, and the depth profiles of nitrogen and fluorine in the buried oxide, which are obtained by secondary ion mass spectrometry (SIMS) analysis, each are nearly identical for all the implanted wafers although there are the obvious differences in the buried oxide radiation hardness between the different samples. Additionally, the rebound and fluctuation phenomena of the buried oxide radiation responses have been observed, which can be attributed to the charge trapping and de-trapping in the buried oxide due to irradiation.

TF-ThP27 The Effect of Vacuum Ultraviolet Irradiation on the Dielectric Constant, Leakage Currents and Time-Dependent Dielectric Breakdown of Low-k Dielectric Films*, **Dongfei Pei**, W. Li, P. Xue,* University of Wisconsin-Madison*; S.W. King,* Intel Corp*; Y. Nishi,* Stanford University*; J.L. Shohet,* University of Wisconsin-Madison

Plasma-induced damage is a major concern of the application of low-k dielectric materials in the backend of the line (BOEL) of integrated circuits. Plasma processing, which involves reactive radicals, ion bombardment and vacuum ultraviolet (VUV) irradiation, can cause serious effects on the electrical properties of low-k dielectric materials. The contribution of VUV photons to the damage process was studied in this work. Synchrotron irradiation was used to simulate VUV photon irradiation from processing plasmas without any particle flux. The photon flux varies with the wavelength so the irradiation time was chosen to produce the similar amount of photon fluence at each photon energy. The time dependent dielectric breakdown (TDDB), leakage current, k-value, bandgap and mobile charge of the VUV irradiated low-k dielectric films were measured and compared. FTIR, XPS and ESR analysis were applied to the films. An energy threshold for the VUV photons to induce damage of low-k dielectrics was found. TDDB degradation, leakage current increase and mobile charge generation were observed in low-k dielectric films irradiated by the VUV photon with energy above the threshold.

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TF-ThP28 Fabrication of and Photovoltaic Characterization of SnS Solar Cell*, **YoungKuk Lee**, S.G. Kang, C.G. Kim,* Korea Research Institute of Chemical Technology, Republic of Korea

Tin (II) sulfide (SnS) is a promising candidate to replace current thin film light absorbing materials in photovoltaics. SnS has a moderate band-gap (1.1-1.3 eV) and high absorption coefficient. SnS thin films have been prepared by metal organic chemical vapor deposition (MOCVD) from the reaction of $Sn(dmamp)_2$ and H_2S gas as the source materials. The molecular structure of $Sn(dmamp)_2$ is shown in fig. 1. SnS films were deposited on Si and glass substrates at the deposition temperature of 200-400 °C. Post annealing of SnS thin films was carried out at 400 °C for 1 h under the H_2S ambient. Hall measurement using van der Pauw method indicate that the film has a p-type conductivity with a hole mobility of 13 $cm^2/V{\cdot}s$. Raman spectroscopy and x-ray photoelectron spectroscopy results show that SnS thin film has no impurities or other binary phase detected inside the films

TF-ThP29 Solution Deposition of Pentacene Thin Films for Solar Cells and Organic Electronics*, **Michael Lee**, R. Mendoza, R.T. Rodriguez, B.F. Kunzler,* Northern Arizona University

Since bulk conductivity in organic crystals was discovered in the 1960s,[1] high mobilities for single-crystal organic semiconductors have been reported with 35 $cm^2\ V^{-1}\ s^{-1}$ for pentacene,[2] and even 40 $cm^2\ V^{-1}\ s^{-1}$ for rubrene.[3], [4] However, these large aromatic molecules are generally insoluble for solution-processing.[5] Optimized films have been prepared by solution-processing derivatized molecules, such as TIPS-pentacene. In TIPS-pentacene, the derivitized groups comprise over half of the mass. Optimized devices using modified pentacene can reach a carrier mobility of only 6 $cm^2\ V^{-1}\ s^{-1}$.[6]

While much of the decrease is due to the polycrystalline nature of the films, the added functional groups also play a direct role. Their effect has been tested to some extent by synthesizing pentacene with removable functional groups. Preparing a film and removing of the functional groups gave nearly 50% increased mobility, or 8.8 $cm^2\ V^{-1}\ s^{-1}$.[7]

We present our recent results on using an alternative strategy to directly solution-process unmodified pentacene and other large organic semiconductors into thin films that can be used for organic field-effect transistors and solar cells. This strategy can be extended to other large semiconductors without requiring organic synthesis of new molecules.

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TF-ThP30 Protected Aluminum Mirrors in the DUV Spectral Range for Astronomical applications*, **Hung-Pin Chen**, W.H. Cho, C.-N. Hsiao,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China*; C.C. Lee,* National Central University, Taiwan, Republic of China

Protected or enhanced aluminum is widely used for the preparation of highly reflective coatings in the DUV spectral range. For astronomical applications, the DUV reflector demand high quality on these coatings, not only with regard to their optical performance but also to their environmental stability, their thermal properties, and their radiation resistance. In this article, we prepare the protected aluminum mirrors by electron-beam evaporation with ion beam assisted, and optimize the beam voltage and beam current of ion source to improving film quality. Explore the refractive index, absorption and the microstructure by difference ion source parameters. The corresponding optical and mechanical properties of multilayer optical thin film were investigated by in-situ optical monitoring, spectrometer, ellipsometry, and Atomic Force Microscope (AFM). Space environment was partially simulated through the employment of a Co60 gamma (γ) radiation source (Nuclear Science and Technology Development Center), to determinate the optical stability of optical thin films for aerospace applications. The reflectance results were measured at the BL04B Beamline of National Synchrotron Radiation Research Center (Taiwan) in DUV spectral region.

TF-ThP31 Physical Characteristics of TiO_x Thin Films Obtained by DC Reactive Sputtering*, **Victor Lima**, I. Doi, J.A. Diniz, R.R. César,* State University of Campinas, Brazil

This work presents the results of the physical characterization of TiO_x thin films obtained under different deposition conditions such as O_2/Ar ratio and deposition plasma power using dc reactive sputtering process. Two sets of the films were prepared, one set varying the sputtering discharge power ranging from 600 W to 1500 W, at constant gas flow ratio of Ar = 60 sccm and O_2 = 40 sccm, and 10 minutes deposition time. Other set of the TiO_x films were prepared with constant 1000 W deposition power for 10 minutes and gas flow O_2/Ar ratio ranging from 0.166 to 0.5. The obtained samples of both sets were all characterized by different techniques, ellipsometry, Raman spectroscopy, Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) to determine thickness and refractive index of the films, crystalline structure, roughness and surface morphology, respectively. The ellipsometry results show that deposition rate of the samples increases linearly as the power increases, and that the refractive index slightly decreases with the power increment, remaining however between 2.44 and 2.47, therefore close to the typical value of titanium oxide. As for the crystalline structure, the results of the Raman spectroscopy showed Raman shift peaks at 150, 230, 420, 600, 670 and 810 cm^{-1}, corresponding to anatase and rutile form of TiO_x thin films, which agree to those results observed by different researchers. The obtained spectra demonstrate also that the brookite structure was not found on the studied TiO_x samples. AFM images showed rms roughness ranging from 0.150 nm for the samples obtained at 600 W deposition power to 0.872 nm for those obtained at 1500 W deposition power, that may explained considering increase of temperature at the sample surface and sputtered materials from the target. The c haracterization of the second set of the TiO x samples, showed that deposition rates increases as more Ar is provided to the sputtering atmosphere, as well as the refractive index, this one exhibiting a small increment as O_2 ratio is increased, with low standard deviation values, showing deposition of the films with quite homogeneous surface. AFM and Raman results showed very small variations in rms roughness of the samples and crystalline structure when gas flow ratio were varied, remaining around the values of 0.441 nm roughness and Raman peaks of anatase and rutile crystalline structure, similar results as those observed for the first set of the samples. These exhibited properties of TiO_x obtained by dc reactive magnetron sputtering technique, make it a interesting material for several applications, for instances for dielectric in semiconducting FETs.

TF-ThP32 Modification of the Vacuum-ultraviolet Absorption Spectrum during Plasma Exposure of Low-k Dielectrics: A Time-dependent Density Functional Theory Analysis*, **Ha Nguyen**, F.A. Choudhury, J.L. Shohet,* University of Wisconsin - Madison

Methyl depletion of organosilicate (SiOCH) films due solely to the absorption of plasma vacuum-ultraviolet (VUV) photons has been a crucial concern in plasma processing of interconnects. Research on determining VUV photon penetration into SiOCH films is still of great interest. Several systematic studies [1,2] have been published on how parameters such as absorption coefficient, penetration depth, and quantum yield of methyl depletion chemical processes depend on film porosity, VUV dose, and particularly VUV wavelength. These studies contributed significantly to the advance of this research field. However, these studies did not address an important question of how VUV photoabsorption changes during the course of VUV irradiation. This results in the concentration of Si-CH3 bonds being reduced with time. This in turn affects how the VUV-penetration depth varies with time. In this work, we aim at addressing this question by using time-dependent density functional theory (TDDFT) to model the absorption spectrum in a continuous photon energy range of 0 to 20 eV for an octamethylsilsesquioxane, $(CH_3)_8Si_8O_{12}$, molecule, which is chosen from among siloxane-based molecular precursors of low-k films as a benchmark case as the first step to understand VUV photoabsorption of SiOCH films. Our calculated results show that for the whole range of VUV photoabsorption energies, the absorption cross-section decreases substantially as the number of Si-CH3 broken bonds increases. This decrease of the absorption cross-section, however, occurs at different rates, which depend strongly on VUV photon energy (e.g., the highest and lowest rates are in the ranges of 10-15 eV and 7-10 eV, respectively). These interesting results suggest that the modification of VUV photoabsorption during plasma processing is a paramount factor to determine the penetration of VUV photons into low-k dielectric films.

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TF-ThP33 High Moisture-Barrier Films using Roll-to-Roll-Plasma CVD grown SiO_x on Room-Temperature ALD treated PEN Substrates*, **Nobuyuki Kawakami**, N. Jiko, T. Okimoto,* Kobe Steel, Ltd., Japan*; K. Kanomata, F. Hirose,* Yamagata University, Japan

Flexible electronic devices are expected to extend its commercial applicability for the bendable applications. Barrier coating depositions on plastic substrates, such as, polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), are essential, because water vapor passes through the plastic films, which might degenerate the performance of electronics devices. It is also essential to enhance the productivity of the barrier coating while minimizing its process costs, where the roll-to-roll process is expected to be a candidate. So far, the roll-to-roll type plasma enhanced chemical vapor deposition (PECVD) system for the SiO_x coating was developed where its barrier ability of water vapor transmission rate (WVTR), was at as low as 5×10^{-4} g/m^2/day with the 500 nm thick coating on PEN [1]. However, further improvement of WVTR down to below 10^{-6} g/m^2/day is still demanded for organic light emitting diodes (OLEDs) . In this study, the SiO_x coating is deposited by the roll-to-roll PECVD, combined with room temperature atomic layer deposition (ALD) of AlO_x to form a stacked structure on the PEN substrate. The SiO_x coating was processed by a PECVD roll coating system (Kobe Steel, Ltd., W35-350CS), where hexamethyldisiloxane (HMDSO) was used as precursor mixed with oxygen. The ALD of AlO_x was performed using trimethylaluminum (TMA) and remote-plasma-exited water vapor, where the plasma was generated with a mixture of water vapor and argon by an induction coil with a frequency of 13.56 MHz [2]. In order to simplify the whole process, the single ALD layer was inserted for the barrier film formation. The stacked structure consisting of CVD-SiO_x/ALD-AlO_x/PEN substrates was used for the experiment. The barrier performance was measured by Aquatran^{TM} produced by MOCON Inc. with a temperature of 40 °C and a relative humidity of 90 %.

The stacked structure of 300 nm thick CVD-SiO_x on 10 nm thick ALD-AlO_x exhibited the WVTR below 5×10^{-4} g/m^2/day (This is the detection limit of Aquatran^{TM}), whereas the film with a single layer of 300 nm thick CVD-SiO_x deposited directly on PEN had a WVTR of 3.38×10^{-3} g/m^2/day. As a view point of productivity, it is notable that the thin inserting ALD layer drastically effects on the barrier performance. We consider that the present layer-stacking approach is used for the high moisture-barrier films since this technique goes well with the roll-to-roll production.

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TF-ThP34 Determination of the Characteristic Times of Surface Coverage of HfO_2 in Si Substrates by ALD*, **Pierre Giovanni Mani-Gonzalez**,* UACJ, Mexico*; M.M.M. Contreras-Turrubiartes,* UASLP, Mexico*; P.E. Garcia-Casillas, H. Leos-Mendez,* UACJ, Mexico*; H. Hernandez-Arriaga,* UASLP, Mexico*; J.A. Hernandez-Marquez, J.L. Enriquez-Carrejo,* UACJ, Mexico*; M. Melendez-Lira,* CINVESTAV-IPN, Mexico*; E. Lopez-Luna,* UASLP, Mexico

Actually atomic layer deposition has been used for electronic devices ensemble. The high quality at the interface allows the use of this technique as a deposition method. But when growing any material it is important to think in three important points: the aperture-times of each precursor, the number of ALD cycles and the time of surface saturation. The present work shows the process of surface saturation as function of pressure and physical models. This way of obtaining films is innovative because it has not been considered in every ALD equipment. Also, increasing the superficial area, stoichiometric control and thickness. Those features can be controlled using variables such temperature. In previous research it was found that an interface is formed and some defects in film when it is grown by ALD. Those works do not consider this proposed model.

TF-ThP37 Linear Scanning Magnetron for Solar Cell PVD Applications*, **Vladimir Kudriavtsev**, A. Riposan, L. Mandrell, C.W. Smith, T.M. Bluck,* Intevac

In this presentation we discuss Linear Scanning Magnetic Array (LSMA) technology for magnetron sputtering in

conjunction with in-line substrate processing. In this approach, the magnet array (pole) scans over planar target

spreading the erosion pattern in a controlled fashion. Thus, high quality, dense metal films with good uniformity can be

produced at significant advantages over static magnetrons, such as significantly higher target utilization, longer

uptime, and prevention/removal of target defects related to re-deposition.

We review the influence of magnet motion acceleration/deceleration, the influence of endpoint motion offset

(stagger), and the influence of magnet - to - substrate velocity ratio, on target utilization and lead-to-trail edge film

uniformity. Trade-offs between uniformity and target utilization were established and characterized.

The optimization method we use employs a combination of theoretical simulations and experimental

measurements. Theoretical analysis utilizes ANSYS static magnetic field simulations, erosion profile calculations

including motion integration effects, and ray tracing method for sputtering film thickness calculations

(MATLAB). The structure and uniformity of LSMA-deposited thin films was characterized experimentally by

XRF, 4 point probe and SEM, and the target erosion measured by weight and erosion profiles of spent targets.

We have demonstrated that, with a judicious design approach, an optimal range of operating parameters can be

defined and target utilizations in 60-70% range can be reached, while maintaining deposition uniformity below 2% with

excellent film properties. This makes the LSMA plasma source (using planar targets) more economically

competitive than static and rotatable magnetrons.

TF-ThP39 Chemical Vapor Deposition of Manganese Nitride from bis(2,2,6,6 tetramethylpiperidido) Manganese (II), Mn(tmp)$_2$, and Ammonia*, E. Mohimi, B. Trinh,* ***Shaista Babar****, G.S. Girolami, J.R. Abelson,* University of Illinois at Urbana Champaign

Manganese nitride can be synthesized in numerous phases whose solid-state properties are attractive for spintronic, magnetic or microelectronic applications. It is desirable to develop chemical vapor deposition (CVD) routes for manganese nitride films compared to physical vapor deposition (PVD) paths, since CVD can conformally coat high aspect ratio (deep) features, which are increasingly used in the architecture of nanoscale devices. However, lack of suitable precursors for deposition of manganese nitride hindered its development in novel applications where a conformal thin film is required.

Here, we report CVD growth of amorphous manganese nitride films, from a novel and practical precursor, bis(2,2,6,6 tetramethylpiperidido)Manganese (II) Mn(tmp)$_2$ and ammonia as co-reactant. Growths are done in a high vacuum chamber at substrate temperature of 50-350 °C. Precursor container is heated at 60 °C and Ar carrier gas passes through the container at flow rates of 5-40 sccm to deliver precursor to the chamber. Ammonia is delivered through a separate line at pressures from 0-13 mTorr.

XPS reveals a bulk Mn:N ratio of 2.6:1 to 2.8:1 for films grown in the temperature range examined, with no carbon contamination within the detection limits of instrument. All films show a nodular microstructure in cross-section SEM, with rms roughness of 0.4 and 0.5 nm for films grown at 50 and 150 °C, respectively. We propose a transamination reaction between precursor and ammonia to be responsible for the nitride growth, as no reaction is observed in the absence of ammonia. Films are conformal in micro-trenches of aspect ratio 3, while having a directional growth component which led to higher thickness at the opening of the features. Copper diffusion barrier properties of a 12nm manganese nitride film is investigated by deposition on 300 nm thermal silicon oxide/Si substrate, and e-beam evaporation of 200 nm copper on top of manganese nitride film, followed by annealing at 500 °C under Ar for 1 hour. Samples were analyzed by Auger electron spectroscopy for depth profile composition, and compared with a reference sample of no diffusion barrier. Results show that manganese nitride performs well as copper diffusion barrier for microelectronic applications.

TF-ThP40 Effect of Substrate Temperature and Pulse Frequency on the Properties of SiC Film on Si (111) Deposited by Pulsed dc Magnetron Sputtering*, H.-P. Chen, C.-T. Lee, P.-K. Chiu, D. Chiang,* ***Wei-Chun Chen****,* ITRC, National Applied Research Laboratories, Taiwan, Republic of China*; S.-L. Ou,* Da-Yeh University, Taiwan, Republic of China

In this work, the SiC thin film was deposited on Si(111) substrate by a pulsed dc magnetron sputtering deposition for developing the suitable buffer-layer between GaN film and Si substrate. The SiC thin film was prepared from a high purity (99.999%) SiC target and deposited on Si(111) at conditions with various substrate temperatures (600~900 °C) and pulse frequencies (10~100 kHz) by a pulsed-dc magnetron sputtering. Effects of process parameters on the film composition, microstructure, surface roughness, and electrical properties were investigated by field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FESEM-EDX), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), Raman spectrometer, and Hall-effect measurement, respectively. The research goal is to obtain preferred orientation along SiC (111) and root-mean-square surface roughness below 0.5 nm. It is expected that the high quality GaN layer can be epitaxial grown on Si substrate with SiC interface layer.

TF-ThP41 Reactive Magnetron Sputtering of Epitaxial Scandium Nitride for High Performance Electronics*,* ***Amber Reed****,* Air Force Research Laboratory, Wright Patterson Air Force Base*; D.C. Look, V. Vasilyev,* Air Force Research Laboratory, Wright-Patterson Air Force Base*; H.M. Jeon, H.A. Smith, M.R. Schmitt,* Air Force Research Laboratory, Wright Patterson Air Force Base*; J.S. Cetnar,* Air Force Research Laboratory, Wright-Patterson Air Force Base*; B.M. Howe,* Air Force Research Laboratory, Wright Patterson Air Force Base

With technological advances in electronics increasing the need for high performance devices (i.e. high power-high speed), there has recently been a surge in research in transition metal nitrides. The inherent mechanical, chemical and high temperature stability of transition metal nitrides make them ideal candidates for high-performance high-temperature electronics. Scandium nitride (ScN) is of particular interest for incorporation into gallium nitride (GaN) based electronics. Stoichiometric ScN is an n-type III-V semiconductor with a moderate band-gap (2.1-2.4 eV) and high reported carrier concentrations (up to 10^{21} cm^{-3}). With its rock salt structure and lattice constant of 4.51 nm, ScN has great potential for hetero-epitaxial growth on sapphire (Al_2O_3) and magnesium oxide (MgO). In addition, its close lattice match with GaN (<0.1% mismatch) makes ScN a good candidate for use as a buffer layer for hetero-epitaxial GaN on silicon (Si), in ScN-GaN heterostructures, or as an ohmic contact for GaN devices. Incorporation of ScN films into GaN devices requires high quality (i.e. low surface roughness, large grain-oriented crystals, low oxygen contamination) films.

In this work we investigate hetero-epitaxial growth of ScN films on GaN, Al_2O_3 <0001>, and MgO <100> substrates using unbalanced reactive magnetron sputtering with external electro-magnetic coils. The effect of coil current, target power and nitrogen gas fraction on film stoichiometry, microstructure and surface morphology was investigated by correlating film properties, determined through x-ray photoelectron spectroscopy, x-ray diffraction, transmission electron microscopy and atomic force microscopy, with the deposition parameters and plasma conditions during film growth. Hall measurements of the films showed that resistivity and mobility were strongly dependent on crystalline quality and ScN crystal orientation. The Hall mobility of (111)-oriented ScN films on (0001) sapphire increased from 0.95 cm^2/(V*S) to 7.8 cm^2/(V*S) and the resistivity decreased from 1.57x10^{-3} W cm^{-3} to 6.52x10^{-4} W cm^{-3} as the full width half maximum of the ScN (001) x-ray diffraction peak decreased. The transport properties of the (100)-oriented ScN were significantly better than those of the (111)-oriented films with mobilities > 80 cm-2/(V*s) and resistivities < 1.77 x10^{-5} W cm^{-3}.

TF-ThP42 Amorphous Phase Content Determination in TiO_2 Thin Films on Glass Substrates using the PONKCS Approach*, T. Malek,* ***Stanislav Danis****,* Charles University in Prague, Czech Republic*; L. Matejova,* Technical University of Ostrava, Czech Republic*; M. Cerhova,* Czech Academy of Sciences, Czech Republic

Polycrystalline titania oxide are of great interest recently namely for their photocatalycal properties. Samples of TiO_2 could be prepared as polycrystalline powder (nano-powder) and/or in the form of polycrystalline thin films. In our contribution we will present structural studies of thin layers prepared on different substrates (amorphous glass and crystalline silicon) by dip-coating method. A set of layers were analysed all of them synthetized via sol-gel process controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane combined with pressurized water extraction and/or supercritical/pressurized methanol drying. Obtained thin films were heated up to 400ºC for 4 hours in order to obtain crystalline phase. However, some amount of non-crystalline phase of TiO2 could be expected due to preparation procedure. In case of powder the amount of the non-crystalline part can be determined using internal standard, for example. Unfortunately, this technique cannot be used in the case of thin layer. We show how to apply PONKCS method [1] in order to at least estimate the amorphous phase concentration within prepared samples on the glass substrate.

The presented work is supported by the Grant Agency of the Czech Republic by the project No.14-23274S.

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Keywords: thin films , quantitative phase analysis, amorphous phase

TF-ThP43 The Atomic Layer Deposited SrTiO$_3$Films using Thin Seed Layer and their Improvement of Dielectric Properties for DRAM Capacitor

Sang Hyeon Kim, Samsung Electronics, Republic of Korea*; C.S. Hwang,* Seoul National University, Republic of Korea

Dynamic random access memory (DRAM) plays the role as main memory in computers and mobile electronic devices. Further evolution of DRAM requires increase in change density of capacitors. However, the currently using ZrO$_2$/Al$_2$O$_3$/ZrO$_2$ stacked dielectric layer is facing its limitation for further scaling due to the increased leakage current. Thus, perovskite structured SrTiO$_3$ (STO) material is attracting great attention as a future dielectric material in DRAM capacitors. Atomic layer Deposition (ALD) is the most suitable method for DRAM capacitor application which requires excellent conformality on complicated three-dimensional structure with an aspect ratio of 100:1.

ALD of STO films has been researched at a high growth temperature of 370 °C in a series of investigations by the authors' group in order to achieve in-situ crystallization. (1),(2) However, abnormally too high growth rate at initial stage of film growth on Ru electrode, which is the most probable electrode material, was observed,(2) due to the involvement of CVD-like growth behavior. In this study, therefore, 1.5-nm very thin seed layers were deposited under low temperature to make dense seed layers. As a result, the dielectric constant was improved from ~160 to ~270 which was one of the best results of the STO dielectric material. STO films were deposited in a traveling-wave-type ALD reactor (CN-1 Co, Plus-100) for a 4-in.-diameter single wafer. Sr(iPr$_3$Cp)$_2$ and Ti(Me$_5$Cp)(OMe)$_3$ (synthesized by Air Liquide) were employed as the Sr and Ti precursors, respectively. H$_2$O and high density (250g/m^3) O$_3$ were employed as oxygen source for SrO and TiO$_2$ sublayers, respectively. The ALD saturation curve was confirmed in SrO and TiO$_2$ deposition, and the deposition showed a linear growth behavior with respect to the number of deposition cycle with no indication of abnormal growth at the initial stage. In STO deposition, cation composition (Sr/(Sr+Ti)) was evaluated from 50% - 70%. Electrical properties of the (top) RuO$_2$ / STO / Ru (bottom) planar capacitor were estimated to confirm the feasibility of the next generation DRAM capacitor applications.

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TF-ThP44 Water Cooled Low Temperature Evaporation (LTE) Source for Thin Film Organic Semiconducting Materials

Salahud Din, Kurt J. Lesker Company, UK

Rapid advances in research and development in organic electronics have resulted in many exciting discoveries and applications, including organic light-emitting devices for information display and illumination, solar cells, photodetectors, chemosensors, and logic devices. Organic semiconducting materials are broadly classified as polymeric or small molecular. For the latter category, solvent-free thin film deposition techniques are generally preferred to form well-defined interfaces and improve device performance. Controlled deposition of organic semiconductor materials has become more and more important. Due to lower process temperatures (up to ~500C), the manufacturing of organic electronic devices such as light emitting diodes (OLEDs) and other electronic devices is less energy consuming than conventional silicon based electronics. Additionally, these low temperatures also make it possible to use flexible substrates, e.g. plastic films, which can serve as a basis for elastic electronic devices. The crucial part of the fabrication is the deposition of the active organic layers (films) with a layer thickness between 10 and 100 nanometres. It is mostly done by thermal evaporation in a high vacuum environment. The mobility of the charge carriers within the layers and the layer morphology strongly depend on the deposition rates, i.e. the increase in layer thickness with time during the deposition process. The desired deposition rates range between 0.01 and 5 Angstrom per second.

Kurt J. Lesker Company has developed thin film LTE deposition sources which can deposit a wide range of organic materials with precise deposition rates and thickness control. These sources can be coupled with quartz crystal monitors (QCM) and closed loop PID control systems to ensure consistent high-quality results. The process can be performed at very high levels of vacuum allowing for a long mean free path and therefore lower tendency to introduce film impurities. High deposition rates can be achieved and lower energy particles can reduce substrate damage. Low temperature evaporation sources can take hours to cool in a vacuum system before venting is possible to replenish. This increases device fabrication tact times, reduces throughput and creates the need for more sources in larger platforms. Kurt Lesker's water cooled LTE source has the ability to cool down 3.7x times faster against the standard LTE source, saving precious time while maintaining precise thin film growth during deposition process.

TF-ThP45 Reactive RF Magnetron Sputtering of Vanadium Oxides: Substrate Bias Issues

Sergey Jr. Maklakov*, V.I. Polozov, I.A. Ryzhikov, V.N. Kisel,* Institute for Theoretical and Applied Electromagnetics RAS, Russian Federation

Thin films of vanadium oxides are widely applied functional coatings for electronics. Non-stoichiometric nanocrystalline VO$_x$ films possess low thermal activation energy (~ 0.1 eV). These films serve as infrared detectors in uncooled bolometers. Under certain annealing conditions, VO$_x$ films undergo recrystallization, and stoichiometric VO$_2$ oxide may be formed. Crystalline VO$_2$ films possess metal-insulator transition at 68C. These VO$_2$ films works as switches for transmission lines for terahertz and microwave range. All these VO$_x$ coatings are frequently deposited through magnetron sputtering.

Although reactive sputtering of vanadium in oxygen-containing atmosphere has been studied since 1960's, there are several points that still not clear. It is well known, that when a negative DC bias are applied to substrate, it provides additional energetic treatment of a growing film. It causes re-sputtering of a surface layer and increases effective surface temperature of a growing coating. As a result, films, grown under the bias conditions, are depleted with light elements and show decreased concentration of admixtures. These effects are studied well for biases more than -20 V *(J. Phys. D: Appl. Phys. 39 (2006) 2220–2223)*. We present experiment which shows that substrate bias of low value may influence chemical reactivity of reactive components, giving similar results to large biases.

Series of VO$_x$ thin films was deposited by means of unbalanced RF magnetron source in Ar + O$_2$ gas mixture. Oxygen-depleted films appear as black coatings with metal conductivity. Oxygen-rich films are yellow dielectrics. Oxygen content may be easily controlled through gas composition, which is a common knowledge. Gas mixture (13.6 % O$_2$ for a vacuum facility applied) which gives transient VO$_x$ films between oxygen depleted and oxygen rich compositions, was applied for the experiment. Negative bias of a few volts (starting from -1 V), which is comparable to a floating potential, reduces vanadium oxidation state from V^{+5} down to V^{+2}. No biased substrate, under designated conditions, results in VO$_x$ films, substantially consisting of V^{+5}. Observed effect cannot be explained by resputtering process. Resistivity of VO$_x$ films in the series varies by 5 orders in magnitude. Reduction of vanadium oxidation state also changes the Meyer-Neldel rule type from conventional to inverse. This phenomenon may be caused by changes in oxygen reactivity associated with variations in RF discharge characteristics.

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Spectroscopic Ellipsometry Focus Topic
Room 104C - Session EL+AS+EM+MI+TF-FrM

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Morten Kildemo, Norwegian University of Science and Technology, Nikolas Podraza, University of Toledo

8:20am **EL+AS+EM+MI+TF-FrM1 Magnetoopticalproperties of Metals, Half-Metals, and Garnets Probed by Vector-Magneto-Optical Generalized Ellipsometry***, **Heidemarie Schmidt**,* Technische Universität Chemnitz, Nano-Spintronics Group, Germany **INVITED**

Magnetotransport measurements are a standard technique for the electrical characterization of single layers on insulating substrates. However, magnetotransport measurements require electrical contacts and known current paths, which excludes application to multilayer stacks. Motivated by the recent development of fast Mueller matrix ellipsometers, we have set-up a vector magnetooptical generalized ellipsometer (VMOGE) with an 0.4 T octupole magnet [1] and have investigated magnetooptical response of a single layers and multilayer stacks in a magnetic field of arbitrary orientation and magnitude up to 0.4 T at room temperature. We assume that the off-diagonal element of the magnetooptical dielectric tensor of every magnetizable layer in the multilayer stack is a product of the magnetic field independent and wavelength dependent complex magnetooptical coupling constant and the magnetic field dependent and wavelength independent magnetization of the layer. As an example, the complex magnetooptical coupling constant of nominally 10, 20, and 30 nm thick ferromagnetic Ni films obtained from modelling corresponding VMOGE data is discussed. It was challenging to identify the magnetization direction of Ni films from different sets of magnetic field dependent Mueller matrix elements [2]. In the future knowledge of complex magnetooptical coupling constant of all magnetizable materials in a multilayer stack will allow for modelling and optimizing the magnetooptical response of given stack. As a second example, the modelled complex magnetooptical coupling constant of capped, ferromagnetic Fe, Ni20Fe80, Co, Ni80Fe20, and Ni thin films on ZnO substrates is discussed and related with the spin-dependent electronic bandstructure of given weakly correlated, magnetizable materials [3]. For this comparison the experimental complex off-diagonal elements of the magnetooptical dielectric tensor have been converted into theoretical complex off-diagonal elements of magnetooptical conductivity tensor. Finally, the experimental magnetooptical response of strongly correlated, magnetizable materials [4], e.g. half-metals and garnets, is presented and as an outlook development of new theoretical frameworks for calculating the bandstructure of such strongly correlated, magnetizable materials for a comparison with experiment is motivated. [1] K. M. Mok, N. Du, H. Schmidt, Rev. Sci. Instrum. 82 (2011) 033112; [2] K.M. Mok, C. Scarlat, G. J. Kovács, L. Li, V. Zviagin, J. McCord, M. Helm, H. Schmidt, J. Appl. Phys. 110 (2011)123110; [3] K.M. Mok, G. J. Kovács, J. McCord, L. Li, M. Helm, H. Schmidt, Phys. Rev. B 84 (2011) 094413; [4] G. Kotliar and D. Vollhardt, Physics Today 57 (2004) 53

9:00am **EL+AS+EM+MI+TF-FrM3 *In Situ* Terahertz Optical Hall Effect Measurements of Ambient Doping Effects in Epitaxial Graphene***, S. Knight,* University of Nebraska-Lincoln*; C. Bouhafs, N. Armakavicius, P. Kühne, V. Stanishev, R. Yakimova,* Linköping University, Sweden*; S. Wimer, M. Schubert,* University of Nebraska-Lincoln*; V. Darakchieva,* Linköping University, Sweden*; **Tino Hofmann**,* University of North Carolina at Charlotte

Recently, the cavity-enhanced THz optical Hall effect (THz-OHE) has been demonstrated as non-contact method to obtain free charge carrier properties using low-field permanent magnets [1,2]. A tunable, externally-coupled cavity is used to enhance the THz-OHE signal which allows the accurate determination of a sample's free charge carrier properties even at low magnetic fields. In this work we take advantage of this approach by integrating the permanent magnet into a gas flow cell. We demonstrate for the first time the application of the cavity-enhanced THz-OHE for the *in-situ* characterization of free charge carrier properties of monolayer graphene on Si-face 4H-SiC as a function of ambient conditions. The experiments were performed using a new rotating-analyzer THz ellipsometer at Linköping University. Upon changing the CO_2, H_2O, and O_2 concentration in the cell, large variations in both free charge carrier sheet density N_S and mobility μ are observed for the *n*-type graphene. The lowest N_S was found for the as-grown sample with $N_S = 5.9(1) \times 10^{11}$ cm^{-2} where $\mu = 2507(57)$ cm^2/Vs. The highest N_S was found after purging the sample with nitrogen for 6 hours with $N_S = 2.43(4) \times 10^{12}$ cm^{-2} where $\mu = 1604(23)$ cm^2/Vs. These significant changes are attributed to a redox-reaction of oxygen and water at the graphene surface which results in the extraction of electrons from graphene [3]. This will be discussed in detail in our presentation. We further observe that this doping mechanism is only partially reversible at room temperature upon removal of oxygen, carbon dioxide, and water by purging the cell with nitrogen. In conclusion, we demonstrate *in-situ* THz-OHE as a new and powerful technique to determine ambient-dependent doping mechanisms which is illustrated here using monolayer epitaxial graphene on Si-face 4H-SiC.

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9:20am **EL+AS+EM+MI+TF-FrM4 Excitons at Interfaces in Ellipsometric Spectra***, **Nuwanjula Samarasingha**, C. Rodriguez, J.M. Moya, N.S. Fernando, S. Zollner,* New Mexico State University*; P. Ponath, K. Kormondy, A. Demkov,* University of Texas at Austin*; D. Pal, A. Mathur, A. Singh, S. Dutta, J. Singhal, S. Chattopadhyay,* Indian Institute of Technology Indore, India

The presence of excitonic features in the optical constants and ellipsometry spectra of bulk semiconductors and insulators has been known for many years. In Si, Ge, and GaAs, the E_1 critical points are strongly enhanced by two-dimensional excitons, even at room temperature. Three-dimensional excitons have been seen in ellipsometry spectra for GaP and Ge. Excitons also influence the dielectric function of $SrTiO_3$. An exciton is an electron-hole pair bound by the Coulomb interaction, with properties similar to a hydrogen atom. The influence of excitonic absorption on the dielectric function was described by Tanguy.

In a thin epitaxial layer (with a thickness below or near the Bohr radius) on a substrate with a different band gap, the wave functions of the electron and hole are strongly modified. In a thin type-I quantum well, consisting of a narrow-gap semiconductor grown on a large-gap substrate, both the electron and the hole are confined, which leads to an increase in the dipole overlap matrix element. Therefore, the dominant absorption peak at 4.2 eV is larger in a 20 nm thick $SrTiO_3$ layer on a $LaAlO_3$ substrate than in bulk $SrTiO_3$. (The band gap of $LaAlO_3$ is larger than that of $SrTiO_3$.)

On the other hand, in a staggered type-II quantum well, either the electron is confined, or the hole, but not both. Therefore, the overlap dipole matrix element (and thus the excitonic absorption) is strongly reduced, because one quasiparticle resides in the quantum well and the other one in the substrate. If a $SrTiO_3$ layer is grown on Si or Ge, the valence band maximum occurs in the substrate, while the conduction band offset is very small. Therefore, the exciton wave function is delocalized (deconfined), which reduces the dipole overlap matrix element. Therefore, the real and imaginary part of ε of thin $SrTiO_3$ layers on Si or Ge are much smaller than in the bulk and decrease monotonically with decreasing thickness. A similar effect can be seen for thin ZnO layers on Si as a function of thickness.

The dielectric function of $SrTiO_3$ is not only affected by layer thickness. A very thick polycrystalline $SrTiO_3$ layer on Si has a much lower dielectric function than a single-crystalline $SrTiO_3$ substrate. In this case, we speculate that the magnitude of the dielectric function is related to other Tanguy parameters, perhaps the excitonic binding energy or the exciton decay rate (broadening). To investigate this further, we will perform temperature-dependent ellipsometry measurements on bulk zinc blende GaP, which has a much simpler band structure than wurtzite ZnO or the correlated metal oxide $SrTiO_3$, but shows similar excitonic effects.

9:40am **EL+AS+EM+MI+TF-FrM5 Infrared and Visible Dielectric Properties of $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$***, **Jacqueline Cooke**, N.T. Nunley, T. Willett-Gies, S. Zollner,* New Mexico State University

Using spectroscopic ellipsometry, we determined the dielectric function of LSAT, from the mid-IR to the deep UV (0.03 to 6.5 eV). LSAT is an acronym for the chemical formula $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$, equivalent to $(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$. LSAT is a common substrate for epitaxial growth of complex metal oxides. Precise knowledge of the optical constants is useful to investigate the properties of epitaxial films grown on LSAT. We also investigated the band gap and the infrared-active phonons. Czochralski-grown LSAT wafers with (001) surface orientation were obtained commercially (MTI Corp., Richmond, CA). Single-side polished wafers were used for spectroscopic ellipsometry and two-side polished wafers with 0.5 mm thickness for transmission. Between 0.8 and 6.5 eV, we measured the normal-incidence transmission and the ellipsometric angles from 60° to 80° incidence in 2° steps on a J.A. Woollam variable angle of incidence ellipsometer with a computer-controlled Berek waveplate compensator. We also measured in the mid-IR on a rotating compensator FTIR ellipsometer. Transmission measurements show a steep rise of the absorption coefficient (α) between 4.6 and 4.8 eV, where LSAT becomes opaque. Fitting the ellipsometry data with a model containing two Tauc-Lorentz oscillators and 19 Å surface roughness thickness yields an excellent fit to the data. The Tauc gap is 4.9 eV and the high-frequency dielectric constant $\varepsilon_\infty= 4.0$. Plotting α^2 versus photon energy yields a direct band gap of 5.8 eV. An Urbach tail extends towards lower energies. The resulting dielectric function is in agreement with previous ellipsometry and minimum-deviation prism measurements. The mid-IR dielectric function shows four ε_2 peaks due to TO phonon absorption. The loss function shows four LO peaks. A fifth TO phonon was seen at 155 cm^{-1} in far-IR ellipsometry. An ideal ABO3 perovskite has only three IR-active TO phonons. FCC ordering on the B-site as in (Sr_2AlTaO_3) adds a fourth phonon. We argue that the TO phonons at 155 and 283 cm^{-1} are vibrations of the tetrahedra against the La/Sr sublattices, respectively (mode splitting due to disorder). On the other hand, the 397 and 442 cm^{-1} modes are B-O bending modes due ordering in the Al/Ta sublattice. Finally, a B-O stretch mode at 664 cm^{-1} and broad two-phonon absorption at 765 cm^{-1} are also found. Fitting the spectra with a factorized TO/LO model yields better results than a sum of Lorentzians, because the individual TO/LO pairs are not well separated. The presence of FCC ordering was also confirmed with x-ray diffraction. We will also discuss temperature dependent ellipsometry and transmission measurements.

10:00am **EL+AS+EM+MI+TF-FrM6 A New Constant of Product of Electronic Scattering Time and Resistivity in Thin Silver Refractive Index Calculation from Ellipsometry and Resistivity Measurements***, **Guowen Ding**, C. Clavero, D. Schweigert, M. Le,* Intermolecular, Inc.

The optical and electrical response of metal thin films is highly affected by electronic scattering with the interfaces and defects. We are able to successfully model the electrical resistivity and near infrared (IR) optical response using a thickness dependent electronic scattering time. We investigated Ag films thickness in the range of 3 nm to 74 nm and determined that the product of electronic scattering time (τ) and resistivity (ρ) remains constant regardless of the thickness ($\tau \times \rho = C$), with a value of 59±2 μΩ cm·fs for Ag films. As a result, determining the constant C for a given thin film will allow to calculate the propreties of the film over a large range of wavelengths while limiting the number of measurements.Our findings enable us to develop a theoretical framework to determine the optical response of metal thin films in the near IR by using single wavelength ellipsometer measurements. An excellent agreement is found between experimental measurements and predicted values. We first reported this constant $\tau \times \rho = C$ for silver, and we posit that such constant concept could be applied for other conducting films. Application of the model presented here will allow rapid characterization of the IR optical response of metal thin films, with important application in a broad spectrum of fundamental and industrial applications, including optical coatings, low-emissivity windows and semiconductor industry.

10:20am **EL+AS+EM+MI+TF-FrM7 Realization of an *In Situ* Mueller-matrix Imaging Ellipsometer for the Real Time Observation of Surface Properties in an Ultra-high Vacuum EUV Facility***, **Pim Muilwijk**, N.B. Koster, F.T. Molkenboer, E. Sligte, te, A.F. Deutz, P. Walle, van der,* TNO Technical Sciences, Netherlands

TNO is realizing EUV Beamline 2 (EBL2), a facility to investigate the effects of Extreme Ultra-Violet (EUV) radiation on surfaces to enable future EUV High Volume Manufacturing (HVM) production. In this facility, samples with sizes up to 152x152x20 mm (6” EUV reticles) can be exposed to EUV radiation of up to 500W equivalent at intermediate focus (IF) under realistic environmental conditions and analyzed by in-situ ellipsometry and XPS. EBL2 consists of EUV source, automated handling system, beam line and an exposure chamber with an in-situ dual wavelength Mueller-matrix imaging ellipsometer.

Light from the dual wavelength light source (405 & 640nm) enters the exposure chamber through a polarizer, configurable retarder and a vacuum window producing a defined polarization state. After reflecting off of the sample, the light exits the exposure chamber through a vacuum window, configurable retarder and polarizer. The sample position is imaged on two camera’s, one for each wavelength. By combining all combinations of 4 polarization illumination states with 4 analyser states the full Mueller matrix of the sample can be recovered.

Calibration is performed in-situ with two insertable polarizers and two different calibration samples. The calibration procedure does not require prior knowledge of the polarizer orientation nor of the calibration samples.

This presentation will focus on the design and realization of the ellipsometer and will also touch upon the process of interpreting the data.

EBL2 will be publicly accessible as a test facility for EUV lithography related research after qualification, which is expected to be finished end of Q1 2017.

10:40am **EL+AS+EM+MI+TF-FrM8 Conducting, Semi-Conducting and Insulating 2D-Materials Characterized by Spectroscopic Imaging Ellipsometry***, **Matthias Duwe**, S. Funke,* Accurion GmbH, Germany*; U. Wurstbauer,* Technical University of Munich, Germany*; A. Matkovic,* University of Belgrade, Serbia*; A. Green,* SUNY College of Nanoscale Science and Engineering*; A. Molina-Mendoza,* Universidad Autonoma de Madrid, Spain*; A. Castellanos-Gomez,* IMDEA Nanoscience, Spain*; P.H. Thiesen,* Accurion GmbH, Germany

Finding thin-film flakes of 2D-materials after the fabrication and identifying their layer thicknesses often is a challenging and time-consuming task. Here, we present various applications of spectroscopic imaging ellipsometry (SIE) to a variety of conducting, semi-conducting, and insulating 2D-Materials such as graphene, molybdenum disulfide (MoS_2), hexagonal boron nitride, and black phosphorus. As a combination of polarization-contrast microscopy and spectroscopic ellipsometry, SIE measurements localize microscopic flakes of the 2D-materials, yield the samples’ optical dispersion functions, and determine the layer thicknesses.

Matkovic et al. [1] characterized monolayers of graphene by SIE, and they obtained the optical dispersion by Fano-resonance modelling. Using this dispersion, SIE offers a straightforward search for and identification of few-layer graphene flakes on various opaque or transparent substrates. As this flake search uses ellipsometric measurements, it depends far less on the used substrate compared to e.g. conventional light-microscopy. In a similar procedure, SIE identified monolayers of insulating hexagonal boron nitride, and it yielded the material‘s optical properties.

SIE measurements on MoS_2 revealed the repercussion of the used substrate [2]. Ellipsometric contrast micrographs showed the lateral variation of the optical parameters for a structured flake. Spectroscopic measurements of the ellipsometric values (Ψ & Δ) obtained from selected regions of interest on the flake yielded the optical dispersion for the in-plane and out-of-plane components of the dielectric function in the visible spectral range.

Finally, we will present imaging Mueller-matrix ellipsometry (IMME) for the characterization of thin-film flakes of the semi-conducting 2D-material black phosphorus. In contrast to MoS_2, black phosphorus also features an optical in-plane anisotropy. IMME-micrographs easily reveal this anisotropy as the Mueller matrix's off-diagonal blocks deviate from zero. By performing spectroscopic Mueller-Matrix mapping and rotational Mueller-matrix measurements combined with atomic force microscopy, we obtained the flake’s layer thickness, the orientations of the optical axes, and the material's optical properties in the visible spectral range.

[1] A. Matković, A. Beltaos, M. Milićević, U. Ralević, B. Vasić, D. Jovanović, and R. Gajić, *Spectroscopic imaging ellipsometry and Fano resonance modeling of graphene*, *J. Appl. Phys.*, **112** 123523, (2012)

[2] S.Funke, E. Parzinger, B. Miller, P. H. Thiesen, A.W. Holleitner, U. Wurstbauer, *Imaging Ellipsometry of Mono- to Multilayer ofMoS_2 on Tranparent Sapphire Substrate*, Manuscript in preperation

Thin Film

Room 105A - Session TF-FrM

CVD, ALD and Film Characterization

Moderators: David Adams, Sandia National Laboratories, Halil Akyildiz, North Carolina State University

8:20am **TF-FrM1 Assessing the Role of Temperature and Pressure on the Tungsten ALD Selectivity Window on Si/SiO$_2$ Substrates***, **Paul Lemaire**, G.N. Parsons,* North Carolina State University

Operating conditions such as temperature and pressure are critical variables for atomic layer deposition (ALD) processes. The ALD "temperature window" describes the temperature range in which the growth per cycle is relatively constant. Yet the temperature window typically is in reference to the growth surface and does not include deposition on less thermodynamically favored surfaces. Pressure is typically maintained at ~1 Torr in order to maintain a balance between gas interdiffusion and entrainment, but there has been little work investigating how pressure affects ALD nucleation. In this work we discuss how process temperature and pressure can be adjusted to improve an ALD "selectivity window" aka deposit more material on a growth surface over a non-growth surface. We specifically study a tungsten hexafluoride (WF$_6$) - silane (SiH$_4$) ALD process (W-ALD) to selectively deposit tungsten on silicon (Si) over silicon oxide (SiO$_2$). Ellipsometric and x-ray photoelectron spectroscopy (XPS) analysis shows that the W-ALD selectivity window increases at lower temperatures and at higher pressure. We suggest that this improved selectivity is due to the lowered probability of the WF$_6$ reacting with defect sites on the non-growth SiO$_2$ surface. In addition, we discuss how cyclic gas exposures during the ALD deposition can be used to rapidly change the operating pressure and temperature in order to improve the selectivity window. Results from ellipsometric, and XPS analysis show that dosing He, H$_2$, and CH$_4$ immediately prior to the WF$_6$ exposure improves the selectivity window. We attribute the improved selectivity window to rapid substrate heating which assists in desorption of WF$_x$ species from the SiO$_2$ surface and helps limit undesired tungsten nucleation.

8:40am **TF-FrM2 X-ray Absorption Spectroscopy Study of Nanocomposite Thin Films Grown by Atomic Layer Deposition***, **Anil Mane**, S. Babar, A. Yanguas-Gil,* Argonne National Laboratory*; A. O'Mahony,* Incom, Inc.*; T. Wu, J.W. Elam,* Argonne National Laboratory

We have established an ALD approach to synthesize nanocomposite coatings comprised of conducting, metallic nanoparticles embedded in an amorphous dielectric matrix. These films are nominally composed of M:Al$_2$O$_3$ where (M= W and Mo) and are prepared using alternating exposures to trimethyl aluminum (TMA) and H$_2$O for the Al$_2$O$_3$ ALD and alternating MF$_6$/Si$_2$H$_6$ exposures for the metal ALD. By varying the ratio of ALD cycles for the metal and the Al$_2$O$_3$ components during material growth, we can tune precisely the various material properties such as microstructure, electrical, optical and chemical properties. We have exploited these nanocomposite coatings in several applications such as resistive coatings for large-area microchannel plates suitable for large area photodetectors, charge drain coatings for electron-optic MEMS devices (Digital Pattern Generation chips) for maskless reflection electron beam lithography, protective barrier coatings for Li-ion battery cathodes and solar selective absorber coating for high temperature concentrated solar power (CSP) components.

The ALD surface chemistry for these M:Al$_2$O$_3$ nanocomposite films is complex, particularly during the transitions between the Al$_2$O$_3$ and the metal ALD since the surface functional groups are completely different for these two types of processes. To better understand the relationship between the ALD surface chemistry and the resulting microstructure and composition of these nanocomposite materials, we used a suite of analytical methods including transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and synchrotron X-ray absorption spectroscopy (XAS) performed at the Argonne Advanced Photon Source to characterize W:Al$_2$O$_3$ films while varying the W cycle ratio, W%=(W cycles)/(total cycles)*100. A key result was that for W% < 50, W is present in both metallic and sub-oxide states whereas for W% ≥50, only metallic W is seen. This transition from dielectric to metallic character at W% ~50 is accompanied by an increase in the electrical conductivity and the disappearance of a clear bandgap in the absorption spectrum. TEM revealed that the conducting phase is composed of 1-2 nm metallic nanoparticles embedded in an amorphous matrix. We believe that these nanoparticles form spontaneously during the TMA exposure following a W ALD cycle, and that the TMA acts as a reducing agent.

9:00am **TF-FrM3 A Fundamental Study of Thermal Conductivity in ALD-deposited Amorphous Oxide Thin Films of Varying Density***, **Brandon Piercy**,* Georgia Institute of Technology*; K.E. Meyer, P.E. Hopkins,* University of Virginia*; M.D. Losego,* Georgia Institute of Technology

Non-crystalline materials are believed to follow the minimum thermal conductivity model first proposed by Einstein in 1911. This model predicts that the thermal conductivity (Λ) of an amorphous solid is proportional to the atomic density (n) via a Λ proportional to n$^{2/3}$ relationship. This theory implies that the thermal conductivity of amorphous oxide materials can be controlled via their density. While processing conditions in the microelectronics industry often focus on optimizing the dielectric and electrical resistivity properties of amorphous oxide materials, less attention is given to these layers' thermal properties. However, in high-power applications, the thermal conductivity of these materials begins to have importance. In this presentation, we will report on our new fundamental understanding of two industrially important amorphous metal oxide thin films: Al$_2$O$_3$ and TiO$_2$. ALD deposition of these materials—besides having industrial relevance—also enables direct control over atomic density of these amorphous materials via deposition temperature. In this study, amorphous thin films of Al$_2$O$_3$ and TiO$_2$ of varying density were deposited with ALD over a range of temperatures from 25 °C to 250 °C. The atomic density of these films is assessed with multiple techniques including ellipsometry, x-ray reflectivity, and gravimetric measurements. Time-domain thermoreflectance (TDTR) is used to measure thermal conductivity. TDTR is an ultrafast optical pump-probe measurement that is particularly well-suited for evaluating the thermal conductivity of thin films and other nanostructures. In this study, the density of Al$_2$O$_3$ films was increased by 15%, leading to an increase in thermal conductivity from 1.2 W/m-K to 1.7 W/m-K, a 42% change. TiO$_2$ films saw an increase from 1.4 W/m-K to 1.9 W/m-K (36%) with a 12% increase in density. Thermal conductivities as a function of film densities were fit with the Einstein minimum effective limit model modified with a differential effective-medium approximation, affirming the applicability of the amorphous limit to metal oxide systems. For the case of TiO$_2$, a discrete jump in thermal conductivity to 2.5 W/m-K was detected at the onset of film crystallization (125°C). This result suggests that TDTR can be more sensitive than XRD in detecting the onset of crystallization in amorphous thin films.

9:20am **TF-FrM4 The Development of ALD Barrier Layers for Harsh Environment Applications***, **Ankit Singh**,* Georgia Institute of Technology*; A. Perrotta,* Eindhoven University of Technology, Netherlands*; S. Graham,* Georgia Institute of Technology

Encapsulation of electronic devices using vacuum deposited moisture barrier films is a critical step for their protection and enhancement of lifetime. Devices like implantable devices, OLEDs, OPVs, thin film transistors and thin film solar cells are prone to rapid degradation through chemical reactions with surrounding gas or liquid media. Barrier layers help in avoiding direct exposure of these devices to their surrounding environment thus enhancing their lifetime. Several deposition techniques can be used for preparation of such layers. Atomic layer deposition (ALD) is known to be able to produce ultra-barrier films with water vapor transmission rates lesser than 10-4 g/m2/day. However, performance and reliability of ALD based barrier films is governed by their stability in corresponding environments where resistance to corrosion and material stability will remain a key parameter to their durability.

In this work, we explore the use of TiO2, HfO2, ZrO2, and Al2O3 ALD based barrier films in harsh conditions like high temperature and a range of chemical exposure. The barrier layers were coated over ZnO sensors in order to test their ability to protect the ZnO in harsh environments and can be detected optically using photoluminescence. The exposure included DI water, salt water, phosphate buffer saline solution and low pH (HCl) solution. Degradation in ZnO films was monitored by photoluminescence testing in order to track the decrease in PL signal with time. To compliment the PL study, electron microscopy and a detailed EIS study was conducted in order to understand the mechanism of ALD barrier degradation in different environments. Several of ALD based metal oxides have shown enhanced corrosion resistance outperforming aluminum oxide which showed the least resistance. Finally, application of these barrier layers in protection of organic electronics and inorganic solar cells has been demonstrated.

9:40am **TF-FrM5 Conformal CVD Growth of HfB_xC_y and HfB_xAl_y Hard Coatings with Low Coefficient of Friction and High Oxidation Resistance**, ***Elham Mohimi***, *T. Ozkan, S. Babar, Z. Zhang, S. Liu, G.S. Girolami, A.A. Polycarpou, J.R. Abelson,* University of Illinois at Urbana Champaign

Conformal hard coatings with low coefficient of friction, high oxidation resistance and chemical stability are desired for applications such as components with convoluted structures, cutting tools that sustain high temperature, thermal protection systems for extreme environments, and machines with relative motion of parts. We previously reported the conformal growth and excellent mechanical properties of HfB_2 and HfB_xN_y hard coatings by chemical vapor deposition (CVD) below 300°C using the high vapor pressure precursor hafnium borohydride, $Hf(BH_4)_4$. Here we report a further improvement in the properties of HfB_2 films by alloying with C to reduce the coefficient of sliding friction, and with Al to impart high temperature oxidation resistance.

All Depositions are performed in a high vacuum chamber using 0.1-0.5 mTorr of the hafnium borohydride precursor. Carbon-alloyed HfB_xC_y films are grown using a co-flow of 0.1-0.4 mTorr dimethylbutene (DMB) as the C source at substrate temperatures of 250-600°C. The resulting films contain 5-33 at. % C. DMB also acts as growth inhibitor that reduces the growth rate by a factor of 2-6 compared to growth using the precursor alone; this affords almost perfect conformality, e.g., a step coverage > 90% in a trench of aspect ratio 30:1. The nanoindentation hardness varies from 21 to 9 GPa for films with 5-21 at. % C grown at 300°C, and from 23-25 GPa for films with 28-35 at. % C grown at 600°C. The coefficient of sliding friction is remarkably low, 0.05-0.08 for films with the highest and lowest carbon content, respectively. In addition, the elastic response is more compliant, which is expected to improve the tribological wear performance.

Al-alloyed HfB_xAl_y films are grown using a co-flow of 0.05-0.20 mTorr trimethyl amine alane (TMAA) as aluminum source at a temperature of 250-300°C. In the absence of alloying, HfB_2 films exposed to an oxygen ambient at 800°C will oxidize deeply because HfO_2 does not provide a protective layer and B_2O_3 evaporates rapidly. In sharp contrast, films containing 1-20 at. % Al form a protective aluminum oxide surface layer. Compositional depth profiles confirm the absence of oxidation below this surface layer. In addition these films are morphologically stable: whereas HfB_2 crystallizes, densifies and forms a network of cracks at temperatures above ~ 600°C, the HfB_xAl_y films do not crystallize or crack upon annealing to 800°C in inert or oxidizing atmospheres. Future work, including the co-alloying with C and Al, will explore property optimization in which both low friction and oxidation resistance are desired.

10:00am **TF-FrM6 Chemical Vapor Deposition of Silanes for Surface Modification**, ***Brian Johnson***, *M.R. Linford,* Brigham Young University

Silanes are arguably the most important reagents for chemically modifying surfaces. They have the unique ability to attach to silanol (SiOH) groups while imparting desired functionality. Indeed, they are extensively used to modify silica for chromatography and silicon wafers to create attachment layers for biosensors and bioarrays. Of course, HMDS is an important silane that is widely used in the semiconductor industry. Interestingly, most of the reports in the literature on silane deposition describe their liquid phase deposition. The obvious drawbacks of this approach are its lack of reproducibility and the consumption of large amounts of solvent both in the deposition and rinsing of the surfaces. Clearly there are health/safety issues associated with this use of solvent. Its advantages are simplicity – only beakers/simple glassware are required. The gas phase deposition of silanes has exactly the opposite advantages. It offers greater reproducibility and control, but the equipment required is much more complex and expensive. Nevertheless, the semiconductor and related industries much prefer the latter chemical vapor deposition (CVD) direction. Here we describe the CVD of various silanes under the controlled conditions offered by a commercial deposition system. We describe the effect of reactive functionality in the silane on deposition. We show how varying the temperature substantially changes film growth (silane deposition). We describe system cleanliness issues and the means by which carry over between runs can be nearly eliminated. We discuss the deposition of both monofunctional and trifunctional silanes. Films are characterized by X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and contact angle goniometry. Water contact angles and film thicknesses of hydrophobic silanes are strongly correlated. Best conditions for the gas phase deposition of some important silanes are presented.

10:20am **TF-FrM7 Iron CVD from Iron Pentacarbonyl: Growth Inhibition by CO Dissociation and Use of Ammonia to Restore Constant Growth**, *P. Zhang, E. Mohimi, T. Talukdar, G.S. Girolami,* ***John Abelson,*** University of Illinois at Urbana Champaign

The precursor $Fe(CO)_5$ can be used to deposit Fe and Fe alloy thin films by CVD. However, at temperatures of 200-300°C this system exhibits undesirable behaviors – a reduction in growth rate with increasing temperature, a change in morphology from faceted to irregular, and a self-limiting film thickness – that make film growth very difficult to control and reproduce. We hypothesize that decomposition of CO ligands poisons the growth surface with graphitic carbon, on which further precursor reaction is suppressed.

Here, we report a novel solution based on surface chemistry: injection of NH_3 along with $Fe(CO)_5$ eliminates the poisoning effect, i.e., Fe CVD becomes stable and reproducible in the temperature range of 200-300°C with little change in morphology or growth rate. We propose that NH_3 removes CO from the growth surface before it can decompose based on mechanisms that were previously investigated for CO on static Fe surfaces[1].

We report that co-flow of NH_3 entirely restores the growth rate and morphology of pure Fe and of Fe_xCo_{1-x} films. The use of NH_3 may be applicable to other set carbonyl-based CVD precursors.

1. Johnston, Colin, Norman Jorgensen, and Colin H. Rochester. "Infrared study of ammonia–carbon monoxide reactions on silica-supported iron catalysts."*Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 84.10 (1988): 3605-3613.

10:40am **TF-FrM8 New Insights on the Structure and Chemistry of the Tin Oxide-emitter Interface in CdTe Solar Cells as revealed by Thermomechanical Cleavage and Electron Spectroscopy**, ***Craig Perkins***, *C. Beall, J.M. Burst, A. Kanevce, M.O. Reese, T.M. Barnes,* National Renewable Energy Laboratory

CdTe solar cells having superstrate architectures have a poorly understood, complex front surface formed via interdiffusion of the CdS-based emitter and the CdTe absorber. Interfaces in this region of the cell are difficult to probe by standard surface analytical methods because they are bound by glass on one side and microns of CdTe on the other. Post-growth processing with $CdCl_2$ and for back contacting is likely to further change these buried interfaces, making the traditional scheme of interface analysis – interleaved depositions and analyses – impractical. Yet these front interfaces are important. Recent modeling shows that recombination at the cell front will be increasingly critical to cell efficiency as doping levels are improved from ~$10^{14}/cm^3$ to $10^{16}/cm^3$. In this study we make use of a LN2-based thermomechanical cleavage technique and a surface analysis cluster tool to probe in detail the tin oxide-emitter interface in completed CdTe solar cells. We show that this thermomechanical cleavage occurs within a few angstroms of the SnO_2-emitter interface. An unexpectedly high concentration of chlorine, ~20%, was determined from a calculation that assumed a uniform chlorine distribution. Angle-resolved X-ray photoelectron spectroscopy was used to further probe the structure of the chlorine containing layer, revealing that both sides of the cleave location are covered by a single unit cell of $CdCl_2$. Exposing these newly formed surfaces to water showed that CdTe solar cells made using $CdCl_2$ and CdS:O emitters contain water-soluble components at their front surfaces, raising questions pertinent to cell reliability. We show that the SnO_2-emitter interface is also characterized by an extremely strong gradient in oxidation of the chalcogens present as well as a high fraction of oxidized tellurium. Selenium addition to the front of the device, done to improve carrier lifetimes, also affects the extent of chalcogen oxidation. Our work provides new and unanticipated details about the structure and chemistry of front surface interfaces and should prove vital to improving materials, processes, and reliability of next generation CdTe-based solar cells.

11:00am **TF-FrM9 Defect Tolerance in Methylammonium Lead Triiodide Perovskite**, ***Xerxes Steirer***, *P. Schulz, G. Teeter, V. Stevanovic, M. Yang, K. Zhu, J.J. Berry,* National Renewable Energy Laboratory

X-ray photoelectron spectroscopy (XPS) is used to track dynamic chemical and electronic changes in hybrid perovskite ($CH_3NH_3PbI_3$) thin-films used in photovoltaic applications. We report in detail X-ray induced transformations with implications on theoretical predictions of hybrid perovskite defect tolerance. Large changes in perovskite composition are analyzed with simultaneously acquired valence band spectra. A clear and reproducible trend is found that provides evidence for vacancy-type defect formation upon X-ray irradiation as $CH_3NH_3PbI_3$ is continuously converting to PbI_2. Remarkably, the position of the valence band edge with respect to the Fermi level (E_F) is invariant to significant losses of both CH_3NH_3 and I. It is not until the I/Pb ratio drops below 2.5 that E_F shifts toward the valence band edge indicating that the $CH_3NH_3PbI_3$ film becomes less *n*-type. This shift is correlated with the formation of PbI_2 as demonstrated in Pb 4f and I 3d core level spectra. Results gained from these XPS studies demonstrate that the electronic structure of the hybrid perovskite compound investigated is tolerant to defects (CH_3NH_3 and iodine vacancies) on the order of one defect pair per octahedron.

11:20am **TF-FrM10 Non Uniform Deposition Rate Profile during the Growth of SiO_2 Films Deposited by Atmospheric Pressure PECVD***, **Anna Meshkova**,* FOM Institute DIFFER, Netherlands*; F.M. Elam, S.A. Starostin,* FUJIFILM Manufacturing Europe, Netherlands*; M.C.M. van de Sanden,* FOM Institute DIFFER, Netherlands*; H.W. de Vries,* FOM institute DIFFER, Netherlands

It was recently demonstrated that high quality dense inorganic oxide films can be synthesized on polymers utilizing the roll-to-roll Atmospheric Pressure PECVD process assisted by the diffuse dielectric barrier discharge (DBD) between cylindrical drum electrodes. In such a reactor configuration the local deposition rate as well as the local plasma chemistry is highly non-uniform along the gas flow due to the depletion of the precursor and spatial-temporal non uniformity of the discharge.

It is therefore expected that the properties of the film will vary depending on deposition location within the reactor. Hence the analysis of the spatially averaged layer deposited on the substrate roll-to-roll transported through the active reactor length is not sufficient for understanding the film growth process. The aim of the present contribution, therefore, is to study the local kinetics, gas phase transport and film growth mechanisms by means of spatially resolved analysis of the film properties in the gas flow direction of the AP-PECVD reactor, by analysis of the deposition rate profile, morphology, chemical composition and microstructure.

The set of SiO_2 films was grown in an AP-PECVD reactor with parallel bi-axial cylindrical electrode geometry on PEN foil. TEOS was used as a precursor for silica-like thin films and the process gasses were argon, nitrogen and oxygen. The variation the of deposition rate along the gas flow was accessed by measuring the film thickness profile by means of a focused beam SE with a beam size of 120 µm. The composition and microstructure was analysed by spatially resolved XPS and ATR-FTIR.

Surprisingly it was found that deposition rate profile along the gas flow has two distinct maxima. The presence of two maxima indicates a difference in the transport kinetics of the precursor fragments arriving to the surface. This coincides well with the observed variation in film microstructure in the downstream direction, assessed by ATR-FTIR analysis, with higher network porosity for lower gas residence time and denser films deposited in high residence time regions. This spatial non-uniformity within the reactor results in a depth gradient of the film properties synthesized on web-rolled substrate. One can conclude that, for the studied AP-PECVD process, the film density will increase from the silica/polymer interface towards silica/air interface when the polymer substrate is transported along gas flow. By controlling the gas flow speed the density of the layer can be modified. The last observation is especially relevant regarding the design of the gas diffusion barrier layers.

11:40am **TF-FrM11 X-Ray Diffraction from Pseudomorphic GaAs/$In_{0.3}Ga_{0.7}$As Superlattice High Electron Mobility Transistor Heterostructures on GaAs (001) Substrates***, **Fahad Althowibi**, J.E. Ayers,* University of Connecticut

Pseudomorphic high-electron mobility transistors (HEMTs) are of great of interest for high-frequency applications. One approach to pseudomorphic transistors involves a superlattice structure, thereby decreasing the individual active layer thicknesses and extending the range of composition for pseudomorphic realization. Generally, X-ray characterization of pseudomorphic HEMTs is difficult to implement due to the complexity of the resulting diffraction profiles. In this work we show for the first time that superlattice implementation of HEMTs aids in the characterization of the pseudomorphic/metamorphic transition by x-ray diffraction means.

Here we report a study of the dynamical x-ray diffraction from GaAs/$In_{0.3}Ga_{0.7}$As superlattice high electron mobility transistor heterostructures on GaAs (001) substrates both with (metamorphic) and without (pseudomorphic) dislocations. We show that the threading dislocation density may be estimated from non-destructive x-ray rocking curve measurements, using the rocking curve peak intensity ratios and widths for superlattice diffraction peaks. Here, the peak widths are obtained from the broadening of the individual rocking curve peaks, while the reduction in peak intensity values may be also used to serve as a sensitive tool for the characterization of threading dislocations. These approaches therefore allow characterization of HEMT structures as pseudomorphic or metamorphic.

12:00pm **TF-FrM12 Flexible CIGS Nanorod Array Photodetectors***, **Emad Badradeen**, M. Brozak, K.M. Al-Mayalee, F. Keles, T. Karabacak,* University of Arkansas at Little Rock

In this study, we fabricated core-shell nanostructured flexible photodetectors on flexible substrates of Kapton. For this purpose, p-type copper indium gallium selenide (CIGS) nanorod arrays (core) were coated with aluminum doped zinc oxide (AZO) films (shell) at relatively high Ar gas pressures. CIGS nanorods were prepared by glancing angle deposition (GLAD) technique using a RF magnetron sputtering unit at room temperature. AZO films were deposited by RF sputtering at Ar pressures of 1.0×10^{-2} mbar (high pressure sputtering, HIPS) for the shell and at 3.0×10^{-3} mbar (low pressure sputtering, LPS) for top contact. The morphological characterization was carried out by field-emission scanning electron microscope. The photocurrent measurement was conducted under 1.5 AM sun under zero electrical bias. GLAD nanostructured flexible photodetectors were shown to demonstrate enhanced photoresponse with a photocurrent density value of 2.88 µA/cm^2. On the other hand, conventional planar thin film devices did not show any notable photoresponse. Improved photoresponse of CIGS nanorod devices are believed to be due to their enhanced light trapping property and the reduced inter-electrode distance as a result of core-shell structure, which allows the effective capture of the photo-generated carriers. This approach can open up a new strategy to boost the performance of flexible photodetectors.

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