Spectroscopic Ellipsometry Focus Topic
Room: 9 - Session EL+AS+EM+TF-MoM

Application of SE for the Characterization of Thin Films and Nanostructures
Moderator: Tino Hofmann, University of North Carolina at Charlotte

8:20am **EL+AS+EM+TF-MoM1 Ultra-thin Plasmonic Metal Nitrides: Optical Properties and Applications**, ***Alexandra Boltasseva***, Purdue University **INVITED**

Transition metal nitrides (e.g. TiN, ZrN) have emerged as promising plasmonic materials due to their refractory properties and good metallic properties in the visible and near infrared regions. Due to their high melting point, they may be suitable for high temperature nanophotonic applications. We have performed comprehensive studies of the temperature induced deviations to the dielectric function in TiN thin films. The studies were conducted on 30 nm, 50 nm, and 200 nm TiN films on sapphire substrates at temperatures up to 900 0C in the wavelength range 350-2000 nm using a custom built in-situ high temperature ellipsometry setup. The results were fitted with a Drude-Lorentz model consisting of one Drude oscillator and 2 Lorentz oscillators. As the temperature is elevated, the real and imaginary parts both begin to degrade. However, the deviations to the optical properties of TiN are significantly smaller compared to its noble metal counterparts, with no structural degradation in the TiN films. In addition to high temperature applications, TiN could also be a potential material platform for investigating light-matter interactions at the nanoscale, since high quality, continuous films of TiN can be grown on substrates such as MgO and c-sapphire down to just a few monolayers. Ultrathin TiN films with thicknesses of 2, 4, 6, 8, and 10 nm were grown on MgOusing DC reactive magnetron sputtering, resulting in high quality films with low roughness. The changes in the linear optical properties were investigated using variable angle spectroscopic ellipsometry at angles of 50° and 70° for wavelengths from 400 nm to 2000 nm. A Drude-Lorentz model consisting of one Drude oscillator and one Lorentz oscillator was used to fit the measurements. As the thickness decreased, an increase in the losses and a decrease in the plasma frequency was observed. However, the films remained highly metallic even at 2nm, demonstrating that they could be used for nanophotonicapplications, including nonlinear optical devices and actively tunable plasmonic devices.

9:00am **EL+AS+EM+TF-MoM3 Magnetron Sputtering of TiN Coatings: Optical Monitoring of the Growth Process by Means of Spectroscopic Ellipsometry**, ***Jiri Bulir***, *J. More Chevalier, L. Fekete, J. Remiasova, M. Vondracek, M. Novotny, J. Lancok*, Institute of Physics ASCR, Czech Republic

The plasmonic applications requires search for novel materials with metal-like optical properties and low optical losses. Transition metal nitrides such as TiN, TaN, ZrN, HfN, NbN exhibit metallic properties depending on concentration of free-carrier of charge. Their plasmonic properties can be tuned by deposition parameters controlling the film structure and the stechiometry.

In this work, we deal with study of growth process of TiN films. The films are grown by RF magnetron sputtering on fused silica, silicon and MgO substrates at substrate temperature ranging from 20°C to 600°C. The growth process is monitored using in-situ spectral ellipsometer in spectral range from 245 to 1690 nm. The ellipsometric data, which are obtained during the deposition process, are attentively analysed using mathematical models based on Drude-Lorentz oscillators.

The Lorentz oscillators are used for description of interband transition in ultraviolet and visible spectral range, whereas the Drude oscillator describes the free-electron behavior in the infrared spectral range. We show that the free-electron behavior is affected by thickness of the ultrathin coatings due to electron scattering effects at the interfaces. Number of physical parameters such as free-electron concentration, Drude relaxation time and electrical conductivity is estimated at each stage of the deposition process by analysis of dielectric functions using the mentioned model. The resulting evolution of the electrotransport properties during the TiN film growth is presented. Special attention is devoted to the initial nucleation stage when the free-electron behaviour is significantly influenced by the interface between the substrate and the TiN film. Based on evolution of electrotransport properties, we discuss differences between polycrystalline growth of TiN film on Si and fused silica substrates and epitaxial growth on MgO substrates.

The accomplished TiN coatings are analyzed using infrared ellipsometer operating in spectral range from 1.7µm to 30µm where the optical constants are infuenced most importantly by free-electron behaviour. The obtained results are compared with those obtained by the in-situ ellipsometer. Special attention is focused on scattering of free electrons at grain boundaries and at the TiN layer interfaces. The estimated parameters are correlated with structure changes such as grain coarsening and surface morphology. The crystallinity is analysed by X-ray Difractometry. The surface morphology of the completed coatings is studied using Atomic Force Microscopy and Scanning Electron Microscopy. The TiN film stechiometry is estimated by X-ray Photoemission Spectroscopy.

9:20am **EL+AS+EM+TF-MoM4 Variable Temperatures Spectroscopic Ellipsometry Study of the Optical Properties of InAlN/GaN Grown on Sapphire**, *Y. Liang*, Guangxi University, China, *H.G. Gu*, Huazhong University of Science and Technology, China, *J. Xue*, Xidian University, China, ***Chuanwei Zhang***, Huazhong University of Science and Technology, China, *Q. Li*, Guangxi University, China, *Y. Hao*, Xidian University, China, *S.Y. Liu*, Huazhong University of Science and Technology, China, *Q. Yang, L. Wan, Z.C. Feng*, Guangxi University, China

Indium aluminum nitride (InAlN), a prospective material for lattice matched confinement layer, possesses the potential to improve the reliability and performance of high electron mobility transistors (HEMTs).[1] One of the important advantages of InAlN alloy is the possibility of growing in-plane lattice-matched to GaN for an indium content of around 17%. However, the bandgap we expected is hindered by the growth of high-quality InAlN films due to the phase separation and nonuniform composition distribution.[1-2]

In this work, InAlN/GaN heterostructures, grown by pulsed metal organic chemical vapor deposition (PMOCVD) on c-plane sapphire substrates, were investigated by a dual rotating-compensator Mueller matrix ellipsometer (ME-L ellipsometer, Wuhan Eoptics Technology Co. Ltd., China). The experimental data (Ψ and Δ), covering the wavelength (λ) range from 193 nm up to 1700 nm at 1 nm step or energy (E) from 0.73 eV to 6.43 eV, were obtained by variable temperatures spectroscopic ellipsometric (VTSE) in three angles (50°, 55° and 60°). The Eoptics software was utilized to fit VTSE data using Tauc-Lorentz multiple oscillator modes. By analyzing the fitting results, the optical constants of the InAlN at variable temperatures (25°C-600°C) were obtained. The peak value of the refractive index increases from 269 nm to 284 nm with increasing temperature. The bandgaps are 4.57 eV and 4.35 eV at the temperature 25°Cand 600°C, respectively. These results demonstrated that InAlN/GaN has a high thermal stability, scilicet no significant performance degradation in high temperature environment.

Reference

[1] Wenyuan Jiao, Wei Kong, Jincheng Li et al, Characterization of MBE-grown InAlN/GaN heterostructures valence band offsets with varying In composition, AIP ADVANCES 6, 035211 (2016).

[2] JunShuai Xue, JinCheng Zhang, Yue Hao, Investigation of TMIn pulse duration effect on the properties of InAlN/GaN heterostructures grown on sapphire by pulsed metal organic chemical vapor deposition, Journal of Crystal Growth 401, 661 (2014).

9:40am **EL+AS+EM+TF-MoM5 Optical Properties of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ Double Perovskite Studied by Spectroscopic Ellipsometry**, ***Honggang Gu***, *S.R. Li, B.K. Song, J. Tang, S.Y. Liu*, Huazhong University of Science and Technology, China

During the past several years, the organic-inorganic lead halide perovskites ($APbX_3$, A = CH_3NH_3 or NH_2CHNH_2, X = Cl, Br, or I) have been promising materials for photovoltaic, photoelectric -detecting and light-emitting devices due to their outstanding photoelectric properties, such as broad absorption range, high quantum efficiency, ultrafast charge generation, high charge carrier mobility and long charge carrier lifetime and diffusion length. However, there are two remaining challenges that need to be addressed in order to apply these materials to photoelectric productions, namely the compound stability and the presence of lead. Most recently, lead-free metal halide double perovskites, such as $Cs_2AgBiCl_6$ and $Cs_2AgInCl_6$, have attracted extensive attention because of their nontoxicity and relative air-stability. In the study and application of these perovskite materials, the knowledge of their optical properties, such as the bandgap and the basic optical constants, is of great importance to predict the photoelectric characteristics and dig the potential of the materials.

Spectroscopic ellipsometry (SE) has been developed as a powerful tool to characterize the optical properties as well as structure parameters of novel materials, thin films and nanostructures. In this work, we study the optical properties of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ perovskites by a spectroscopic ellipsometer (ME-L ellipsometer, Wuhan Eoptics Technology Co., Wuhan, China). The refractive index and the extinction coefficient of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ with different composition coefficient *x* of bismuth are determined by the ellipsometer over the wavelength range of 250-1000nm. We find that the presence of bismuth introduces two critical points in the optical constant spectra of the perovskites, i.e., 315nm and 382nm in the refractive index spectra and 300nm and 375nm in the extinction coefficient spectra, respectively. Moreover, there is a red shift in the bandgaps and significant increase in both the refractive index and the extinction coefficient with the increase of composition coefficient *x* of bismuth.

10:00am **EL+AS+EM+TF-MoM6 Charge Carrier Dynamics of Aluminum-doped Zinc Oxide Deposited by Spatial Atomic Layer Deposition**, ***Daniel Fullager***, *G. Boreman, T. Hofmann,* University of North Carolina at Charlotte, *C.R. Ellinger*, Eastman Kodak Company

Transparent conductors for displays, backplanes, touchscreens and other electronic devices are an area of active research and development; in this manner, aluminum-doped zinc oxide (AZO) has shown promise as an ITO replacement for some applications. Although there have been numerous reports on the optical properties and electrical conductivity of AZO, there has not yet been a Kramers-Kronig consistent dispersion model fully describing the charge carrier dynamics. In this presentation, we will report on the model dielectric function of AZO from the combination of UV-Vis and IR spectroscopic ellipsometry. A model dielectric function that describes the optical response over this wide spectral range will be presented and discussed. In particular, we will present a comparison between the commonly used extended Drude models and the dielectric function developed here in light of results obtained from density functional theory calculations.

The AZO films analyzed in this study were deposited using a spatial atomic layer deposition (SALD) process. While AZO can be deposited by several techniques, including sputtering, chemical vapor deposition (CVD), and atomic layer deposition (ALD), ALD does allow for the greatest ability to control the aluminum-doping level of AZO. However, the range of substrate sizes and form factors addressable by traditional chamber ALD are limited. Conversely, spatial ALD (SALD) is an atmospheric pressure, roll-compatible ALD process that enables the materials property control of ALD to be translated into a wider range of applications spaces. Furthermore, the use of selective area deposition in a "patterned-by-printing" approach enables the high-quality AZO deposited by SALD to be easily patterned, offering an integrated and facile path for manufacturing optical and electronic devices.

10:40am **EL+AS+EM+TF-MoM8 Broad Range Ellipsometry Shining Light onto Multiphase Plasmonic Nanoparticles Synthesis, Properties and Functionality**, ***Maria Losurdo***, CNR-NANOTEC, Italy **INVITED**

How rich are the physics, interface chemistry and optical properties associated with the surface plasmons of metal nanostructures and their potential for manipulating light at the nanoscale! For many technological applications nanoparticles (NPs) are supported on a substrate, and at the nanoscale, interaction and interfaces with the support become very important. We have demonstrated that the substrate/NPs interaction is the key to engineering not only the shape but also the crystalline phase of NPs.

This contribution will present and explore fundamental and applied aspects of multiphase core-shell plasmonic NPs supported on substrates of technological interest using various diagnostic tools, which comprise: (i) spectroscopic ellipsometry spanning the THz, IR, visible, and UV wavelength ranges, (ii) variable angle Muller Matrix ellipsometry to qualify size effects on anisotropy and depolarization of samples, (iii) *in-situreal-time* spectroscopic ellipsometry to understand growth and tailor particle size which ultimately controls the plasmon resonance, and (iv) various imaging and microscopies techniques to elucidate the interplay between the nanostructure of multiphase nanoparticle and their functionality.

The case studies involve liquid-shell/solid-core plasmonic NPs (Ga, Ga/Mg), plasmon-catalytic core/shell Ga/Pd and plasmon-magnetic Ni/Ga NPs supported on various substrates (glass, plastics, sapphire) that control their crystalline phases.

We will start with a description of the *real-time* ellipsometry capabilities in monitoring the growth of those multiphase core/shell NPs to detect the formation of the various phases in situ and to control the resulting plasmon resonance.

The discussion then will shifts to a description of fundamental of thermodynamics of substrate supported multiphase NPs and how their growth dynamics is controlled by the interface energies, and how those new phenomena can be highlighted by real-time ellipsometry.

Ex-situ corroborating measurements of Mueller-matrix ellipsometry and hyperspectral cathodoluminescence spectroscopy and imaging will be presented to discuss phenomena of depolarization and of interaction of NPs resulting from the self-assembly.

Finally, since those NPs enable active plasmonics, we demonstrate the implications of the multi-phase nature of NPs, as well as solid-liquid phase coexistence on the plasmon resonance (LSPR) of supported NPs and on its exploitation to follow in real time phenomena in their application in catalysis (hydrogen storage and sensing) and optomagnetism and possible future directions.

The contribution of the H2020 European programme under the project TWINFUSYON (GA692034) is acknowledged

11:20am **EL+AS+EM+TF-MoM10 Use of Evolutionary Algorithms for Ellipsometry Model Development and Validation using Eureqa**, ***Neil Murphy***, Air Force Research Laboratory, *L. Sun*, General Dynamics Information Technology, *J.G. Jones*, Air Force Research Laboratory, *J.T. Grant*, Azimuth Corporation

Eureqa, developed by Nutonian Inc., is a proprietary modeling engine based on automated evolutionary algorithms. In this study, we utilized Eureqa to parameterize both the amplitude and phase difference data for reactively sputtered thin films. Specifically, evolutionary algorithms are used to develop and validate models for fitting raw ellipsometric data for a variety of optical materials including SiO_2, Ta_2O_5, and Aluminum Zinc Oxide. These films, deposited using pulsed DC magnetron sputtering, were deposited on both silicon and fused quartz substrates, and measured using a J.A. Woollam VASE system. The resulting models are then compared to traditional models that are currently utilized to fit the candidate materials systems.

11:40am **EL+AS+EM+TF-MoM11 Excitonic Effects on the Optical Properties of Thin ZnO Films on Different Substrates**, ***Nuwanjula Samarasingha***, *Z. Yoder, S. Zollner*, New Mexico State University, *D. Pal, A. Mathur, A. Singh, R. Singh, S. Chattopadhyay*, Indian Institute of Technology Indore, India

The presence of excitonic features in the optical constants 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. Three-dimensional excitons have been seen in ellipsometry spectra for GaP and Ge. In addition to these semiconductors, wide band gap materials like ZnO exhibit strong excitonic features in the dielectric function (ε) which is directly related to the electronic band structure. The top valence band at the Γ point in the Brillouin zone is split into three bands by spin orbit and crystal field splitting. The corresponding free exciton transitions between the lowest conduction band and these three valence bands are denoted by A, C (Γ_7 symmetry) and B (Γ_9 symmetry). The transition from the B subband is forbidden for light polarized parallel to the optical axis (extraordinary dielectric function). ZnO is attractive for optoelectronic device applications due to its large excitonic binding energy of 60 meV at room temperature.The influence of this excitonic absorption on ε was described by Tanguy [1].

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

In a thin epitaxial layer on a substrate with a different band gap, the wave functions of the electron and hole are strongly modified. In ZnO (band gap 3.37 eV) grown on a large-gap SiO_2 substrate (type-I quantum well), both the electron and the hole are confined, which leads to an increase in the dipole overlap matrix element. Therefore, the real and imaginary part of ε of thin ZnO layers on SiO_2 are much larger than in the bulk and increase monotonically with decreasing thickness.

On the other hand, in a staggered type-II quantum well (ZnO on Si), either the electron is confined, or the hole, but not both. Therefore, the overlap dipole matrix element is strongly reduced. Therefore, ε of thin ZnO layers on Si is much smaller than in the bulk and decreases monotonically with decreasing thickness. We will fit our ellipsometric spectra by describing the dielectric function of ZnO using the Tanguy model [1]. We will analyze the dependence of the excitonic Tanguy parameters on quantum well thickness and substrate material.

Reference:

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

Electronic Materials and Photonics Division
Room: 14 - Session EM+MI+TF-MoM

Growth, Electronic, and Magnetic Properties of Heusler Compounds

Moderators: Rehan Kapadia, University of Southern California, Seth King, University of Wisconsin - La Crosse

8:20am **EM+MI+TF-MoM1 Semiconducting Half-Heusler Heterostructures Grown by Molecular Beam Epitaxy**, ***Anthony Rice***, *S.D. Harrington, D.J. Pennachio, M. Pendharkar, C.J. Palmstrøm*, University of California at Santa Barbara

Half-Heusler (hH) compounds are an attractive family of materials for a number of applications due to their wide range of properties, including half-metallic ferromagnetism and topologically non-trivial surface states. Additionally, those containing 18 valence electrons per formula unit are predicted to show a semiconducting band gap [1]. This suggests the possibility of a single multifunctional material composed of compounds with the same crystal structure throughout which makes use of the diverse hH properties not accessible by traditional III-V technology as well as more traditional band gap engineering.

In this presentation, the heterointerface formed between the 18 valence electron semiconducting hHs, CoTiSb and NiTiSn, is investigated. Layered structures with both NiTiSn and CoTiSb, have been successfully grown on MgO(001) substrates using molecular beam epitaxy. Transmission electron microscopy and X-ray diffraction (XRD) data suggest separate layers with sharp interfaces. X-ray photoelectron spectroscopy (XPS) data shows no evidence of intermixing, with component peaks attenuating as expected. XPS is used to measure the valence band offset, which suggests a type-I heterojunction.

Through the use of CoTiSb buffer layers, the integration of NiTSn with III-V substrates is demonstrated. Previous attempts at direct growth of NiTiSn on III-Vs has proven unsuccessful due to the high reactivity of nickel with III-Vs. Reflection high-energy electron diffraction intensity oscillations during growth are observed for these structures, consistent with layer-by-layer growth. XRD interference fringes suggest abrupt interfaces. Higher quality NiTiSn is ultimately achieved, with lower carrier concentrations and higher mobility. Interface transport, both laterally and vertically, is also explored.

This work was supported in part by the Vannevar Bush Faculty Fellowship (ONR-N0014-15-1-2845) and NSF-MRSEC (DMR-1121053). The UCSB MRL Shared Experimental Facilities are supported by the MRSEC Program of the NSF under Award No. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network. A part of this work was performed in the UCSB Nanofabrication Facility which is a part of the NSF funded National Nanotechnology Infrastructure Network.

[1] T. Graf, C. Felsar, and S. Parkin. Progress in Solid State Chemistry 39 (2011) 1-50

8:40am **EM+MI+TF-MoM2 Towards Topotronics: Combining Chemical Potential Tuning and Strain Engineering to Realize Surface Dominated Transport in Topological Heusler Thin Films**, ***Shouvik Chatterjee***, *J.A. Logan, N.S. Wilson, M. Pendharkar, C.J. Palmstrøm*, University of California at Santa Barbara

Heusler compounds have emerged as an exciting material system where realization of functional and tunable novel topological phases might be possible[1-4]. PtLuSb is one such compound that has been shown to host topologically non-trivial surface states[5]. However, being a semi-metal without a bulk band gap, exotic transport and thermodynamic properties expected from topological surface states are obscured by contributions from trivial bulk carriers that limits possible device applications[6]. Furthermore, natural defects in the compound leads to unintentional p-type doping resulting in the surface Dirac point lying above the chemical potential[5,6,7].

In this talk, I will present our efforts to address both these issues by a combination of carrier doping and substrate induced bi-axial strain to shift the chemical potential and attempt to open up a bulk gap, respectively. I will show experimental evidence of chemical potential tuning in Au alloyed $Pt_{1-x}Au_xLuSb$ thin films where the surface Dirac point can be pushed below the Fermi level. In addition, it is possible to open a bulk-band gap by application of compressive bi-axial strain on thin films synthesized on lattice mismatched substrates. Realization of surface dominated transport in topological Heusler thin films will open up avenues for realization of many exotic phenomena such as quantum anomalous Hall effect[8], axion insulators[9], topological superconductivity[10] and their potential device applications.

References:

S. Chadov *et al*, Nature Mater, 9, 541 (2010)

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L. Fu and C. Kane, Phys. Rev. Lett,100, 096407 (2008)

9:00am **EM+MI+TF-MoM3 Topology, Magnetism, and Superconductivity in Ternary Half-Heusler Semimetals**, ***Johnpierre Paglione***, University of Maryland, College Park **INVITED**

In materials with non-centrosymmetric crystallographic structures, it has long been known that the lack of inversion symmetry can give rise to odd-parity spin-triplet pairing states. We report superconductivity and magnetism in a new family of topological semimetals, the ternary half Heusler compounds RPtBi and RPdBi (R : rare earth). In this series, tuning of the rare earth f-electron component allows for simultaneous control of both lattice density via lanthanide contraction, as well as the strength of magnetic interaction via de Gennes scaling, allowing for a unique tuning of both the normal state band inversion strength, superconducting pairing and magnetically ordered ground states. Antiferromagnetism with ordering vector (0.5,0.5,0.5) occurs below a Néel temperature that scales with de Gennes factor, while a superconducting transition is simultaneously linearly suppressed. With superconductivity appearing in a system with non-centrosymmetric crystallographic symmetry as well as p-orbital derived spin-3/2 quasiparticles, the possibility of high-spin Cooper pairing (i.e. beyond triplet) with non-trivial topology analogous to that predicted for the normal state electronic structure provides a unique and rich opportunity to realize both predicted and new exotic excitations in topological materials.

9:40am **EM+MI+TF-MoM5 Electron Counting, Surface Reconstructions, and Electronic Structure of 18 Electron Half Heuslers**, ***Jason Kawasaki***, University of Wisconsin - Madison, *A. Janotti*, University of Delaware, *C.J. Palmstrøm*, University of California at Santa Barbara

Half Heusler compounds (composition *ABC*) show great promise for the development of earth abundant thermoelectrics, half metallic ferromagnets for spin injection, and topological heterostructures. In these applications, the electronic structure of surfaces and interfaces are critical to materials performance. However, little is known about how and why the surfaces of these materials reconstruct or their direct effect on electronic properties. Using a combination of molecular beam epitaxy, angle resolved and core level photoemission, scanning tunneling microscopy, and density functional theory (DFT), we investigate the stability, reconstructions, and electronic surface states on the (001) surfaces of CoTiSb, NiTiSn, and FeVSb. These compounds are representative of a large class of 18 valence electron Half Heuslers that are expected to be semiconducting. We find that reconstructions in these compounds are characterized by *C* site (group IV or V) dimerization, as in III-V semiconductors, and this dimerization coincides with *B* site vacancies at the surface. We explain these trends using a simple electron counting model, and predictions from the model are in good agreement with both the experimental data and with DFT calculations. Our combined theoretical and experimental studies provide a rationale for understanding and controlling reconstructions and resultant electronic surface states in Heuslers.

10:00am **EM+MI+TF-MoM6 Computational Investigation of Heusler Compoundss for Spintronic Applications**, ***Jianhua Ma***, University of Virginia, *W.H. Butler*, University of Alabama

We present first-principles density functional calculations of the electronic structure, magnetism, and structural stability of 378 *XYZ* half-Heusler, 405 X_2YZ inverse-Heusler, 576 X_2YZ full-Heusler compounds. We find that a "Slater-Pauling gap" in the density of states in at least one spin channel is a common feature in Heusler compounds. We find that the presence of such a gap at the Fermi energy in one or both spin channels contributes significantly to the stability of a Heusler compound. We calculate the formation energy of each compound and systematically investigate its stability against all other phases in the open quantum materials database (OQMD). We represent the thermodynamic phase stability of each compound as its distance from the convex hull of stable phases in the respective chemical space and show that the hull distance of a compound is a good measure of the likelihood of its experimental synthesis. We find low formation energies and mostly correspondingly low hull distances for compounds with X = Co, Rh, or Ni, Y = Ti or V, and Z = P, As, Sb, or Si in half-Heulser compounds. In the half-Heusler family, we identify 26 18-electron semiconductors, 45 half-metals, and 34 near half-metals with negative formation energy that follow the Slater-

Pauling rule of three electrons per atom. In the inverse-Heusler family, we identify 14 asymmetric 18-electron semiconductors, 50 half-metals, and 42 near half-metals with negative formation energy. In the full-Heusler family, we identify 8 24-electron semiconductors and 23 half-metals with negative formation energy. Our calculations predict several new, as-yet unknown, thermodynamically stable phases, which merit further experimental exploration—RuVAs, CoVGe, FeVAs in the half-Heusler structure, and NiScAs, RuVP, RhTiP in the orthorhombic MgSrSi-type structure. Further, two interesting zero-moment half-metals, CrMnAs and MnCrAs, are calculated to have negative formation energy. In addition, our calculations predict a number of hitherto unreported semiconducting (e.g., CoVSn and RhVGe), half-metallic (e.g., RhVSb), and near half-metallic (e.g., CoFeSb and CoVP) half-Heusler compounds to lie close to the respective convex hull of stable phases, and thus may be experimentally realized under suitable synthesis conditions, resulting in potential candidates for various semiconducting and spintronics applications.

11:00am **EM+MI+TF-MoM9 Growth, Electronic, and Magnetic Properties of Half-Heusler CoTi$_{1-x}$Fe$_x$Sb**, ***Sean Harrington***, *A.D. Rice, T. Brown-Heft, A.P. McFadden, M. Pendharkar,* University of California at Santa Barbara, *O. Mercan, L. Çolakerol Arslan,* Gebze Technical University, Turkey, *C.J. Palmstrøm,* University of California at Santa Barbara

Recent predictions suggest the semiconducting half-Heusler compound, CoTiSb, exhibits half-metallicity when substitutionally alloyed with Fe. However, to date, few studies have examined the growth of high-quality single crystal thin films of Fe-alloyed CoTiSb. Here, we report the epitaxial growth of the substitutionally alloyed half-Heusler series CoTi$_{1-x}$Fe$_x$Sb by molecular beam epitaxy and the influence of Fe on the structural, electronic, and magnetic properties. CoTi$_{1-x}$Fe$_x$Sb epitaxial films are grown on InAlAs grown on InP (001) substrates for concentrations $0 \leq x \leq 1$. The films are epitaxial and single crystalline, as measured by reflection high-energy electron diffraction and X-ray diffraction. For films with higher Fe content, a lower growth temperature is necessary to minimize interfacial reactions. Using *in-situ* X-ray photoemission spectroscopy, only small changes in the valence band spectra from pure CoTiSb are detected. For films with $x \geq 0.05$, ferromagnetism is observed in SQUID magnetometry with a Curie temperature >400K. The saturation magnetization of the series increases linearly with Fe content as 3.4 μ_B/Fe atom. In comparison, there is a much smaller magnetic moment when the Fe is substituted on the Co site (Co$_{1-x}$Fe$_x$TiSb) indicating a strong dependence of the magnetic moment with site occupancy. A cross over from both in-plane and out-of-plane magnetic moments to only in-plane occurs for higher concentrations of Fe. Ferromagnetic resonance indicates a transition from weak to strong interaction as Fe content is increased. Temperature dependent transport shows a gradual semiconductor to metal transition with thermally activated behavior for $x \leq 0.3$. Anomalous Hall effect and magneto resistance are investigated for the x=0.3 and x=0.5 films revealing large differences in the electronic scattering mechanisms and transport behavior depending on Fe content.

11:20am **EM+MI+TF-MoM10 High Spin-Polarization and Perpendicular Magnetic Anisotropy in Single-Crystal Full-Heusler Co$_2$MnAl/Fe$_2$MnAl Superlattice**, ***Tobias Brown-Heft***, *A.P. McFadden, J.A. Logan,* University of California at Santa Barbara, *C. Guillemard,* University of Lorraine, France, *P. Le Fevre, F. Bertran,* Synchrotron SOLEIL, France, *S. Andrieu,* University of Lorraine, France, *C.J. Palmstrøm,* University of California at Santa Barbara

Ferromagnetic contacts are used as a source of spin-polarized current in many spintronic devices. Desired properties for ferromagnetic contacts used in magnetic tunnel junctions and other next-generation memory elements are perpendicular magnetic anisotropy and 100% spin polarization at the Fermi level (half-metallicity). Heusler compounds are strong candidates for this purpose as many have been predicted and observed to be half-metals (e.g. Co$_2$MnSi), while others exhibit perpendicular magnetic anisotropy (e.g. Co$_2$FeAl/MgO(001)). However, until now both properties have not been observed by experiment in a single material. J. Azadani *et al* have predicted that perpendicular anisotropy can be combined with half-metallicity by growing atomic-period superlattices of two different Heusler compounds [1]. We have successfully grown a single-crystal superlattice formed by layers of Co$_2$MnAl and Fe$_2$MnAl with periodicity of one to three unit cells using molecular beam epitaxy. X-ray diffraction reciprocal space mapping reveals that the superlattice is compliant to the substrate to at least 20 nm film thickness, sustaining strains from -3.0% (tensile) on MgO(001) to +2.3% (compressive) on GaAs(001). The film strain is accommodated via tetragonal distortion of c/a = 0 .96 to 1.06, respectively. The tetragonal distortion on GaAs(001) contributes to perpendicular magnetic anisotropy, resulting in films exhibiting out-of-plane magnetic easy axes at temperatures below 200K. Films with aluminum content higher than nominal stoichiometry may also help to induce perpendicular magnetization by reducing saturation magnetization, thereby lowering thin-film shape anisotropy. Superlattice structure was verified using electron energy loss spectroscopy in TEM, which shows low interface diffusion of cobalt and iron and high elemental contrast between individual superlattice layers. S pin polarization of >90% near the Fermi level has been measured directly via spin-resolved photoemission spectroscopy. Spin-resolved photoemission spectra suggest that the termination layer near a tunnel barrier interface should be Co$_2$MnAl-like, and may benefit from further composition tuning. This work was supported in part by C-SPIN, one of the six centers of STARnet, a Semiconductor Research Corporation program, sponsored by MARCO and DARPA. We also acknowledge support from the Vannevar Bush Faculty Fellowship.

[1] J. G. Azadani *et al*. J. Appl. Phys. 119, 043904 (2016).

11:40am **EM+MI+TF-MoM11 Formation of the Epitaxial MgO/Full-Heusler Co$_2$MnSi Interface: Oxygen Migration and Elemental Segregation**, ***Anthony McFadden***, *T. Brown-Heft, N.S. Wilson, J.A. Logan, C.J. Palmstrøm,* University of California at Santa Barbara

Magnetic tunnel junctions (MTJs) are an increasingly important emerging technology for both magnetic random access memory (MRAM) and spintronics applications. MTJs utilizing CoFeB magnetic electrodes and MgO tunneling barriers have received considerable interest for use in MRAM as desirable properties including perpendicular magnetic anisotropy, high tunneling magnetoresistance ratio, and current induced switching have been demonstrated. While CoFeB/MgO based MTJs have demonstrated remarkable performance, devices utilizing ferromagnetic Heusler compounds have the potential to surpass CoFeB based technologies due to a much higher predicted spin polarization. In addition, many Heusler candidates have even been predicted to be half-metallic (100% spin polarized at the Fermi-level). Of all predicted half-metals, the full-Heusler Co$_2$MnSi has received considerable attention as it is quite stable (ΔH_F = -0.441 eV/atom), has a high Curie temperature (T_c=985K), and a large minority-spin energy gap (571 meV). While Heusler based MTJs have the potential to surpass current CoFeB based technology, the spin polarization of Heusler compounds has been shown to be sensitive to atomic ordering, adding an additional challenge to materials growth and integration.

In the present work, the formation of the MgO/Co$_2$MnSi(001) interface has been studied *in-situ* using X-ray photoelectron spectroscopy (XPS). Co$_2$MnSi layers were grown on Cr-buffered MgO(001) substrates by coevaporation of elemental sources in ultrahigh vacuum while MgO was grown on the Co$_2$MnSi layers using e-beam evaporation of stoichiometric source material. It was found that partial oxidation of the Co$_2$MnSi surface was unavoidable during e-beam evaporation of MgO with oxygen bonding preferentially to Mn and Si. Interestingly, oxidation draws Mn and Si to the surface, resulting in an MgO/Co$_2$MnSi interface with composition significantly different from the unoxidized Co$_2$MnSi surface. In addition, Mn and Si oxides at the MgO/Co$_2$MnSi interface were reduced following annealing in UHV with a corresponding migration of oxygen from the interface into the MgO. The results of XPS studies have been correlated with temperature dependent transport measurements of fully epitaxial CoFe/MgO/Co$_2$MnSi MTJs which were observed to be highly sensitive to post-growth annealing temperature.

Thin Films Division
Room: 20 - Session TF+EM-MoM

ALD for Energy Conversion, Storage, and Electrochemical Processes
Moderator: Mark Losego, Georgia Institute of Technology

8:20am **TF+EM-MoM1 Synthesis and Characterization of All Solid-State SnO$_x$N$_y$/LiPON/Li Batteries**, ***David Stewart***, *A.J. Pearse, K. Gregorczyk, G. Rubloff,* University of Maryland, College Park

Atomic layer deposition (ALD) is excellent for depositing conformal thin films on high aspect ratio substrates, and due to the good thickness control and uniformity, ALD allows us to push the limits of thin film batteries. To produce solid-state lithium ion batteries on such substrates new processes for anodes, high-capacity cathodes, and solid-electrolytes must continue to be developed and characterized. Sn and SnO$_2$ have been well studied as alloy/conversion electrodes in the literature, while the properties of Sn$_3$N$_4$ and SnO$_x$N$_y$ have yet to be explored in any detail. To study the differences in the electrochemical performance of SnO$_2$, Sn$_3$N$_4$, and SnO$_x$N$_y$, an ALD process was developed that allows for highly tunable N/O ratios. In this study tetrakis(dimethylamido)tin (TDMA(Sn)) was used as the metal-organic precursor in combination with remote nitrogen plasma (^{p}N) and H$_2$O was used to introduce oxygen content. For the pure nitride phase, a broad temperature window was found between 150-250 °C, over which the growth rate per cycle (GPC) was ~ 0.55 Å. While only very short pulse times (< 1 s) were required for saturation of the TDMA(Sn), relatively long ^{p}N exposures

(> 20 s) were required for GPC saturation. We then showed that by varying H_2O super cycles the relative concentration of O and N in the film can be controlled between 0% N and 95% N.

To study the electrochemical performance of these materials solid-state half-cells were constructed using SnO_2, Sn_3N_4, and SnO_xN_y thin films versus thermally evaporated Li. A 100 nm thin film of LiPON was deposited as the solid electrolyte by thermal ALD [1]. This electrolyte layer is thick enough to provide good electrical insulation and thin enough to allow fast ionic diffusion, however when cycled to voltages below 0.4 V vs Li/Li^+ the half-cells shorted, possibly due to mechanical breakdown of the LiPON layer from significant volume expansion of the anodes during the alloying reaction with Li. The Li_2O matrix formed from SnO_2 is expected to be more stable, but with lower ionic conductivity than the Li_3N matrix formed from Sn_3N_4. Galvanostatic intermittent titration and electrochemical impedance spectroscopy were used to analyze the ionic conductivity of the anodes before and after the initial conversion reaction and as a function of N/O ratio. The high capacity of the SnO_xN_y electrodes in combination with the excellent ionic conductivity and mechanical properties of the ALD LiPON makes these films attractive for applications in 3D Li-ion batteries.

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[1] A. J. Pearse, T. E. Schmitt, E. J. Fuller, *et. al*. Chemistry of Materials **2017** *29* (8), 3740-3753 DOI: 10.1021/acs.chemmater.7b00805

8:40am TF+EM-MoM2 Molecular Layer Deposition for Applications in Lithium-Ion Batteries

*K. Van de Kerckhove, F. Mattelaer, J. Dendooven, **Christophe Detavernier***, Ghent University, Belgium

Molecular layer deposition (MLD) of hybrid organic-inorganic thin films called *titanicones*, *vanadicones*, *tincones*, and *alucones* was investigated for electrode and solid electrolyte applications in lithium-ion batteries.

The titanicone, vanadicone and tincone films were studied as electrode materials, both as anodes and cathodes. Novel MLD processes were developed for these materials and were based on an alkylamine metal precursor (TDMAT, TEMAV, TDMASn) and glycerol (GL) as the organic reactant [1,2]. Linear and self-limited growth could be achieved for these metalcones in a broad temperature range with temperature-dependant growth rates ranging from 0.2 to 1.3 Å/cycle. Film growth was studied in situ with spectroscopic ellipsometry (SE) and infrared spectroscopy (FTIR). The as-deposited films appeared to be electrochemically inactive in all cases. A post-deposition heat treatment up to 500°C in either inert (helium) or oxidizing (air) atmosphere was able to electrochemically activate the films. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements showed that all carbon was removed during calcination in air and that the films crystallized. However, annealing in inert atmosphere conserved the carbon content of the film and thus the films remained amorphous. The performance with increasing charging and discharging rate, and cyclability of the heat-treated MLD electrodes was tested against their respective metal oxide references. The He-annealed metalcones emerged from these tests as the best performing electrodes at higher rates and with improved capacity retention and stability during repeated charging and discharging.

The transformation of alucone films, deposited with the TMA and ethylene glycol (EG) or GL process, into porous aluminium oxide was examined. Porous, non-conducting materials are interesting for lithium-ion battery research since they may serve as the matrix template for solid composite electrolytes. Calcination in air and water etching proved to be the most successful methods. For the calcination treatment, a clear relation was found between the ramp rate during both heating and cooling and the resulting porosity of the film. The aging behaviour of the films in ambient atmosphere was also investigated with FTIR and showed that the films deposited with EG decompose in a matter of only a few hours, as opposed to those deposited with GL.

[1] Van de Kerckhove et al., ***Dalton Trans.***, 2016,**45**, 1176-1184.

[2] Van de Kerckhove et al., ***Dalton Trans.***, 2017,**46**, 4542-4553.

9:00am TF+EM-MoM3 Engineering Hybrid Thin Film Electrolytes for 3D Lithium-ion Battery Applications

***Ryan Sheil**, J. Lau,* University of California at Los Angeles, *P. Moni,* MIT, *C. Choi,* University of California at Los Angeles, *K. Jungjohann,* Sandia National Laboratories, *J. Yoo,* Los Alamos National Laboratory, *K. Gleason,* MIT, *B. Dunn, J.P. Chang,* University of California at Los Angeles

3D battery architectures have the potential to meet the power and energy density demands of next generation microelectronic devices. One requirement in the utilization of 3D based electrodes is the incorporation of a solid electrolyte that can be coated pinhole free and conformally on high aspect ratio structures. Lithium aluminosilicate ($Li_xAl_ySi_zO$, LASO), a solid oxide Li-ion conductor, synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications due to its adequate ionic conductivity (8.2×10^{-8} S/cm) in thin film applications as well as its ability to improve electrode stability. The self-limiting nature of ALD allows precise thickness and composition control when applied to complex metal oxides. Lithium tert-butoxide (LTB), trimethylaluminum (TMA), and tris(tert-butoxy)silanol (TTBS), were precursors used to synthesize LASO by ALD.

In order to further explore potential material properties, ALD deposited LASO was combined with a polymer electrolyte, poly-(tetravinyltetramethylcyclotetrasiloxane) (PV4D4) deposited via initiated chemical vapor deposition (iCVD). The LASO solid electrolyte offers high electrical resistance and chemical stability at the electrochemically active interface, while the pV4D4 solid electrolyte offers improvements in the mechanical integrity of the electrode. A hybrid film consisting of 5 nm LASO and 400 nm PV4D4 demonstrated a room temperature ionic conductivity of 3.4×10^{-7} S/cm, showing no significant increase in interfacial resistance. Integration with both 2D and 3D electrodes has shown substantial improvements in cycling and increased coulombic efficiency.

Current research on Li-ion batteries is directed at creating next generation electrode materials. One of the most viable 3D designs is through the use of nanowire electrodes, in which Si and Ge can offer much larger charge capacities (8444 A h L^{-1} for $Li_{15}Si_4$ and 7366 A h L^{-1} for $Li_{15}Ge_4$, respectively) than traditional carbon based anode materials, but suffer large volume expansion upon lithiation. Using an in-situ TEM electrochemical characterization technique, dynamic processes and structural changes are able to be observed during the lithiation/delithiation of a SiGe nanobattery in real time. Preliminary results show that ALD $Li_xAl_ySi_zO$-coated $Si_{0.4}Ge_{0.6}$ alloy nanowire demonstrates lithiation and delithiation with an intact solid state electrolyte layer with ~39% radial expansion observed upon lithiation.

9:20am TF+EM-MoM4 Carbon Encapsulated CNT Micropillars for Silicon Lithium Ion Battery Electrodes

***Kevin Laughlin**, E. Laughlin, R. Fan, R.F. Davis, R.R. Vanfleet, J. Harb*, Brigham Young University

Here we present work on a hierarchical approach to structuring and encapsulating carbon nanotube (CNT) based carbon monoliths. Prior work has shown silicon has high gravimetric capacity, but increases by ~300%, and forms an unstable solid electrolyte interphase (SEI). High stability and lifetime operation requires nanostructuring of the silicon to alleviate stresses caused by the large expansion of the silicon upon Li alloying, and an encapsulation layer to restrict SEI build up. These CNT structures provide: porous scaffolding for silicon to expand to manage stress on multiple scales, a long conductive path for lithium transfer resulting in tall electrodes, and protection from unstable SEI formation. At high silicon loadings even nanoscale layers of silicon result in stresses large enough to cause mechanical damage to the electrode and encapsulation layer, resulting in lower capacity and cell lifetimes. By patterning the CNT scaffolding, we can contain the stresses caused by lithiation.

9:40am TF+EM-MoM5 Porous Oxide Shell on the Supported Gold Nanoparticles Synthesized via Polymer-Templated Atomic Layer Deposition

***Haoming Yan**, X.Z. Yu, Q. Peng*, University of Alabama

Ultra small (≤ 5 nm) metal nanoparticles (USMNPs), especially Au, have attracted increasing attention due to their remarkable catalytic activity and selectivity in many important reactions. However, their catalytic properties are greatly affected by the poor thermal stability and the macro-molecular capping ligand (MCL) layer on their surfaces. Encapsulating the USMNPs with a porous oxide shell (pOXIDE) is a solution for both issues. So far, there has been limited success in generating the pOXIDE shell on the supported USMNP without significantly blocking its active sites. The objective of this work is to demonstrate the MCL layer templated atomic layer deposition (ALD) can be applied to synthesize the pOXIDE shell on the USMNPs to improve their thermal stability while keeping most of the surface active sites on USMNPs for the catalytic reaction.

10:00am TF+EM-MoM6 Three-Dimensional Solid State Batteries Grown Via Atomic Layer Deposition

***Alexander Pearse**, T. Schmitt, D. Stewart, E. Sahadeo, K. Gregorczyk,* University of Maryland, College Park, *K. Gerasopoulos,* Johns Hopkins Applied Physics Lab, *G. Rubloff,* University of Maryland, College Park

Thin film solid state batteries have multiple attractive properties, including low interfacial impedance, exceptional cycling stability, and intrinsic safety, but have not seen significant implementation because their overall capacity is very low (on the order of 0.1 mAh/cm^2). This is a consequence of their growth by physical vapor deposition, which limits them to planar substrates. In this configuration, increasing areal capacity necessarily sacrifices rate performance due to slower ionic diffusion in thicker electrodes. Realizing practical energy or power densities in thin film SSBs will involve the development of entirely new fabrication processes in order to allow the integration of thin film SSBs with 3D substrates, such as micromachined silicon or conductive fabrics. In particular, 3D designs allow the decoupling of capacity and rate performance for area-normalized metrics.

We describe the development and synthesis of a solid state lithium-ion battery film stack grown entirely by atomic layer deposition (ALD), which allows us to successfully integrate solid state energy storage with 3D structures. The entire device is fabricated at temperatures at or below 250C, allowing for compatibility with a broad variety of substrates and processing environments. We utilize a simple electrochemical process for inserting free lithium ions into a crystalline cathode, avoiding the need to integrate lithiation into the ALD growth process itself. The solid electrolyte is a lithium polyphosphazene compound (a variant of LiPON) grown by a 2-precursor thermal process (Pearse et al. Chemistry of Materials 2017). The battery itself is comprised of a LiV_2O_5 – Sn_xN_y couple, providing a reversible capacity of approximately 35 μAh/cm$_2$ μm$_{LVO}$ with an average discharge voltage of 2V. By growing these batteries into micromachined silicon structures with aspect ratios of up to 10, we are able to increase areal capacity by nearly one order of magnitude while simultaneously improving capacity retention at high rates- a type of scaling not possible for planar devices. We also discuss challenges associated with interface chemistry in the ALD growth environment and with patterning highly conformal films, and compare device performance to finite element electrochemical simulation.

10:40am **TF+EM-MoM8 Systematic Investigation of Geometric Effects in Porous Electrodes for Energy Conversion Reactions**, ***Julien Bachmann***, University of Erlangen, Germany **INVITED**

Inexpensive energy conversion devices necessitate novel strategies towards reducing the need for rare functional materials. One such strategy consists in accurately controlling the interface's geometry.

In our work, the pore walls of an anodic nanoporous template are coated with either galvanic deposition or atomic layer deposition (ALD) to obtain structured electrode surfaces that provide the experimentalist with a well-defined, tunable geometry. Indeed, the platform consists of a hexagonally ordered array of metallic or oxidic nanotubes of cylindrical shape, embedded in an inert matrix. The diameter of the tubes can be defined between 20 and 300 nm and their length between 0.5 and 100 μm, approximately. They can be utilized as a model system in which the electrode's specific surface area can be increased and its effect on the electrocatalytic current characterized systematically.

Diffusion-limited electrochemical transformations remain unaffected by changes in the length of the electrode's pores, whereas the steady-state galvanic current density observed for slow multielectron transformations increases linearly with the pore length. In particular, this approach enables us to achieve an increase of the electrochemical water oxidation turnover at neutral pH on iron oxide surfaces by three orders of magnitude. These results highlight a strategy for optimizing electrochemical energy transformation devices which could be generalized: the geometric tuning of catalytically mediocre but abundant and cost-effective material systems.

11:20am **TF+EM-MoM10 Development of a Reduction-resistant Oxide Electrode for Dynamic Random Access Memory Capacitor**, ***CheolJin Cho***, *M.-S. Noh*, *W.C. Lee*, Korea Institute of Science and Technology, Republic of Korea, *C.H. An*, Seoul National University, Republic of Korea, *C.-Y. Kang*, Korea Institute of Science and Technology, Republic of Korea, *C.S. Hwang*, Seoul National University, Republic of Korea, *S.K. Kim*, Korea Institute of Science and Technology, Republic of Korea

Rutile phase TiO_2/RuO_2 structures have attracted great interests as a new material system for next-generation dynamic random access memories (DRAM) capacitors because of the high dielectric constant (> 80) of the rutile TiO_2. A conducting oxide electrode, RuO_2, enables the TiO_2 dielectric to be crystallized into a rutile phase at low temperatures (< 300 ºC). Since RuO_2 has a high work function, it is effective to suppress leakage current by Schottky emission which is a main conduction mechanism of TiO_2/RuO_2. However, the RuO_2 electrode is easily reduced during the post-annealing under forming gas atmosphere for trap passivation at the gate oxide/Si interface. Subsequently, the dissociated oxygen ions from RuO_2 cause problems such as the oxidation of W plug. The oxidation of W plug causes a fatal deterioration in device operation because the W plug acts as a path through which the charges of the capacitor move. Also, physical damage such as cracks will also occur when RuO_2(rutile) is reduced to Ru(hexagonal close-packed, HCP). For these reasons, we suggest a SnO_2-based electrode, which is a reduction-resistant material, as a new oxide electrode for DRAM capacitors. The reduction reaction of SnO_2 is thermodynamically more difficult than that of RuO_2. Also, a small amount of Ta ions is incorporated into the SnO_2 films to enhance the conductivity of the electrode. The resistivity of SnO_2 is reported to reach down to $10^{-4}\Omega\cdot cm$ by Ta doping, which is sufficient for use as an electrode of DRAM capacitor. Furthermore, the Ta-doped SnO_2 films are well crystallized into a rutile phase, thereby leading to the formation of rutile TiO_2 at a low growth temperature (< 270 ºC). Therefore, we demonstrate that Ta-doped SnO_2 would be a promising candidate for the electrodes for next-generation DRAM capacitors.

Thin Films Division
Room: 20 - Session TF-MoA

Emerging Applications for ALD

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

1:40pm **TF-MoA1 Probe the Reaction Chemistry during Atomic Layer Deposition onto $CH_3NH_3PbI_3$**, ***Qing Peng***, *X.Z. Yu*, University of Alabama

The rapid development of organic-inorganic hybrid halide perovskites, represented by $CH_3NH_3PbI_3$, based solar cells is one of the major scientific breakthroughs of recent years. It is superior optoelectronic properties inspired applications beyond solar cells, including LEDs, transistors, and sensors. Thin metal oxide coatings are promising electron extraction layer, moisture barrier, electron injection layer, electron blocking layer, and high-k dielectrics for semiconducting $CH_3NH_3PbI_3$. Atomic layer deposition (ALD) is a promising method to directly put these metal oxides onto $CH_3NH_3PbI_3$. The pure heterogeneous reaction mechanisms provide ALD the capability to deliver conformal films on substrates of complex morphology with sub-nanometer control of the composition and thickness of the film. On the other hand, the heterogeneous-reaction-driven film growth mode in ALD process demands a molecular level understanding of the heterogeneous reaction chemistry. In this presentation, we will show the surface reaction mechanisms of ALD oxide on $CH_3NH_3PbI_3$ by using a suite of in-situ and ex-situ analytic methods. Our results show that the heterogeneous reaction chemistries of ALD during the nucleation stage of ALD oxide on $CH_3NH_3PbX_3$ is complex. Based on these fundamental understandings, we will further show that one can control the formation of the oxide layer by ALD through the careful control of the ALD chemistry and process conditions.

2:00pm **TF-MoA2 Digital Doping of ALD Nb:VO_2 Thin Films for Thermochromic Applications**, ***Alexander Kozen***, *M. Currie, B.P. Downey, C.R. Eddy, Jr., V.D. Wheeler*, U.S. Naval Research Laboratory

Vanadium Dioxide (VO_2) is a thermochromic material that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 68˚C. This structural phase transition is accompanied by major changes in electrical and optical properties, particularly in the infrared. As such, VO_2 is suitable for many applications including microbolometers, adaptive thermal coatings, and passive spacecraft thermal shielding.

While the T_c of VO_2 is appropriate for many current applications, it is desirable to modify the T_c to other values for improved performance of current applications or to address new emerging application needs. The T_c of VO_2 has been shifted by doping with other transition metals on the order of 1-5%.[1], [2], however these doped VO_2 films were deposited by PLD, MBE, and sputtering, all line of sight physical vapor deposition techniques.

We demonstrate digital doping of ALD Nb:VO_2 by incorporation of ALD Nb_2O_5 (TBTDEN + O_3) into the conventional ALD VO_2 process (TEMAV + O_3). Inclusion of Nb into the ALD VO_2 process in amounts between 1% and 5% makes minimal impact on as-deposited film morphology. After annealing, the Nb:VO_2 films also exhibit minimal physical changes from their undoped analogues. We find that Nb doping can lower the T_c of the VO_2 films by -13.5˚C/Nb% while maintaining acceptable optical modulation behavior, critical for use of doped VO_2 in emerging applications.

[1] W. Burkhardt, T. Christmann, B. K. Meyer, and W. Niessner, "W-and F-doped VO 2 films studied by photoelectron spectrometry," *Thin Solid Films*, vol. 345, no. 2, pp. 229–235, 1999.

[2] X. Wu, Z. Wu, C. Ji, H. Zhang, Y. Su, Z. Huang, J. Gou, X. Wei, J. Wang, and Y. Jiang, "THz Transmittance and Electrical Properties Tuning across IMT in Vanadium Dioxide Films by Al Doping," *ACS Appl. Mater. Interfaces*, vol. 8, no. 18, pp. 11842–11850, May 2016.

2:20pm **TF-MoA3 Mechanisms in Organic and Hybrid Organic-Inorganic Molecular Layer Deposition**, ***David Bergsman****, *S.F. Bent*, Stanford University

Molecular layer deposition (MLD) has seen increased interest in recent years for the deposition of organic and hybrid organic-inorganic ultrathin films. This vapor-phase, layer-by-layer technique, which relies on the same self-limiting precursor saturation as atomic layer deposition, has shown promise for the development of many applications that require conformal organic-containing coatings, such as in photoresists, porous catalysts, and metal organic frameworks. Despite recent developments in MLD, there is a significant gap in our understanding of the mechanisms behind MLD and the microscopic properties of MLD-grown films, such as their molecular-level structure or degradation mechanisms. In this presentation, we will present results of our recent studies to understand such mechanisms, and discuss how that understanding can be used to better control the thermal, mechanical, electrical, and catalytic properties of these materials.

First, we discuss our exploration of the growth behavior of organic MLD films by examining trends in film properties as a function of backbone flexibility [1]. Our results suggest that changes in growth rate between the most rigid and most flexible backbones (4 Å/cycle vs 1 Å/cycle) are not caused by differences in length of molecular precursors, chain orientation (~25° on average for each backbone), or film density (1.0 – 1.2 g/cm^3), but are instead caused by an increased frequency of terminations in the more flexible chemistries. Because of the physisorption of precursors, which reintroduce reactive sites, these terminations do not lead a complete cessation of film growth. We further elaborate on the structure of the films by examining crystal orientation and infrared absorption data, which suggest that films consist of a mixture of upward growing chains and horizontally aligned layers of paracrystalline polymer segments.

Second, we discuss manganese/ethylene glycol hybrid films, which have promise as nanostructured, earth-abundant catalysts for electrochemical water splitting. Time-dependent ellipsometry, infrared absorption, and x-ray photoelectron spectroscopy data indicate that the organic component of the films is unstable in air, as seen in other hybrid MLD materials. The degradation pathway will be discussed, based on the observation that the organic linkers primarily degrade into carboxylate ions. Thermal annealing and chemical treatments, such as exposure to oxygen and water, are further shown to affect this degradation and can be used to control the formation of nanoporous, catalytically active catalysts for the oxygen reduction reaction.

1. D. S. Bergsman, et. al., Chem. Mater, 2017, 29, 1192

2:40pm **TF-MoA4 Inorganic Modification of Cellulosic Fibers for Enhanced Oil Sorption Capacity**, ***Andrew Short***, *S. Pamidi, Z. Bloomberg, M.D. Losego*, Georgia Institute of Technology

A few atomic layer deposition (ALD) cycles of metal oxides onto cellulosic fibers is known to modify the fiber's surface energy and make the fiber hydrophobic. In this research we use the trimethylaluminum-water chemistry to make cellulosic fibers highly hydrophobic (WCA ~160°) and oleophilic, transforming natural cotton into an ideal material for oil spill remediation. The ALD-treated cellulose floats on water for over 12 months and readily sorbs oil, whereas untreated cellulose preferentially sorbs water over oil (Figures 1 and 2). ALD-treated cellulose has a significantly higher oil sorption capacity (e.g., 20 g g^{-1} vs. 0.11 g g^{-1}) than raw cotton across a range of experimental conditions approximating those encountered in real-world oil spill remediation efforts (Figure 3). While studies in the literature report ultra-high oil sorption capacities (~200 g g^{-1}), this study finds that reporting oil sorption capacity in terms of g g^{-1} can be misleading, and recommends this measure be reported in tandem with the material's volumetric oil sorption capacity (g cm^{-3}) because of its greater relevance to use-case effectiveness. The comparison of g g^{-1} and g cm^{-3} oil sorption capacities given in Table 1 demonstrate that the sorbent produced here is comparable to some of the best reports in the literature. This talk will detail how the oil sorption capacity of these new materials change with differing real-world conditions and explain the efficacy of Al_2O_3 ALD applied to cellulosic fibers as a scalable, cost-effective method for creating biodegradable, on-demand materials for oil spill remediation.

3:20pm **TF-MoA6 Atomic Layer Deposition of Nano-Coatings on Fabrics for Antibacterial Applications**, ***Renee Puvvada***, *M. Bellavia, T.A. Sulchek, M.D. Losego*, Georgia Institute of Technology

About 1.7 million Americans contract hospital-acquired infections every year resulting in 99,000 inadvertent deaths and an estimated $20 billion in healthcare costs. Here, we investigate the use of atomic layer deposition (ALD) to treat various fabrics (e.g., polyester, cotton, and blends) with antimicrobial inorganic materials to create unique antibacterial linens, scrubs, and hospital gowns. Our protocols include biological testing of the antibiotic performance of ALD-treated fabrics against DH5-α, a strain of *E. coli* that is engineered to be suitable for laboratory purposes. Antibacterial performance is tracked as a function of ALD cycle number at various deposition temperatures. Fabrics were exposed to *E. coli* and then incubated for 20 hours, after which cultures are serially diluted up to 7 times, spotted onto

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*** TFD James Harper Award Finalist**

Petri dishes, and incubated for another 20 hours. Colony counting is then used to quantify antibiotic effectiveness.

For ZnO ALD coatings of 0, 1, 10, and 100 cycles, we find that only the 100 cycle sample is sufficiently cytotoxic to kill all of the E. colibacteria. Interestingly, for only a few cycles of ZnO (1, 3, and 10 cycles) the bacteria appears to grow more rapidly. We attribute this increased bacterial growth rate to the Zn^{2+} ions acting as a nutrient for the bacteria. It is known that in order to be an effective antimicrobial agent, ZnO must be "nano-sized" or larger; atomic forms of Zn and ZnO, which ionize into Zn^{2+} in nutrient broth, act instead as nutrients. A more detailed investigation of this transition from nutrient to antimicrobial will be discussed during this talk. We will also examine the effectiveness of other oxide materials including TiO_2 and ZrO_2 as well as compare the long-term performance of ZnO against common disinfectants like Lysol® and their stability in aqueous environments of varying pH.

4:00pm **TF-MoA8 ALD-based Functionalization of Biomaterials: Recent Developments and Future Challenges**, ***Christos Takoudis***, University of Illinois at Chicago **INVITED**

Biomaterials are engineered to interact with biological systems for therapeutic and diagnostic clinical applications. Biomaterials can be synthesized in a lab or can directly be obtained from natural resources, and they constitute whole or part of a biomedical device or a living structure that can be utilized to execute, improve, enhance or restore a natural function. The surface of a biomaterial controls the interactions occurring at the interface between the biomaterial surface and its surrounding living environment. Hence, successful performance of a biomaterial relies on its appropriate surface properties. Many biomaterials do not have appropriate surface functions and properties to cater to specific needs and applications. Therefore, surface modification and functionalization leading to significantly improved performance of biomaterials would be highly desirable and sought after.

In modern surface science and engineering, bio-nanotechnology is a potent tool to functionalize surfaces incorporating nanometer size thin films and nano-structural features into materials. Among the available deposition techniques, atomic layer deposition (ALD) offers unique advantages in yielding conformal thin films of metal oxides or metals (from a few Å to hundreds of nm thick), uniformly, with precise control at atomic or molecular level; in this manner, the performance and functionality of functionalized biomaterials could be selectively altered, optimized and controlled as needed.

ALD is a relatively new technique for optimizing materials in bio-nanotechnology. Here, after a brief review of the more widely used modes of ALD, ALD's potential in bio-nanotechnology is presented with a few of its latest developments in biotechnology. ALD is promising means in tuning the hydrophilicity/hydrophobicity characteristics of biomedical surfaces, forming conformal ultra-thin coatings with desirable properties on high aspect ratio biomedical substrates, tuning the anti-bacterial properties of substrates surfaces of interest, and yielding multifunctional biomaterials for medical implants and other devices.

Recent developments on ALD at low (room or near room) temperature to functionalize the surface of heat-sensitive biomaterials with complex nanostructures are presented and discussed. Surface characterizations are done to investigate the morphology, chemical composition, crystallinity and wetting behavior of ALD-nanofilm coated biomaterial surfaces. The bioactivity of ALD TiO_2-coated surfaces, for example, is presented using in-vitro and in-vivo biocompatibility and biomineralization studies. Future challenges of ALD-based functionalization of biomaterials will be discussed.

4:40pm **TF-MoA10 Titanium Nitride ALD using Ultra-high Purity Hydrazine at Low Temperature**, ***Dan Alvarez***, *J. Spiegelman, R. Holmes, S. Allanson,* RASIRC*, A.C. Kummel, S. Wolf, M. Kavrik,* University of California, San Diego, *K. Andachi*, RASIRC

Overview

New channel materials such as SiGe, Ge and InGaAs create challenging thermal budgets (<400°C) for metal nitride deposition. TiNx metal gate electrodes in particular need new low temperature ALD methods.

Hydrazine has shown viable reactivity in previous studies but practical use has been limited due to purity concerns, especially water contamination [1-3]. Commercially available anhydrous hydrazine typically has a water concentration ranging from 0.2-2.0%. In addition to this low purity issue, oxygen concentration in metal-nitride films made using hydrazine is a high 4-15% for SiNx and TiNx.

Previous reports detail the safe delivery of gaseous hydrazine using a solvent-based formulation and membrane delivery system [4]. This presentation details studies on water measurement and removal, plus low resistivity films resulting from hydrazine-based low temperature TiNx ALD.

Hydrazine Purification, Measurement

Studies show that water contamination levels can be reduced to <50 parts-per-million (ppm) using new hydrazine source purification methods as measured by Karl-Fischer and GC-MS methods. Gas phase output of the ultra-dry materials was measured below the FT-IR moisture measurement method lower detection limit of 0.83ppm (Figure 1). Standard commercially available hydrazine has a comparatively high gas phase moisture measurement of 31ppm.

Titanium Nitride Deposition

Sequential pulsing of TiCl4 and N2H4 precursors at substrate temperatures of 275°C-350°C achieved atomic layer deposition TiNx. Initial measured resistivity at 350°C was a low $R_{average}$ = 130 ohm, R_{sheet} = 50 ohm. Growth rate is approximately 0.5A per cycle. Films were characterized by XPS (Figure 2), AFM, KPFM, TEM and four-point sheet resistance. Little to no oxygen was present in the TiNx film, which had a near stoichiometric ratio of Ti/N. The presentation will include additional optimization to reduce residual chlorine content at lower temperatures. In addition, a correlation with regards to residual Chlorine content/Resistivity versus deposition temperature will be discussed.

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5:00pm **TF-MoA11 ALD Barriers for Protection of Electronic Devices in Biological Environment**, ***Ankit Singh***, *K. Adstedt, S. Graham*, Georgia Institute of Technology

Encapsulation plays a significant role in the protection and lifetime enhancement of electronic devices. Devices like OPVs, OLEDs, biological implants, and thin film solar cells are susceptible to rapid degradation on exposure to the surrounding media containing moisture and ionic species. Encapsulation barriers hermetically seal the devices and thus, prevent the ingress of moisture or any other fluid that can affect the function and stability of the devices. It involves use of inorganic barrier layers deposited using vacuum deposition processes. Out of several vacuum deposition techniques used for this purpose, atomic layer deposition (ALD) has shown an outstanding performance by producing films which have water vapor transmission rate less than 10^{-4} g/m^2/day. However, the performance and reliability of ALD barrier films is subject to their stability and resistance to corrosion in the surrounding environment.

Recently, miniaturized medical devices have gained popularity because of their new treatment and monitoring capabilities, ease of application and enhanced portability. These devices include artificial pacemakers, cochlear implants, artificial heart valves, etc. These devices are exposed to different bodily fluids that have varying pH and salt concentrations. Any electronic device cannot be expected to last for long enough time to be used as an implant with any protective covering. Thus, it becomes imperative to look for a robust solution.

In this work, we explore the use of different metal oxides deposited using ALD at 100°C in biological environment. The materials include Al_2O_3, HfO_2, TiO_2 and ZrO_2. Chemical stability of the ALD films is determined by using electrochemical impedance spectroscopy (EIS) whereas, biocompatibility of the ALD films is determined using MTT cell proliferation assay measurements. For chemical stability test using EIS, a 3 electrode setup was used to understand the mechanism of material degradation. The ALD deposited materials were exposed to phosphate buffer saline (PBS) solution, simulated sweat and saliva, and Dulbecco's Modified Eagle Medium (DMEM) for 21 days. Besides ALD Al_2O_3, other metal oxides have demonstrated enhanced corrosion resistance and stability in different solutions. ALD HfO_2 has better stability as compared to ALD Al_2O_3 but tends to develop crack with long exposure time. However, ALD TiO_2 and ZrO_2 were found to be most stable in all the biological solutions used for testing. All the ALD materials used during the test have been found to be biocompatible using MTT cell proliferation test. Finally, we demonstrate the application of these ALD materials for protection of active implantable devices.

Thin Films Division
Room: 20 - Session TF-TuM

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

Moderators: Halil Akyildiz, Uludag University, Turkey, Paul Poodt, Holst Centre / TNO, Netherlands

8:00am **TF-TuM1 Aluminum-Doped Zinc Oxide via Spatial ALD: Process Impact on Film Morphology, Electrical Conductivity and Stability**, *S.F. Nelson*, ***Lee Tutt***, *C.R. Ellinger*, Eastman Kodak Company

Aluminum-doped zinc oxide (AZO) is an attractive transparent conductive material because of to its nontoxic, earth-abundant material composition. A wide range of electrical properties have been reported for AZO deposited using a variety of techniques and a range of process conditions. This talk will focus on the AZO grown using spatial atomic layer deposition (SALD), and the impact of process conditions on the electrical, optical and crystallographic properties of the resultant AZO films. We will report primarily on those AZO films deposited using a co-flow of dimethyl aluminum isopropoxide (DMAI) and diethyl zinc (DEZ) as the metal precursors, and water as the oxygen source.

We will share our current understanding of the mechanisms responsible for the interplay between process parameters and material properties, including the correlation of film properties such as doping-level and crystallographic structure to the end-use properties of conductivity and optical transparency. For reference, we have deposited AZO having a bulk resistivity of 2.7×10^{-4} Ω-cm and an average visible transmission of 85%, obtained from 204 nm thick AZO films deposited at 300°C. This compares well to commercially available ITO coatings having, for example, about 1.2×10^{-4} Ω-cm and 82% average visible transmission for film thicknesses between 150 nm and 200 nm.

In addition, the impact of passivating the AZO surface with very thin aluminum oxide (Al_2O_3) will also be reported. We have found that passivation with Al_2O_3 enhances conductivity through an increase in both mobility and carrier concentration. Improved thermal stability during elevated annealing conditions in air was also observed for alumina-passivated AZO samples

8:20am **TF-TuM2 Fast Pulsing of Precursor and Reactant to Merge ALD and CVD Processes: Example of Thick Al_2O_3 Deposition**, ***Fabien Piallat***, *L. Bonnet*, *J. Vitiello*, KOBUS, France

A specific pulsed-CVD reactor was developed for the chemically enhanced deposition of materials. In this specific reactor, both reactant and precursor can be pulsed or sent continuously to the deposition chamber. Thus, many materials can be deposited by one of the three following methods, Atomic Layer Deposition (ALD), Chemical Vapor Deposition (CVD) or pulsed-CVD.

In this presentation, an investigation of Al_2O_3 deposition will be presented, with detailed process comparison for each of the three techniques in order to highlight the variability brought by the process on the material properties. Al_2O_3 deposition was done with TriMethylAluminium (TMA) precursor and O_2 in-situ plasma.

Influence of the pulse length on the deposition rate shows a gap between the surface saturation growth mode of the ALD and the continuous growth of the CVD. Starting with pulse length in the order of seconds, in the case of the ALD mode, a reduction of the pulse length leads first to a reduction of the growth rate, because the precursor does not have enough time to adsorb at the sample surface to form a monolayer. Then, in a second time, for pulse time in the order of hundreds milliseconds, there is an increase of the growth rate, due to the change in the growth mode, from the surface saturation to the continuous growth. Further reduction of the pulse length, in the order of tens milliseconds, the growth can be assimilated to a CVD growth, with properties similar to the one of material obtained in continuous growth.

Additionally, extraction of the activation energy of the deposition reaction, using the Arrhenius law from deposition at temperature ranging from 100°C up to 450°C, will give some insight on the importance of the process on the favoring of the deposition reaction.

Finally, to address the photonic and MEMS applications, thick layers of Al_2O_3 will be deposited by the three methods and will be characterized by ellipsometry, Fourrier Transformed Infra-Red (FTIR), Raman measurement and X-ray Diffration (XRD). Pro and cons of each technique will be discussed based on these characterizations.

8:40am **TF-TuM3 Employing Atmospheric Pressure Micro-Plasma Printer for ALD of TiO_2 Thin Films**, ***Morteza Aghaee***, *J. Verheijen*, Eindhoven University of Technology, The Netherlands, *A. Stevens*, InnoPhysics B.V., The Netherlands, *W.M.M. Kessels*, *M. Creatore*, Eindhoven University of Technology, The Netherlands

A broad range of devices such as thin film transistors (TFTs), solar cells, sensors and microfluidic channels benefit from micron-scale patterns in their structure. These micron-scale patterns are often fabricated by means of costly methods such as (photo-)lithography. For this reason, there is a large interest in alternative simple and cost-effective approaches for micron-scale to sub-millimeter patterning that reduce the number of etch and lithography process steps.

A micro-plasma printer [1], which is based on a unique needle-to-plate micro-plasma dielectric barrier discharge (DBD), has recently been developed for spatially-resolved surface functionalization [2] and deposition of organic films [3] with sub-millimeter range resolution. In this contribution, the potential of the micro-plasma printer in delivering patterned, ultra-thin inorganic films at atmospheric pressure is addressed. Specifically, the setup is adopted to carry out thin film TiO_2 deposition in two configurations, namely plasma enhanced chemical vapor deposition (PE-CVD) and plasma-assisted atomic layer deposition (PA-ALD).

The properties of the TiO_2 layers as well as the patterning resolution have been investigated. The TiO_2 films deposited by PE-CVD mode have not shown satisfactory results in terms of purity and density of the layers (more than 5% C and refractive index of 1.8). However, the PA-ALD mode has been able to deliver patterns of amorphous TiO_2 films with low level of impurity and sub-nanometer thickness control. A growth rate of 0.15 nm/cycle has been obtained for 500 ms and 400 µs of TTIP and N_2/O_2 plasma exposures in each PA-ALD cycle, respectively. Rutherford backscattering spectroscopy (RBS) has revealed a growth rate of 2.4 Ti atoms per nm^2.cycle in saturation condition. Improvement of density and reduction of film impurities (H, C and N content) have been observed by prolonging the plasma exposure time. TiO_2 films with refractive index of 2 and less than 1% C have been deposited by 2 ms of plasma exposure. The width of the smallest features deposited by PE-CVD and PA-ALD modes have been determined by XPS line scan measurements to be 1.8 mm and 900 µm, respectively, for 7 nm thick layers.

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9:00am **TF-TuM4 Large-Area Atmospheric Pressure Spatial ALD**, *C. Frijters*, *F. van den Bruele*, *F. Grob*, ***Paul Poodt***, Holst Centre / TNO, Netherlands

Atmospheric spatial ALD (sALD) is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD are flat panel (OLED) displays. We have developed spatial ALD processes for making high mobility oxide semiconductors for the TFT backplane as well as thin-film encapsulation for the OLED front plane. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area sALD deposition technology that is able to combine high throughput with uniform performance across large areas.

As an intermediate step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates, able to deposit uniform films across a deposition width of 300 mm. The whole tool is operated under an atmospheric but inert N_2 atmosphere. We will present the basic deposition performance of the tool, where large-area thickness non-uniformities of less than 1% have been achieved for alumina on glass. Furthermore, we will demonstrate excellent compositional uniformity for binary oxides.

One of intended applications is thin-film encapsulation of OLED devices. In order to test the encapsulation performance of the films deposited by the large area spatial ALD tool, we deposited single layer and double layer alumina films, in combination with printed organic planarization layers, on PET foils laminated on 325 mm x 325 mm glass panels. The encapsulation performance was tested under damp-heat conditions. The deposited encapsulation stacks show excellent results, with virtually no visible defect appearing after more than 1000 hrs. at 60 ºC 90 %RH, corresponding to a potential device lifetime of at least 2.5 years. These results demonstrates the potential of spatial ALD for manufacturing large-area OLED devices.

9:20am **TF-TuM5 High Speed ALD of Multifunctional ALD Ultrabarriers for Flexible OLED Encapsulation**, ***Jacques Kools***, Encapsulix, France **INVITED**

In recent years, Atomic Layer Deposition (ALD) has established itself as a viable technology for deposition of ultrabarriers on large area electronic devices such as photovoltaics, OLED's and organic electronics. As a first generation material, Alumina (Al2O3) has been established as the workhorse material to deliver excellent water vapor and oxygen barrier properties. However, many devices require protection from a multitude of invasive fluxes, such as UV light, salt water, electromagnetic radiation, ... etc. A nanoengineered synthetic barrier material allows to tune the different physical properties of the barrier.

In this paper we will describe our recent work on the development of hardware and process for industrial deposition of nanoengineered barriers, with properties that have been optimized to the specific device requirements. Leveraging the unique ability of ALD to control materials on the atomic scale, multilayered barriers are constructed atomic layer by layer from a set of up to ten precursor materials. In this way, it is possible enhance the flexibility (by the use alucone layers), the UV resistance (by the use of TiO2), the resistance to liquid water.. etc.

Process development and manufacturing experience in the OLED industry will be discussed.

11:00am **TF-TuM10 Simulation of Atomic Layer Deposition**, ***Paul Moroz***, TEL Technology Center, America, LLC, *D. Moroz*, Harvard University

Semiconductor industry overcomes many challenges by advancing materials processing to new levels of precision, accuracy, manufacturability, and reliability, while the role of numerical simulations grows. Here we present new results on Monte Carlo feature-scale simulations of Atomic Layer Deposition (ALD) conducted with a feature-scale simulator, FPS3D [1-5], as well as comparison of obtained simulation results with corresponding experiments. The ALD processes are often complex, involving large molecules and, to our knowledge, have not been addressed by other feature-scale simulations except via FPS3D [4-5]. ALD has a potential for conformal and precise deposition. However it requires definite conditions for being successful, and those conditions are very important to understand. The main factor of all of ALD schemes is the cyclic change of flux parameters and the corresponding chemistry, producing a single monolayer or, most typically, a fraction of a monolayer of the deposited film after application of a cycle. We consider two very different cases of SiN film deposition. The first one uses cycles of dichlorosilane and ammonia plasma, while the second one applies cycles of disilane and hydrazine. The SiN deposition rate for the former corresponds to a half of a monolayer per cycle, while for the later, it saturates at values close to a full monolayer per cycle. Steric hindrance was found to be an important factor in explaining those phenomena.

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11:20am **TF-TuM11 Boron Nitride Film Growth at Room Temperature Using Electron Enhanced Atomic Layer Deposition (EE-ALD)**, ***Jaclyn Sprenger***, *H. Sun, A.S. Cavanagh, S.M. George*, University of Colorado Boulder

Electron-enhanced atomic layer deposition (EE-ALD) can drastically reduce the temperatures required for film growth. The temperature reduction occurs because electrons can desorb surface species by electron stimulated desorption (ESD) to create very reactive "dangling bonds". Precursors can then adsorb efficiently on the dangling bonds. EE-ALD lowers the thermal budget and enables the deposition of thin films on thermally sensitive substrates. EE-ALD has been demonstrated previously for the deposition of polycrystalline GaN [1] and amorphous Si [2] at room temperature.

BN film growth by EE-ALD was performed at room temperature on Si (111) substrates using alternating doses of borazine ($B_3N_3H_6$) and low-energy electrons. Borazine is a single-source precursor for BN deposition. *In situ* ellipsometry was performed during the BN EE-ALD. These ellipsometry measurements yielded a linear growth rate of ~3 Å/cycle for electron energies of 100 eV with an electron current of 300 μA for 240 s. This *in situ* growth rate was confirmed by *ex situ* spectroscopic ellipsometry. A BN film with a thickness of 150 nm was deposited after ~500 EE-ALD cycles (see supplemental Figure 1). *Ex situ* ellipsometry measurements show flat BN thickness spatial profiles (see supplemental Figure 2) which are consistent with self-limiting reaction conditions including hydrogen desorption.

Film composition was studied with *ex situ* XPS (see supplemental Figure 3). The BN composition is consistent throughout the film with a B/N ratio of 1.3/1. The films are pure with C and O concentrations of only <3 at.% in the bulk of the film. A thin, self-passivating surface oxide resulting from atmospheric exposure is present. In addition, *ex situ* FTIR transmission was performed on the BN films. These FTIR measurements yielded an absorption peak at ~1370 cm^{-1} that is consistent with hexagonal BN.

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11:40am **TF-TuM12 CVD of sp^2-BN on Si(111) Substrates**, ***Laurent Souqui***, *H. Pedersen, H. Högberg*, Linköping University, Sweden

Boron nitride (BN) is a wide bandgap semiconductor related to the other 13-nitrides (or III-nitrides), aluminium nitride (AlN) or gallium nitride (GaN). As BN is isoelectronic to carbon, it demonstrates graphite-like structure (sp^2-BN) in hexagonal BN(h-BN) and rhombohedral BN, (r-BN). In addition, BN exists as disordered phases such as amorphous (a-BN) or turbostratic (t-BN). Crystalline h-BN and r-BN films are promising materials for application such as UV-devices, power electronics and neutron detectors. Furthermore the similarities between graphene and sp^2-phases such as h-BN and r-BN make BN a commensurate insulating growth template for graphene.

Our previous works were focused on the CVD of epitaxial sp^2-BN films on Al2O3(0001) and 6H-SiC(0001) substrates [1] and found the optimal condition for BN growth to be around 1500°C. We now study the growth of boron nitride on silicon substrates (Si) as silicon is cheap, abundant and is a mature technology. However, due to its low melting point (1414°C), Si cannot withstand such high temperature processes. Because of the necessity of growing at lower temperature, CVD BN films grown on silicon usually show low crystallinity i.e. often a-BN, t-BN or nano-crystalline BN.

In this work, thin BN films were grown on Si(111) substrates in a horizontal hot-wall CVD reactor. Triethylborane (TEB) and ammonia (NH_3) were used as precursors and reacted at temperatures between 1200°C and 1300°C. The substrates were in-situ annealed in silane (SiH_4) and NH_3 before the deposition. Further, a small fraction of SiH_4 was also introduced during the growth as this has been shown to favour growth of crystalline sp^2-BN films [2]. Fourier-Transform Infra-Red spectroscopy (FTIR) confirms the presence of sp^2-BN. Adjustment of the SiH_4 concentration in the growth flux results in the deposition of crystalline films attributed to sp^2-BN in X-ray diffraction. In contrast, films deposited on Si at the same conditions but without SiH_4/NH_3 pre-treatment hardly nucleates and is amorphous to X-rays. This shows the importance of surface preparation in order to grow crystalline BN films on Si. In addition to growth of boron nitride, we observe the growth of SiC grains either due to a reaction between alkyl by-products from TEB and either the substrate or SiH_4 from the gas phase.

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12:00pm **TF-TuM13 Microcontroller-based Sequential Deposition Control Systems using Behavior Tree Algorithms: ALD for the "App Generation"**, ***Brandon Piercy***, *J. Crane, M.D. Losego*, Georgia Institute of Technology

A major challenge for researchers developing custom deposition equipment is the design and creation of the control software and electronics. While a simple loop-based control logic is often sufficient for sequential deposition applications like atomic layer deposition (ALD), it becomes cumbersome and difficult to reprogram when integrating more complex functionality or decision making. Furthermore, there are limited examples of publicly available control code or hardware schematics that can be easily integrated into an existing system. The "behavior tree" algorithm, developed in the robotics and artificial intelligence communities, is a highly adaptable and intuitive method to create complex behaviors. With behavior trees, we have created unique deposition recipes that would be challenging to implement using simpler control algorithms. We have written the core algorithm to run on widely available microcontrollers, making it possible to control equipment remotely using mobile “apps” or a centralized computer. In this talk, we will describe our microcontroller implementation and how it can be rapidly integrated into new or existing sequential deposition systems.

Applied Surface Science Division
Room: 13 - Session AS+TF-TuA

Problem Solving Using Surface Analysis in the Industrial Laboratory

Moderators: Jeffrey Fenton, Medtronic, Paul Vlasak, The Dow Chemical Company

2:20pm **AS+TF-TuA1 TOF-SIMS MS/MS for Industrial Problem Solving**, *G.L. Fisher, D.M. Carr,* Physical Electronics, *T. Miyayama, S. Iida,* ULVAC-PHI, Japan, ***Scott Bryan***, Physical Electronics

One of the most common requests in an industrial analytical lab is to distinguish between "good" and "bad" samples of supposedly the same composition. For failure analysis labs, the goal is often to determine the source of contamination or defects in a production process with poor yield. Identifying contamination left behind from different cleaning procedures or after extended use is also a common request. In all these circumstances, one does not know ahead of time what chemical compounds are present. TOF-SIMS is an ideal technique for these applications because it has high sensitivity, high specificity, and parallel detection of all masses. One complication is that real-world samples usually have a complex mixture of compounds on the surface, making the TOF-SIMS spectrum difficult to interpret. Further, the use of a wide variety of different primary ion beams (e.g. Ga^+, In^+, Au^+, Bi^+, C_{60}^+, and Ar_n^+) has complicated the use of TOF-SIMS spectral databases for compound identification due to large changes in relative peak intensities from one beam to another.

A MS/MS capability was recently integrated into a TOF-SIMS instrument to make compound identification easier [1,2]. It allows unambiguous identification of both organic and inorganic peaks above *m/z* 200, where the mass accuracy is insufficient to identify the composition of a peak by its exact mass. A MS/MS spectrum from a single precursor mass is much easier to match using a spectral database compared to using the original complex TOF-SIMS spectrum. In addition, the MS/MS spectrum of a given precursor ion is independent of the primary ion used to generated it.

Several case studies will be given where MS/MS was needed to identify compounds from an analysis of industrial samples. Two modes of MS/MS will be compared and contrasted. One is based on collision induced dissociation (CID) with inert gas and the other is based on post source decay (PSD).

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2:40pm **AS+TF-TuA2 *In Situ* Molecular Imaging of Switchable Ionic Liquids**, ***Juan Yao****, D. Lao, X.F. Yu, S. Nune, D. Heldebrant, Z.H. Zhu, X.Y. Yu,* Pacific Northwest National Laboratory

Switchable ionic liquids (SWILs) are emerging green solvents in industry for cleaner separation and efficient biomass production, for instance. However, the liquid structure and composition of SWILs are not fully understood. Besides some off-line analyses using NMR and IR, our knowledge of the SWIL is quite limited. We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study SWILs in this work. SWILs are introduced into a vacuum compatible microfluidic channel for analysis by liquid SIMS. Two model systems have been investigated. The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings. The second is primarily made of koechanol with various CO_2 loadings. Koechanol acts as both acid and base in the latter. Our results show two coexisting liquid phases in the two SWIL systems. This phenomenon was only hypothesized in previous theory prediction. We are able to provide the first physical evidence of the complex liquid-liquid interface using three-dimensional chemical mapping with submicrometer resolution. In addition, more complex stoichiometry is discovered as a result of SWIL formation. More importantly, we provide the first chemical spatial mapping elucidating the evolved liquid-liquid interface as a result of SWIL formation. We anticipate the more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis and more versatile industrial applications.

3:00pm **AS+TF-TuA3 Employing a Surface and Bulk Analytical Approach for the Synthesis and Characterization of Ophthalmic Biomaterials**, ***Daniel Hook****, A. Hoteling, W. Nichols, I. Nuñez, K. Wygladacz,* Bausch + Lomb, Inc. **INVITED**

Background:

During the development of a new soft contact lens material three areas of focus; regulatory requirements, manufacturing requirements and customer needs, are often used to guide the overall activities of the material development process.

Regulatory requirements are associated with material properties that are collected using methods defined by standards organizations and accepted by regulatory bodies globally. While this data is mandatory for the registration and approval of a contact lens material it is incomplete in that it only defines the basics of the material.

Manufacturing requirements such as speed of polymerization and completeness of reaction provide critical information so that an effective material can be made in a cost effective manner.

Finally, patients will demand a material that can be worn comfortably while correcting vision over the course of the wearing schedule. Patient focused parameters such as incorporation of wetting agents that create a wettable surface as well as a robust surface that will withstand handling of the course of several weeks of wear area also critical to success.

Methods:

The ISO methods 18369-4:2006, 4.6, 18369-4:2006, 4.4, 18369-4:2006, 4.5 were used to collect bulk properties of water content, oxygen permeability and refractive index while ANSI method Z80.20.2010, 7.10 was used to collect captive bubble contact angle data (CBCA). Photo-Differential Scanning Calorimetry (Photo DSC), Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid Chromatography - Mass Spectrometry (LC-MS) were used to measure polymerization kinetics and monomer consumption. X-ray Photoelectron Spectroscopy (XPS) data was collected to understand surface uniformity and product consistency while Atomic Force Microscopy (AFM) was used to assess surface morphology over the course of the wearing schedule.

Results and Conclusion:

Data summarizing the submission for samfilcon A, a 46% water, 114 Dk material will be presented. CBCA coupled with XPS data will demonstrate a consistent surface wettability and chemistry across multiple lens powers and lens lots. Photo DSC, GC-MS and LC-MS will illustrate how the lens polymerizes in two distinct time resolved phases enabling the incorporation of polyvinyl pyrrolidone wetting agent into the lens bulk and surface. Together the analytical data will provide a unique picture of the data set needed for regulatory approval along with satisfying the manufacturing requirements and patient needs for a successful ophthalmic biomaterial.

4:20pm **AS+TF-TuA7 Surface Properties and Interfacial Bonding of Anodic Aluminium Oxides and Organic Resins**, ***Shoshan Abrahami****, T. Hauffman,* Vrije Universiteit Brussel (VUB), Belgium, *De KoK,* Fokker Aerostructures BV, Papendrecht, The Netherlands, *Gudla, Ambat,* Technical University of Denmark (DTU), Denmark, *J.M.C. Mol*, TU Delft, Netherlands, *H. Terryn*, Vrije Universiteit Brussel, Belgium

Aluminium pretreatment for bonding purposes needs to produce a stable oxide with optimal chemical and structural characteristics for adhesion with the organic resin. Contributions at the interface region can be related to adsorptive interactions as well as mechanical interlocking between the two phases. To separate between these two effects, we applied either barrier-type or porous-type oxides on two sets of specimens. This paper presents an overview of a study on the relation between oxide properties and interfacial bonding, as affected by the nature of electrolyte and the anodizing conditions, as well as changes in the chemistry of the organic resin (epoxy, phenol, silanes). A detailed characterization of different anodic oxides and its effect on the adsorption of resin-derived functional molecules was performed using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Results indicate significant changes in the chemical composition of the oxides as a function of the electrolyte[1]. Mechanical peel test performance indicate that the initial bond strength is independent of the oxide surface chemistry, while the stability under the ingress of water is correlated to the amount of surface hydroxyls[2]. The presence of phosphates and sulphates did not alter bonding mechanisms, only the availability of hydroxyls. Further, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize the geometrical modifications to the pore- and oxide structure in porous-type oxides. In addition, energy-dispersive X-ray spectroscopy (EDS) profiles were acquired on TEM cross-sections to assess the oxide structure and concentration of resin inside the pores. Linking these morphological features to peel results show that two types of modifications are crucial for the formation of a strong and durable bonding[3]. A minimum pore size is needed for the resin to fill the oxide pores for good initial adhesion. Surface roughness, on the other hand, was found beneficial for the durability of the bond upon the ingress of water. Overall, the results demonstrate that both surface chemistry and oxide morphology contribute to the strength and durability of an adhesive bond.

1. Abrahami, S. T., et al., XPS Analysis of the Surface Chemistry and Interfacial Bonding of Barrier-Type Cr(Vi)-Free Anodic Oxides. J. Phys. Chem. C 2015, 119, 19967-19975.

2. Abrahami, S. T., et al., Effect of Anodic Aluminum Oxide Chemistry on Adhesive Bonding of Epoxy. J. Phys. Chem. C 2016, 120, 19670-19677.

3. Abrahami, S. T., et al., Interface Strength and Degradation of Adhesively Bonded Porous Aluminum Oxides npj Materials Degradation 2017, in press.

4:40pm **AS+TF-TuA8 Practical Considerations of Different Ion Sources for Industrial Applications: The Good, the Bad, and the Indifferent**, ***William Stickle***, *C.N. Young*, *M.D. Johnson*, HP Inc., *B. Schmidt*, Physical Electronics USA

In recent years advances in ion gun technology have resulted in the routine application of cluster ion sources for analyses in industrial R&D labs. Most industrial laboratories study a wide variety of material systems ranging from polymers to inorganic thin films; many of these material systems require analysis not just of the as received surface, but also of and through the depth of a thin film. The purpose of this talk is to compare and contrast the benefits and drawbacks of performing routine XPS analyses using a mono atomic argon ion source compared with a C_{60}^+ ion source and an argon gas cluster ion source. From a practical standpoint, it is important to understand the sputter induced chemistry that may be created by these various sources and the trade-offs for applying these different primary ion sources for routine surface chemical analyses. The effects of preferential sputtering and chemical changes or reactions of metal oxides will be discussed. Several different material systems are examined and discussed by comparing the information obtained using mono atomic argon, an argon gas cluster source and a C_{60}^+ ion source for enhancing and clarifying ‘routine’ analyses. The different types of samples to be discussed will include polymers, fluoropolymer systems, amorphous metals and their oxides and multilayer thin films.

5:00pm **AS+TF-TuA9 Surface Analysis in an Industrial Setting: Non-ideal Real World Samples**, ***Vincent Smentkowski***, General Electric Global Research Center **INVITED**

The top few nanometers of a sample is defined as the surface. The surface is where most chemical reactions take place. There are many instances where the surface of materials are designed/functionalized in order to optimize properties and improve device performance; there are other instances where the surface becomes compromised and the material/device performance degrades following treatment and/or use. Accurate characterization is essential in order to understand material/device performance.

Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Scanning Probe Microscopy (SPM) are the most common, and commercially available, surface analysis techniques. These techniques provide complimentary information regarding both the composition and microstructure of the surface of a sample and often compliments bulk analysis.

In my talk, I will discuss the characterization challenges faced in an industrial setting where the surface analyst is often provided non-ideal samples and is asked to provide both a rapid and complete analysis of the sample. The criticality of talking with the person that submits the sample to understand their issue(s) and what they expect from the analysis (as well as being certain they realize possible complications) will be highlighted via real samples. I will also show a few examples where proof of principle results provided interesting data, however the data were not scientifically meaningful.

5:40pm **AS+TF-TuA11 C 1s Peak of Adventitious Carbon Aligns to the Vacuum Level: Dire Consequences for Material’s Bonding Assignment by Photoelectron Spectroscopy**, ***Grzegorz Greczynski***, *L. Hultman*, Linköping University, Sweden

X-ray photoelectron spectroscopy (XPS) is an irreplaceable analytical tool in materials research providing information about surface chemistry and composition. The unambiguous bonding assignment relies, however, on the correct measurement of binding energy (BE) values, which is often a nontrivial task due to the lack of an internal BE reference. C 1s signal from ubiquitous carbon contamination on samples forming during air exposure, so called adventitious carbon (AdC) layers, is the most common BE reference in XPS studies. Our literature review shows that in 58% of the top-cited papers dealing with XPS studies of magnetron sputtered films published between 2010 and 2016 in peer-reviewed journals, C 1s of AdC was used as a BE reference, while, alarmingly, the remaining papers lack information about any referencing method used. Within the first group, C 1s peak was set quite arbitrary at the BE varying from 284.0 to 285.2 eV. This serious inconsistency contradicts the very notion of a BE reference, which per definition should be connected with one single-energy value.

In this work, we examine the reliability of using AdC for XPS BE referencing by measuring the position of C 1s peak for a series of transition metal (TM) nitride thin film layers that exhibit a well-defined Fermi edge cut-off serving as an internal BE reference. Measurements are performed as a function of the AdC layer thickness, which scales with the air exposure time. We show that the BE of C 1s peak E^F_B varies by as much as 1.44 eV, depending on the underlying (TM)N.[i] This is a factor of ten more than the typical resolvable difference between two chemical states of the same element, *which makes BE referencing against the C 1s peak unreliable and thus inadvisable for the purpose*. Surprisingly and reassuringly, we find that C 1s shifts correlate to changes in sample work function Φ_{SA}, such that the sum $E^F_B+\Phi_{SA}$ is constant at 289.50±0.15 eV, irrespective of materials system and air exposure time, indicating vacuum level alignment. This discovery allows for significantly better accuracy of chemical state determination through a complementary measurement of Φ_{SA} and referencing to C 1s set at $289.50-\Phi_{SA}$, which as we demonstrate, yields consistent results for the whole series of TM nitrides, irrespective of air exposure time. Our findings are not specific to nitrides and likely apply to all systems where charge transfer at the AdC/substrate interface is negligible.

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[i] G. Greczynski and L. Hultman, *ChemPhysChem* 18 (2017) 1507

6:00pm **AS+TF-TuA12 Band Energy Alignment Studies at Heterojunction by X-ray Photoelectron Spectroscopy (XPS)**, ***Jisheng Pan***, Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Singapore

The performance of any type of hetero-junction device is determined by two kinds of interface parameters: the band discontinuities and the built-in potential. Therefore, determining heterojunction band offsets and tuning them to a desired application would have an obvious impact on the optimization of the devices. Many techniques have been developed to determine the interfaces and to understand the microscopic origin of the interface properties. XPS is more widely used technique to study band alignment of heterojunction, probably due to its capability to simultaneously detect interface chemical and electronic properties which can be exploited for fully understanding of distinct correlations between the thin film material characteristics and device performance. There are two ways to obtain energy band offsets using XPS. One is direct measurement of valence band spectrum from interface, and this spectrum is simply considered as a superposition of substrate-related and overlayer-related valence band spectra. A nonlinear least squares fit is performed to separate it to substrate-related and overlayer-related valence band spectra to determine two valence band maxima and, valence band offset (VBO) of interface. The conduction-band offset CBO is deduced from VBO and suitable reference gap values of two materials at interface. It can be seen that the accuracy of the band offsets determined through this way depends on the fitting procedure. In order to overcome the above problem and obtain reliable band offset data, a method was proposed to determinate band offsets by combination of core level and valence band spectra. No fitting procedure is involved in this method. However, accurate XPS determination of band alignment in this way requires careful consideration of many other possible effects. In this paper, we have studied the effects of chemical shift, differential charging, band bending and photoemission final state on the determination of heterojunction band offsets using Kraut’s method. The method has also been applied to determinate energy-band alignments of molybdenum disulphide (MoS_2) monolayer on high-k dielectric oxides such as Al_2O_3 and ZrO_2. The VBO at monolayer MoS_2/Al_2O_3 (ZrO_2) interface was measured to be 3.31 eV (2.76 eV), while the CBO was 3.56 eV (1.22 eV). For bulk MoS_2/Al_2O_3 interface, both VBO and CBO increase by 0.3 eV, due to the upwards shift of Mo $4dz^2$ band. The symmetric change of VBO and CBO implies Fermi level pinning by interfacial states. Our finding ensures the practical application of both p-type and n-type MoS_2 based complementary metal-oxide semiconductor and other transistor devices using Al_2O_3 and ZrO_2 as gate materials.

Thin Films Division
Room: 20 - Session TF-TuA

ALD Precursors and Surface Reactions
Moderators: Qing Peng, University of Alabama, Riikka Puurunen, Aalto University, Finland

2:20pm **TF-TuA1 Accelerated Searching of Potential Precursors for Silicon Carbide-atomic Layer Deposition from Ab-initio Machine Learning Methods**, ***Zhigang Mei***, *S. Bhattacharya*, *A. Yacout*, Argonne National Laboratory

Due to the superior thermophysical properties of silicon carbide at high temperature, silicon carbide (SiC) coatings have the potential to offer excellent resistance to both oxidation and hydriding of zircaloy-based nuclear fuel cladding used in light water reactors. Unfortunately, the current deposition technique for SiC using chemical vapor deposition (CVD) can be only achieved at relatively high substrate temperatures, which can severely degrade the performance of zircaloy cladding. As a comparison, atomic layer deposition (ALD) enables the growth of pinhole free films on large and convoluted substrates with nanometer precision that operates at low temperatures. Developing a new ALD process requires better understanding of how the film growth process takes place, which depends on the chemicals being used. The major obstacle to low-temperature ALD of SiC is to determine the right precursors. To this end, we use high-throughput *ab initio* calculations and state-of-the-art machine learning (ML) techniques to accelerate the precursor screening. The method involves two different types of prediction: the forward and backward predictions. The objective of the forward prediction is to train a set of machine learning models for the free energies of silicon and carbon-containing molecules from the high-throughput *ab initio* database. Inverting the trained forward models through Bayes' law, we quantitatively predict the free energies of all the possible silicon and carbon-containing molecules from the PubChem compound database. By calculating the Gibbs energy of reaction using the ML predicted energy, several potential silicon and carbon precursors are predicted to be promising for ALD of SiC at low temperature. We believe the present method will be helpful to develop novel ALD precursors for other applications.

2:40pm **TF-TuA2 Surface Chemistry of Ru Atomic Layer Deposition Precursors**, *X. Qin*, ***Francisco Zaera***, University of California

The thermal chemistry on nickel, silicon oxide, and aluminum oxide surfaces of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(III), a precursor used for the growth of metallic ruthenium thin films via atomic layer deposition (ALD), was characterized by using a combination of X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and reflection-absorption infrared absorption spectroscopy (RAIRS). Several intermediate steps were identified during the surface decomposition of this precursor on nickel, with the release of carbon monoxide into the gas phase, the formation of tert-butyl species on the nickel substrate, and the reduction of the metal center in stepwise fashion between approximately 300 and 500 K. ALD cycles with oxygen as the second reagent accomplish the efficient removal of all carbon contaminants from the surface and the reversible oxidation-reduction of the metal, indicating the feasibility of growing metallic films with such oxidizing reactant. However, the formation of volatile Ru oxides prevents the buildup of multilayers of the metal. Experiments with other oxidants (nitrous oxide) and other substrates show promise for finding a solution to this problem.

3:00pm **TF-TuA3 Mechanistic Aspects of ALD Ru Thin Film Growth based on Ru(DMBD)(CO)$_3$ and H_2O using Downstream Quadrupole Mass Spectrometry**, ***Zhengning Gao***, Washington University in St. Louis, *R. Kanjolia*, EMD Performance Materials, *P. Banerjee*, Washington University in St. Louis

The precursor 2, 3 - dimethyl butadiene Ruthenium tri-carbonyl (Ru(DMBD)(CO)$_3$), is a volatile molecule with favorable properties for the deposition of both Ru and RuO_2 films via ALD.[1] An intriguing aspect of this precursor is its asymmetric molecular structure with the DMBD ligand coordinated to one side of the Ru^{4+} center, while the 3 carbonyl groups are bonded to the opposite side. This makes the molecule an attractive candidate to study using *in situ* downstream quadrupole mass spectrometry (QMS) since, the release of DMBD vs. carbonyl groups during ALD half-reactions can provide a particularly descriptive view at the atomic level of how Ru(DMBD)(CO)$_3$ interacts with the substrate.

In this talk, we will discuss the mechanism of ALD of Ru thin films using Ru(DMBD)(CO)$_3$ and H_2O. The QMS signal of the Ru(DMBD)(CO)$_3$ consists of three distinct species. First, the mass-to-charge ratio (m/e) of 67 corresponds to the DMBD ligand dissociating from the molecule[2]. Second, a strong m/e = 16 is also observed as the DMBD further cracks into smaller fragments. Finally, m/e = 44 is observed and is related to CO_2 and HCOOH formation from the reaction of the tri-carbonyl groups with H_2O.[3] The QMS signal of these three species will be discussed in the context of varying process parameters such as Ru(DMBD)(CO)$_3$ and H_2O pulse times and the temperature of the ALD process. Additionally, *ex situ* film characterization including atomic force microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectrum and resistivity measurements will be presented to correlate the process signatures obtained via QMS to the film type, morphology and electrical properties.

References:

1. Austin, D. Z.; Jenkins, M. A.; Allman, D.; Hose, S.; Price, D.; Dezelah, C. L.; Conley, J. F., Atomic Layer Deposition of Ruthenium and Ruthenium Oxide Using a Zero Oxidation State Precursor. *Chem. Mater.* **2017**.

2. Chiang, C.-M.; Rowe, J.; Malic, R.; Sen, A.; Steigerwald, M.; Mills, A., A new CVD reaction for atomic layer deposition of silicon. *Applied surface science* **1996,***107*, 189-196.

3. Rosenberg, S. G.; Barclay, M.; Fairbrother, D. H., Electron beam induced reactions of adsorbed cobalt tricarbonyl nitrosyl (Co (CO) 3NO) molecules. *The Journal of Physical Chemistry C* **2013,***117* (31), 16053-16064.

3:20pm **TF-TuA4 Nucleation of Al_2O_3 Atomic Layer Deposition with Water or H_2O_2**, ***Adam Hinckley***, *A.J. Muscat*, University of Arizona

Aluminum oxide (Al_2O_3) is a suitable replacement for SiO_2 in electronic devices such as flash memory due to its wide band gap and higher dielectric constant. Atomic layer deposition (ALD) using sequential pulses of trimethylaluminum (TMA) and an oxidant is a leading method for the formation of nano-scale Al_2O_3 layers. Al_2O_3 layers grown by ALD have been demonstrated with leakage currents of less than 1 nA/cm^3. The quality of the layers depends on both the deposition temperature and choice of oxidant, which is commonly water or oxygen atoms generated using a plasma.

An oxidant more reactive than water, such as H_2O_2, could produce a denser Al_2O_3 film. The growth of Al_2O_3 on hydrogen-terminated silicon using TMA and H_2O_2 was compared to that using TMA and water as a reference. Spectroscopic ellipsometry was used to determine the growth per cycle (GPC), and *in situ* x-ray photoelectron spectroscopy (XPS) was recorded before and after each precursor dose. The O 1s XPS peak at 531.8 eV and the Al 2p peak at 75.5 eV were used to monitor the formation of the Al-O bond and the C 1s peak at 284.5 eV was used to monitor the persistence of the Al-C bond after each half cycle. A second state in O 1s XPS at 533.3 eV assigned to the O-H bond was used to estimate the number of reactive sites present after each oxidant pulse.

The growth-per-cycle (GPC) was equal to 1.2 Å at H_2O_2 pulse times above 0.3 s, which is similar to reported ALD growth rates using water. The Al 2p XPS peak appeared after 4 ALD cycles using anhydrous H_2O_2 and after 7 cycles using water. The aluminum coverage after 10 ALD cycles was 40 % greater for anhydrous H_2O_2 compared to water, although the GPC was similar for each co-reactant. The O-H coverage doubled with each pulse of H_2O_2. The O 1s peak assigned to O-H also broadened with subsequent ALD cycles due to the presence of additional surface states. Each pulse of water increased the O-H coverage by about 1.5 times compared to the subsequent pulse. The ratio between C 1s and Si 2p peak areas showed twice as much carbon present on the surface during H_2O_2 ALD. The C 1s/Si 2p ratio increased during pulses of TMA and decreased during pulses of H_2O_2 due to surface reactions that desorb CH_4. Greater OH densities and C coverages indicate that H_2O_2 activates more surface sites for the metal precursor than water, improving Al_2O_3 film density.

4:20pm **TF-TuA7 Direct Measurements of Half-Cycle Reaction Heats during Atomic Layer Deposition Provide Mechanistic Insights**, ***Charles T. Campbell***, *J. Lownsbury*, University of Washington, *K.S. Kim*, *A.B.F. Martinson*, Argonne National Laboratory

We introduce here a new high-temperature adsorption calorimeter that approaches the ideal limit of a heat detector whereby the signal at any time is proportional to the heat power being delivered to the sample, and prove its sensitivity for measuring pulse-to-pulse heats of half-reactions during atomic layer deposition (ALD) at 400 K. The heat dynamics of amorphous Al_2O_3 growth via sequential self-limiting surface reaction of trimethylaluminum (TMA) and H_2O is clearly resolved. Calibration enables quantitation of the exothermic TMA and H_2O half-reactions with high precision, -343 kJ/mol TMA and -251 kJ/mol H_2O, respectively. A time resolution better than 1 millisecond is demonstrated, allowing for the deconvolution of at least two distinct surface reactions during TMA micro-dosing. It is further demonstrated that this method can provide the heat of reaction versus extent of reaction during each precursor's half-reaction, thus providing even richer mechanistic information on the surface processes involved. The broad applicability of this novel calorimeter is demonstrated through excellent signal-to-noise ratios of less exothermic ALD half-reactions to produce TiO_2 and MnO.

4:40pm **TF-TuA8 Cyclic Silane Precursors in Atomic and Molecular Layer Deposition**, ***Nicholas Strandwitz***, *L. Ju*, Lehigh University

Cyclic azasilanes are a promising class of reactants for atomic and molecular layer deposition due to their volatility, reactivity, and diverse set of peripheral chemical functionalities. The reactivity of this class of molecules stems from ring strain and unstable Si-N bonding. Reaction with water or OH groups results in ring opening and Si-O bond formation and is a useful chemical step for controlled film growth. This work focuses on using and understanding this class of molecules for use in atomic and molecular layer deposition (ALD, MLD). The efficacy of the ring opening reaction and the diversity of functional groups on the cyclic azasilanes deem this precursor group highly promising for MLD. We report the growth of various MLD films based on reaction with anhydrides, metal-organics, and water. The film growth was found to be optimal near 100 °C. The two chemistries reported here are the sequential reaction of (1) a cyclic azasilane, maleic anhydride, and water and (2) a cyclic azasilane, maleic anhydride, trimethylaluminum (TMA), and water. Reaction 1 showed clear evidence of diffusion and reaction within the film as evidenced by large growth rates (~10 nm per cycle) after ~15 growth cycles, regardless of purge time. However, use of TMA in reaction 2 arrested this diffusion, presumably due to consumption of reactive groups or through densification of the film. Film properties were measured as a function of annealing temperature using ellipsometry, x-ray reflectivity, and infrared absorption measurements. These measurements indicate a densification of the films while maintaining low surface roughness. Porosity is evident after removal of organic components by a low dielectric constant for the films derived from reaction 1.These MLD chemistries offer a route to tunable hybrid thin films on high aspect ratio substrates and have potential applications in diffusion barriers, low dielectric constant layers, and passivation layers.

5:00pm **TF-TuA9 Area Selective Atomic Layer Deposition Via Precursor Selective Adsorption: Theory, Strategy, and Applications in Catalysis**, ***Rong Chen***, Huazhong University of Science and Technology, PR China **INVITED**

Atomic layer deposition (ALD) is a powerful thin film deposition method with precise thickness control, good uniformity, and high conformality on entire surface. While in catalysis applications, there are increasing interests for synthesis of catalysts with well-defined nanostructures, thus ALD has become a desired method for catalyst synthesis with precise control of size, composition, nanostructure, etc. Herein we report the area selective growth strategies via ALD precursor selective adsorption to obtain desired metal-oxide composite catalysts. Combining *in-situ* QCM, FTIR and DFT calculations, a series of oxide ALD precursors with $-(CH_3)_n$ $-(N(CH_3)_2)_n$, $-(Cp)_n$, and $–(thd)_n$ ligands are studied on their chemisorption and binding energies to metal surfaces. The selective growth behavior shows a strong correlation with different precursor ligands as well as the counter reactants. Thus with optimal precursor choice and reaction condition, desired nanocomposite structures could be achieved via area selective ALD.

5:40pm **TF-TuA11 AVS 2017 John A Thornton Memorial Award and Lecture: Atomic Layer Deposition: Highlights from the Last 25 Years**, ***Steven George****, University of Colorado at Boulder **INVITED**

The Thornton Memorial Lecture will discuss atomic layer deposition (ALD) highlights from the last 25 years. The lecture will trace the history of ALD starting with the earlier developments in atomic layer epitaxy (ALE). The presentation will recount the importance of semiconductor processing needs to the growth of ALD and the situation that led to the name change from ALE to ALD. The talk will also describe personal highlights in the development of ALD and acknowledge some of the people and circumstances behind those developments. In addition, the lecture will include commentary on the evolution of ALD. The presentation will conclude by looking ahead to the future of ALD.

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* **John A. Thornton Memorial Award Winner**

2D Materials Focus Topic
Room: 15 - Session 2D+EM+SS+TF-WeM

2D Materials Growth and Fabrication
Moderator: Aleksandra Radenovic, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

8:00am **2D+EM+SS+TF-WeM1 Chemical Bath Deposition of Phase Selective MoS_2 on Templated Surfaces**, ***Jenny Hedlund***, *A.V. Walker*, University of Texas at Dallas

Transition metal dichalcogenides (TMDs) have a wide range of physical properties, and consequently have applications in nanoelectronics and biosensors. While TMD materials have been well studied, a simple method for two-dimensional large area thin film deposition of these materials has yet to be achieved. Chemical bath deposition (CBD) is a robust method by which to grow uniform thin films, and offers many advantages over other techniques including low deposition temperatures (≤ 50°C), synthetic flexibility, and it is inexpensive. In this work, CBD is used to deposit large-area ultra-thin molybdenum disulfide (MoS_2), a group VI TMD, and the resulting deposits are investigated by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and time-of-flight secondary ion mass spectrometry (TOF SIMS). These TMDs are most commonly found to possess trigonal prismatic crystalline structure (2H phase) and therefore are semiconductors. Although less widely studied, TMDs can also possess octahedral crystallinity to form the 1T phase. The 1T phase exhibits different properties to the 2H phase, and has applications in sensing, metal contacts and catalysis. By using substrates that mimic the TMD crystalline structure for deposition we have shown that MoS_2 can be deposited with large-area crystallites observed. SEM images of deposition performed on highly oriented pyrolytic graphite show large area flakes, ~100 µm in diameter. Smooth thin films were also deposited on sapphire, and functionalized self-assembled monolayers (SAMs). XPS results show that Mo 3d and S 2s peaks are present in the expected positions and ratios. We further demonstrate that the deposited MoS_2 phase is likely determined by the surface chemistry of the substrate. Using Raman spectroscopy measurements, the thickness and phase of the film are elucidated. CBD of MoS_2 was further characterized using TOF SIMS to elucidate the reaction mechanisms as well as the stability of the deposited film.

8:20am **2D+EM+SS+TF-WeM2 Atomic Layer and Metalorganic Chemical Vapor Deposition of MoS_2 and WS_2 from bis(tert-butylimido)-bis(dialkylamido) Compounds**, ***Berc Kalanyan***, *J.E. Maslar, W.A. Kimes, B.A. Sperling,* NIST, *R. Kanjolia,* EMD Performance Materials

Layered 2D transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness-dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires vapor-phase deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a desirable route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting surface chemistry. However, since ALD conditions are only met at relatively low deposition temperatures, most ALD films are amorphous. Some consider this a useful feature of ALD, since film growth rate and structural development can be decoupled by separating the deposition and crystallization steps. In contrast, metalorganic chemical vapor deposition (MOCVD) enables direct growth of crystalline films, but requires careful process control and precursor selection to achieve the required level of thickness control. The tradeoffs between direct CVD growth and post-sufurization and annealing of amorphous/metallic films is the focus of this work.

In this paper, we present a comparison of process characteristics and film properties, including growth rate, thickness, morphology, composition, and crystallinity, as a function of two deposition routes: ALD and MOCVD. We deposited thin films using $(N^tBu)_2(NMe_2)_2M$ and 1-propanethiol, where M={Mo,W}, at wafer temperatures of 200°C to 400°C for ALD and 400°C to 900°C for pulsed MOCVD on SiO_2/Si substrates. Precursor saturation conditions were evaluated using in situ infrared flow measurements and ex situ X-ray photoelectron spectroscopy. As-deposited and sulfur-annealed films were further evaluated using X-ray diffraction, optical spectroscopies, and microscopy. As-grown ALD films were amorphous and included a mixture of a sulfide and a conductive phase, likely a nitride. Below 300°C, deposition was limited to a thin surface oxide. Higher temperatures resulted in higher growth rates, which also introduced a weak CVD component to the growth. Deposition rates were <1.0 Å/cycle at 350°C. As-deposited films were successfully annealed to 2H-MoS_2 under a sulfur atmosphere, which also removed residual nitrogen. As-grown MOCVD films were polycrystalline 2H-MoS_2 at 600°C. Pulsed injections of precursor enabled Å-level control over aggregate film thickness. For both processes, wafer-scale growth and uniformity in a perpendicular flow reactor were demonstrated on 50 mm substrates. We will also present process characteristics for the analogous WS_2 route and discuss initial data from MoS_2/WS_2 nanolaminates.

8:40am **2D+EM+SS+TF-WeM3 Epitaxial Growth of Atomically Thin Transition Metal Dichalcogenides and their Electronic Structures**, ***Sung-Kwan Mo***, Lawrence Berkeley National Laboratory **INVITED**

Transition metal dichalcogenides (TMDCs) is a versatile material platform with a variety of electrical, optical, and topological properties that can be controlled through thickness, strain, field, and other perturbations. In this talk, I will first discuss the growth of atomically-thin TMDC films, such as $MoSe_2$, WSe_2, WTe_2, $NbSe_2$, and $TaSe_2$, with a layer-by-layer thickness control, using molecular beam epitaxy. Then, I will present how we investigate the electronic structures of these films using angle-resolved photoemission spectroscopy and scanning tunneling microscopy.

9:20am **2D+EM+SS+TF-WeM5 Terminations and Treatments of Silicon Carbide Surfaces to Promote Epitaxial Hexagonal Boron Nitride Deposition by Chemical Beam Epitaxy**, ***Daniel Pennachio***, *N.S. Wilson, A.P. McFadden, T. Brown-Heft,* University of California at Santa Barbara, *K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory, *C.J. Palmstrøm*, University of California at Santa Barbara

This work examines the epitaxial deposition of single-crystal hexagonal boron nitride (h-BN) on silicon carbide substrates through the use of surface treatments which promote suitable nucleation and growth. Silicon carbide, 6H-SiC(0001), was chosen as a candidate substrate due to its market availability, high crystalline quality, temperature stability, and potential coincident lattice match to h-BN. Boron nitride was deposited in ultra-high vacuum (UHV) environments by chemical beam epitaxy (CBE) on SiC substrates through thermal decomposition of borazine at high temperatures. Different SiC surface reconstructions reached through exposure to elemental silicon and subsequent *in-vacuo* annealing were examined for their effect on h-BN nucleation and epitaxial arrangement. Along with reconstructions produced through UHV annealing, CVD-grown epitaxial graphene on 4H-SiC was also utilized as a growth surface. Growth past full single atomic layer coverage of sp^2-bonded material (either h-BN deposited layers or graphene substrates) proved difficult with the accessible temperature range and precursor flux. Various surface treatment approaches were investigated to promote additional layer growth.

Deposited h-BN films on the SiC reconstructed surfaces were found to be near-stoichiometric and of single- to few-atomic layer thickness, as determined by *in-situ* x-ray photoelectron spectroscopy (XPS) B1s:N1s peak area ratios and substrate peak attenuation. Progression of *in-situ* reflection high-energy electron diffraction (RHEED) during h-BN deposition provides evidence of a difference in film nucleation between the Si-rich (3x3) and the C-rich SiC surface reconstructions: while the (3x3) reconstruction quickly transitioned to a (1x1) reconstruction upon precursor dosing, the C-rich reconstruction persisted despite thicker depositions. XPS of the C-rich surface showed a higher binding energy shoulder of the C1s peak, indicative of sp^2-hybridized bonding in a graphene-like buffer layer at the surface. Triangular nuclei seen by scanning electron microscopy after deposition on the C-rich SiC surface suggests epitaxial arrangement to this buffer layer. *In-situ* scanning probe microscopy and *ex-situ* transmission electron microscopy were performed to acquire additional information on film morphology. The influence of different surface treatments for increasing the thickness of h-BN growth will be presented.

9:40am **2D+EM+SS+TF-WeM6 Photo-Chemical Modification of Monolayer Transition Metal Dichalcogenides**, ***Tariq Afaneh***, *P.K. Sahoo, H.R. Gutierrez,* University of South Florida

Fabrication of in-plane 2D heterostructures is a crucial step to advance in the development of a truly 2D optoelectronics. Different approaches have been attempted, including in situ sequential growth of two different materials and post-growth modification of the chemical composition in a 2D monolayer. In this work, we studied a post-growth technique that exploits the radiation-matter interaction under a controlled atmosphere. Using a homemade sealed mini-chamber with a quartz optical viewport, a laser beam (532 nm) was focused onto the sample, consisting on $MoSe_2$ or WSe_2, while keeping a reactive sulfur-rich atmosphere within the chamber. The spatially localized photo-chemical conversion was in situ monitored by mapping the temporal evolution of the Raman active modes. The process can be tuned thereby choosing appropriate laser power, exposure time, and reactive gas environment. The complete or partial conversion was further confirmed by collecting the photoluminescence spectra at the desired exposed sites. The time-dependent intensities of the Raman peaks were fitted to exponentially decaying functions. Depending on the reaction parameters, two different processes with distinct time constants can be identified. The following mechanisms for the photo-conversion are proposed: (i) creation of Se vacancies in the TMD materials due to the energy absorbed from the laser radiation, (ii) cracking of sulfur containing molecules from the gas environment and subsequent incorporation of the sulfur atoms into the Se vacancy sites. The optimization of this process will allow to develop techniques based on photo-induced chemical reactions for local doping, alloying and the fabrication of in-plane TMD heterostructure.

11:00am **2D+EM+SS+TF-WeM10 Bottom-up synthesis of Graphene Nanomembranes with Tunable Porosity**, ***Christof Neumann***, Friedrich Schiller University Jena, Germany, *M. Füser,* Goethe University Frankfurt, Germany, *M. Mohn,* Ulm University, Germany, *D. Kaiser,* Friedrich Schiller University Jena, Germany, *A. Gölzhäuser,* Bielefeld University, Germany, *U. Kaiser,* Ulm University, Germany, *A. Terfort,* Goethe University Frankfurt, Germany, *A. Turchanin*, Friedrich Schiller University Jena, Germany

The potential of atomically thin materials like graphene or carbon nanomembranes (CNMs) [1] for separation or ultrafiltration technologies is based on their negligible thicknesses enabling the ballistic transport of atoms and molecules through the nanomembranes. For such implementations, large scale production of perforated nanomembranes with well-defined sizes of nanopores has to be established. Here we present a scalable method to produce atomically thin graphene nanomembranes with tunable porosity using aromatic self-assembled monolayers (SAMs) as molecular precursors. We employ N-containing 4-(1H-pyrrol-1-yl)thiophenol, 4-(2,5-dimethyl-1H-pyrrol-1-yl)thiophenol and 4-(pyrimidin-2-yl)phenylthiol SAMs on polycrystalline copper foils to convert them into CNMs via low energy electron irradiation induced crosslinking and then to pyrolyze CNMs into nanoporous graphene sheets in vacuum. We characterize the formed supported and suspended graphene nanosheets by different complementary spectroscopy and microscopy techniques including X-ray photoelectron (XPS) and Raman spectroscopy, atomic force (AFM), helium ion (HIM) and high-resolution transmission electron microscopy (HRTEM) as well as by electric transport measurements. We demonstrate that the pore size and the graphene crystallinity can be adjusted by the production parameters and discuss the mechanisms.

[1] A. Turchanin and A. Gölzhäuser, Carbon Nanomembranes, *Adv. Mater.* 28 (2016) 5075

11:20am **2D+EM+SS+TF-WeM11 Cu Single Crystal Substrates for Growth of CVD Graphene**, ***Tyler Mowll,*** University at Albany, SUNY, *Z.R. Robinson,* SUNY Brockport, *C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

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 in-situ analysis with low energy electron diffraction. 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.

11:40am **2D+EM+SS+TF-WeM12 Paper and Circuits, only Atoms Thick**, ***Jiwoong Park***, University of Chicago **INVITED**

2D layered materials are like paper: they can be colored, stitched, stacked, and folded to form integrated devices with atomic thickness. In this talk, I will discuss how different 2D materials can be grown with distinct electrical and optical properties (coloring), how they can be connected laterally to form pattered circuits (stitching), and how their properties can be controlled by the interlayer rotation (twisting). We will then discuss how these atomically thin papers and circuits can be folded to generate active 3D systems.

Scanning Probe Microscopy Focus Topic
Room: 10 - Session SP+SS+TF-WeM

Probing and Manipulating Nanoscale Structure
Moderators: Zheng Gai, Oak Ridge National Laboratory, Qiang Zou, Oak Ridge National Laboratory

8:00am **SP+SS+TF-WeM1 STM-Based Nanofabrication and Integrating Nanostructures with Clean Semiconductor Surfaces**, ***Joseph Lyding***, University of Illinois at Urbana-Champaign **INVITED**

Integrating 1D and 2D nanostructures with clean silicon and III-V semiconductor surfaces represents an interesting route towards future hybrid electronic systems. In this effort, we are exploring the integration of carbon nanotubes, graphene and graphene nanoribbons (GNRs) with clean semiconductor surfaces. A key challenge is the fabrication of ‘clean’ nanostructure-substrate systems. We have addressed this by developing a simple dry contact transfer (DCT) process that enables the deposition of nanostructures onto atomically clean surfaces in ultrahigh vacuum. STM imaging and spectroscopy, coupled with our atomic resolution STM-based hydrogen resist process have been used to study the interactions of carbon nanotubes, graphene and atomically precise graphene nanoribbons with silicon, GaAs and InAs substrates. In these experiments, we have observed the metallic zigzag edge state in graphene[1], carbon nanotube-substrate lattice alignment effects[2], and the electronic structure of GNRs[3]. This talk will also show a method for creating sub-5nm metal wires for contacting nanostructures[4], a SPM probe sharpening technique for producing 1 nm radii probes[5], and a technique for improving the electronic performance of carbon nanotube array transistors as well as the structural and thermal performance of CNT-based composite materials[6].

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8:40am **SP+SS+TF-WeM3 Calcium Mediates Adhesion in Reservoir Fluids**, *S.L. Eichmann,* Aramco Research Center - Boston, ***Nancy Burnham***, Worcester Polytechnic Institute

Oil powers modern economies [1]. Yet only 30% of oil is recovered from a typical reservoir [2]. The reservoirs of Saudi Arabia, which provide over 10% of the world’s oil [3], are unusual . T hey are highly saline, with concentrations of up to 120,000 ppm total dissolved solids (TDS), the temperatures can exceed 100° C, and the emulsion of oil and brine is dispersed within small fissures in carbonate rock. These conditions are challenging for the unhindered diffusion of the nanoparticle tracers that are used to map an oil field from one well to the next [4]. In this study, bare and carboxyl-terminated atomic-force microscope tips and calcite surfaces acted as surrogates for nanoparticle tracers and carbonate rocks, respectively. They were immersed in three fluids: brine (120K ppm TDS), seawater (60K ppm TDS), and calcium-doped seawater (~60K ppm TDS). Surprisingly, the amount of total dissolved solids was not a good predictor of the tip-sample adhesion. Rather, specific ion effects were important; adding calcium to seawater brought the adhesion down to the ~100 pN levels of brine as compared to the ~400 pN levels of seawater . The adhesion for the carboxyl-terminated tips was greater (reaching into the nN-range) than for the bare tips, but the same trends were observed. These results can be used where fresh water for oil recovery is in short supply. The addition of calcium to seawater should mitigate nanoparticle-rock adhesion and allow more efficient diffusion of nanoparticle tracers through a reservoir, which could in turn lead to better oil recovery and help ensure a stable supply of an essential global resource.

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9:00am **SP+SS+TF-WeM4 Nanoscopy of Muscovite Mica**, ***Sampath Gamage***, *M. Howard, A. Fali,* Georgia State University, *K. Bolotin,* Free University of Berlin, Germany, *Y. Abate*, Georgia State University

Muscovite type mica is an inorganic material most commonly used as in various electronic devices. Mica also satisfies many characteristics such as excellent thermal stability, high dielectric strength, larger dielectric constant, high Q factor, and high electrical resistivity needed for organic field effect transistors (OFETs) 1-2. We use the near-field imaging and nano-FTIR techniques to investigate nanoscale absorption properties of mica exfoliated on SiO2 substrate in the frequency range of 4 – 15 µm.

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11:00am **SP+SS+TF-WeM10 Investigation of Energy Transfer and Conversion at a Single Molecule with an STM**, ***Yousoo Kim***, RIKEN, Japan **INVITED**

Excitation of molecules by light irradiation triggers various important processes including luminescence, photovoltaic effect and photochemical reactions, and detailed understanding of the molecular excited states is crucial to improve organic opto-electronic devices. Absorption spectroscopy is a powerful tool to describe the molecular excitations and the combination with emission (luminescence) spectroscopy which deals with deexcitation processes is effective to investigate the excited states. Single-molecule luminescence detection has progressed rapidly and become indispensable in quantum physics, physical chemistry, and biophysics. However, despite considerable effort and progress, absorption spectroscopy is far behind; number of molecules are still necessary to obtain an absorption spectrum. A difficulty lies in the difference between the diffraction limit of excitation light and absorption cross section of a single molecule.

Here I introduce our recent progresses in measurement of luminescence and absorption spectra and in plasmon-induced reaction at a single-molecule level using a scanning tunnelling microscope equipped with optical detection/excitation facilities.

Thin Films Division
Room: 21 - Session TF+EM+MI-WeM

Thin Films for Microelectronics
Moderators: Erwin Kessels, Eindhoven University of Technology, The Netherlands, Adrie Mackus, Eindhoven University of Technology, The Netherlands

8:00am **TF+EM+MI-WeM1 Electrode Modulated Electric Field Capacitance Nonlinearity in ALD Al_2O_3 and HfO_2 Metal-Insulator-Metal Capacitors**, *D.Z. Austin, K. Holden,* ***John Conley, Jr.***, Oregon State University

Back-end-of-line metal-insulator-metal capacitors (MIMCAPs) require increasing capacitance density (C_{ox}) while maintaining low leakage current density (J_{leak}). In addition, analog and mixed signal (AMS) applications are particularly sensitive to nonlinearity of capacitance-voltage (CV), empirically characterized by the quadratic voltage coefficient of capacitance, α_{VCC}. Scaling of MIMCAPs for AMS applications is increasingly challenging as C_{ox}, J_{leak}, and α_{VCC} are all inversely proportional to dielectric thickness (d_{ox}). Despite its technological importance, the fundamental mechanisms responsible for α_{VCC} are not fully understood. It is well established that the "bulk" dielectric material has a dominant effect, where α_{VCC} increases with increasing dielectric constant and roughly as $1/d_{ox}^2$. However, the influence of the electrode interfaces is not currently understood. Of the few studies that have considered the impact of the electrodes on α_{VCC}, most have focused on interfacial layer oxides (ILOs).

In this work, metals with low enthalpy of oxide formation (ΔH_{ox}), are used to examine the influence of the top electrode interface, in the absence of a significant ILO, on the CV nonlinearity of TaN bottom electrode MIMCAPs with various thickness ALD HfO_2 and Al_2O_3. If non-linearity is purely a bulk effect then normalizing for d_{ox}, one would expect that the *electric field* coefficient of capacitance (α_{ECC}) should be independent of d_{ox}. Instead, we find that α_{ECC}*decreases* with decreasing d_{ox}, indicating either an ILO or the direct influence of the interface. A plot of capacitive equivalent thickness vs. optical thickness rules out an ILO. For Au, Ag, Pd, and Ni, α_{ECC} increases with increasing d_{ox}, saturating for thick oxides. It has been proposed that for positive α_{VCC} materials (C_{ox}(V) increases with voltage), electrostriction and Maxwell stress lead to a vertical compression of the oxide under applied fields that results in increased capacitance. We further propose that the oxide must expand horizontally to maintain volume. This expansion results in compressive stress in the oxide and tensile stress in the metal, concentrated near the interface. The electrode then serves to inhibit the lateral expansion of the dielectric, reducing overall α_{ECC}. Indeed α_{ECC} of 10 nm oxides was found to increase roughly linearly with increased oxide/metal % lattice mismatch. As thinner oxides are used to achieve higher C_{ox}, the metal electrodes exert influence over a greater % of the oxide thickness, increasing the electrode importance and its impact on nonlinearity.

New understanding of the impact of electrodes on α_{ECC} should aid in rapid optimization of low α_{ECC} MIMCAPs.

8:20am **TF+EM+MI-WeM2 Difference of the Hysteresis in Capacitance-voltage Characteristics of ALD-Al_2O_3 MIS Capacitors on Si and GaN Substrate**, ***Masaya Saito***, *T. Suwa, A. Teramoto,* Tohoku University, Japan, *T. Narita,* Toyota Central R&D Labs. Inc., Japan, *T. Kachi*, Nagoya University, Japan, *R. Kuroda, S. Sugawa*, Tohoku University, Japan

We evaluated the difference of hysteresis in capacitance-voltage(C-V) characteristics of ALD-Al_2O_3 MIS capacitors for different semiconductors. N-type Cz-Si and n-type GaN wafers which had the bandgap energies of 1.12 and around 3.4 eV, respectively, were used as semiconductor layers for MIS structures. N-type Si wafer was doped with P of 5×10^{14} cm^{-3}. The upper layer (2 µm) of n-type GaN wafer was doped with Si of 5×10^{16} cm^{-3} using a metal-organic vapor phase epitaxy. As the gate insulator layers of the MIS structures, the 10 nm-thick Al_2O_3 films were formed by the Atomic Layer Deposition (ALD) using $Al(CH_3)_3$ and H_2O at 75 ^oC, followed by the formation of aluminum as the gate electrodes. MIS capacitors were irradiated by the light of white LED to only before the voltage sweeps of C-V measurements at -3 V followed by the voltage sweeps of -3 à 3 V and 3 à -3 V without irradiation.

We observed that the clockwise hysteresis in the case of Si gradually decreased as increasing the time of measurement. On the contrary, the hysteresis in the case of GaN was also clockwise and drastically decreased at the second measurement. It is considered that this difference was caused by the difference of bandgap energies between Si and GaN. In the case of Si, some electrons (holes) injected from Si substrate were trapped to the state near the Al_2O_3/Si interface when the positive (negative) bias was applied to gate electrode. When applying the subsequent negative (positive) bias, most of these charges were released because the bandgap energy of Si is small. In the case of GaN, most of these charges trapped to the state near the Al_2O_3/GaN interface were not released within the measurement time because of the interface states far from the both band edges owing to the larger bandgap energy of GaN. Therefore, the different hystereses for their MIS capacitors were probably caused by the difference that the trapped charges to the state in the bandgap were released in the case of Si but not released in the case of GaN.

Acknowledgement:

This research is supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, through its "Program for research and development of next-generation semiconductor to realize energy-saving society. This work was carried out at fluctuation free facility of New Industry Creation Hatchery Center, Tohoku University.

8:40am **TF+EM+MI-WeM3 Monolithic Integration of C-type Erbium Oxide on GaN(0001) by Atomic Layer Deposition**, ***Pei-Yu Chen***, *A. Posadas,* The University of Texas at Austin, *S. Kwon, Q. Wang, M. Kim,* The University of Texas at Dallas, *A. Demkov, J.G. Ekerdt*, The University of Texas at Austin

Motivated by the need for faster device speed, the industry is considering compound semiconductors, such as gallium nitride (GaN) in the III-V family of materials, which have higher electron mobility than silicon. To passivate the nitride surfaces and enable GaN-based electronic devices, a high quality and thermally stable dielectric layer material is required. Recently, rare earth sesquioxides have received attention due to their electrical properties, thermal and chemical stability, and relatively high dielectric constant [1]. Using atomic layer deposition (ALD) with erbium tris(isopropylcyclopentadienyl) $[Er(^iPrCp)_3]$ and water, crystalline cubic (C-type) Er_2O_3 is successfully grown on GaN at 250 °C for the first time. ALD enables the conformal deposition of Er_2O_3 film on GaN and features a stable growth rate of 0.82 Å/cycle in this work. *In-situ* x-ray photoelectron spectroscopy is used to determine film composition and *in-situ* reflection high-energy electron diffraction is used to verify the surface order and the film crystallinity at various stages in the growth process. The cubic structure of Er_2O_3 is confirmed by a combination of both out-of-plane and in-plane X-ray diffraction (XRD). The orientation relationships between C-Er_2O_3 film and GaN substrate are C-Er_2O_3(222) ‖ GaN(0001), C-Er_2O_3(-440) ‖ GaN(11-20), and C-Er_2O_3(-211) ‖ GaN(1-100). The out-of-plane C-Er_2O_3(222) XRD peak shifts as a function of film thickness indicating a slight change in *d*-spacing caused by the presence of strain at the interface as shown in **Fig. 1(a)(b)**. The observed tensile strain results from the lattice mismatch between GaN and Er_2O_3. As the film thickness increases, the C-Er_2O_3 becomes more relaxed. In-plane XRD also displays peak shifts with opposite trend from the out-of-plane scan as expected. Scanning transmission electron microscopy (STEM) is used to examine the microstructure of C-Er_2O_3 and its interface with GaN and is in excellent agreement with the simulated atomic positions (**Fig. 1(c)**). An interfacial layer consisting of 1-3 atomic-layers is observed by STEM. The electron energy loss spectroscopy (EELS) profiles for Ga, Er, O, and N suggest partial oxidization of GaN at the interface. Overall, this work demonstrates a low temperature, all-chemical process for the growth of crystalline C-Er_2O_3 on GaN by ALD.

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9:00am **TF+EM+MI-WeM4 High-Performance p-Type Thin Film Transistors Using Atomic-Layer-Deposited SnO Films**, *S.H. Kim, I.-H. Baek, J.J. Pyeon,* Korea Institute of Science and Technology, Republic of Korea, *T.-M. Chung, J.H. Han,* Korea Research Institute of Chemical Technology, Republic of Korea, ***SeongKeun Kim***, Korea Institute of Science and Technology, Republic of Korea

Since the report of thin film transistors (TFTs) utilizing an amorphous oxide semiconductor of the In–Ga–Zn–O system exhibiting high electron mobility by the Hosono group, considerable efforts have been dedicated to implement these TFTs for emerging applications including flat-panel and flexible displays. Compared with the great progress and success regarding n-type oxide semiconductors, the current status of the development of p-type oxide semiconductors remains far behind.

SnO is a promising p-type oxide with relatively high hole mobility. The low formation energy of Sn vacancies and the more dispersed VBM resulting from hybridization of oxygen 2p and Sn 5s orbitals allow the p-type conduction of SnO. One critical challenge for high-performance SnO TFTs is the instability of the SnO phase. SnO is less stable than SnO_2, indicating the difficulty of growth of SnO.

Here, we demonstrate high-performance p-type TFTs with a single phase SnO channel layer grown by atomic layer deposition (ALD). The performance of the SnO TFTs relies on hole carriers and defects in SnO and near the back-channel surface of SnO as well as the quality of the gate dielectric/SnO interface. The growth of SnO films at a high temperature of 210 °C effectively suppresses the hole carrier concentration, leading to a high on-current/off-current (I_{on}/I_{off}) ratio. In addition, the SnO films grown at 210 °C achieve high field effect mobility (μ_{FE}) compared with the SnO films grown at lower temperatures because of their large grain size and lower impurity contents. However, the SnO films grown at 210 °C still contain defects and hole carriers, especially near the back-channel surface. The post-deposition process – back-channel surface passivation with ALD-grown Al_2O_3 followed by post-deposition annealing at 250 °C – considerably alleviates the defects and hole carriers, resulting in superior TFT performance (I_{on}/I_{off}: 2×10^6, subthreshold swing: 1.8 $Vdec^{-1}$, μ_{FE}: ~ 1 $cm^2V^{-1}s^{-1}$). We expect that the SnO ALD and subsequent process will provide a new opportunity for producing high-performance p-type oxide TFTs.

9:20am **TF+EM+MI-WeM5 Recent Progresses of Atomic Layer Deposited Oxide Semiconductors for Emerging Display Applications**, ***Jin-Seong Park***, *J. Sheng, J.H. Lee,* Hanyang University, Republic of Korea **INVITED**

Recently, transparent amorphous oxide semiconductors have been widely studied for potential use in flat-panel displays, such as active-matrix organic light emitting diodes or liquid crystal displays. Semiconductors based on indium and zinc oxide compounds have been intensively studied since the report on transparent flexible amorphous InGaZnO TFTs based on physical vapor deposition (Hosono group) in 2004.

Among various thin film deposition methods, Atomic Layer Deposition (ALD) has remarkably developed in semiconductor and nano-structure applications since early 1990. The unique properties, including controlling atomic-level-thickness, manipulating atomic-level-composition control, and depositing impurity-free films uniformly, may accelerate ALD related industries and applications in functional thin film markets. One of big and challenging markets, display industry, has been just started to look at the potential to adopt ALD based films in emerging display applications, such as transparent and flexible displays.

In this talk, I will introduce various oxide semiconductor materials such ZnO, SnOx, InOx, ZnSnO, InZnOx, deposited by ALD processes. InOx and SnOx semiconductors were prepared by using a liquid indium precursor ([1,1,1-trimethyl-N-(trimethylsilyl) silanaminato]-indium) and tin precursor (N, N'-tert-butyl-1,1-dimethylethylenediamine stannylene-tin), respectively. The former exhibited highly transparent conducting oxide film property and the latter did the p-type polarity under a water reactant. The Indium oxide films were grown by ALD using as the metal precursor and hydrogen peroxide (H_2O_2) as the oxidant. It is found that the electrical properties of the indium oxide layers strongly depend on the ALD growth temperature. At relatively low growth temperatures below 150 ºC, indium oxide behaves as a transparent semiconducting oxide. Secondly, amorphous indium zinc oxide thin films were deposited at different temperatures. The ALD process of IZO deposition was carried by repeated supercycles, including one cycle of indium oxide and one cycle of zinc oxide. The IZO growth rate deviates from the sum of the respective In_2O_3 and ZnO growth rates at ALD growth temperatures of 150, 175, and 200 °C. Thin film transistors were fabricated with the ALD-grown IZO thin films as the active layer. The amorphous IZO TFTs exhibited high mobility of 42.1 cm^2 V^{-1} s^{-1} and good positive bias temperature stress stability. Finally, flexible InOx and IZO TFTs on polymer substrates were investigated under various mechanical stress conditions, showing interesting degradations of TFTs. It will be discussed about the following issues.

11:00am **TF+EM+MI-WeM10 Silicon Nitride Thin Films Grown by Hollow Cathode Plasma-Enhanced ALD using a Novel Chlorosilane Precursor**, ***Xin Meng***, *H.S. Kim, A.T. Lucero, J.S. Lee, Y.-C. Byun, J. Kim,* University of Texas at Dallas, *B.K. Hwang, X. Zhou, M. Telgenhoff, J. Young*, Dow Chemical

Plasma-enhanced ALD (PEALD) has become an attractive method of depositing silicon nitride (SiN_x) due to its ability to grow high-quality films at low temperatures (≤400°C) for various applications [1]. The use of a chlorosilane precursor, is considered a suitable approach for high-volume manufacturing in the semiconductor industry. Chlorosilane precursors can be applicable to either PEALD SiN_x or thermal ALD SiN_x process. In this work, we have investigated the growth of SiN_x thin films using a novel chlorosilane precursor pentachlorodisilane (PCDS, HSi_2Cl_5)(synthesized by Dow Corning Corporation, vapor pressure ~10 mmHg at 20 °C) in comparison with hexachlorodisilane (HCDS, Si_2Cl_6). A home-made PEALD system equipped with a hollow cathode plasma source (Meaglow Ltd.) was used in this study.

We analyzed the growth per cycle (GPC) and refractive index (R.I.) as a function of the silicon precursor or plasma exposure time, deposition temperature and plasma power. We also investigated the wet etch rate (WER) in dilute hydrochloric acid as a function of the hydrogen content determined by Fourier Transform Infrared Spectrometry (FTIR), and film density determined by X-ray reflectivity (XRR). Using an N_2/NH_3 plasma, saturated growth behavior was demonstrated by PCDS and HCDS with a precursor exposure of ~3×10^5 L. GPC was nearly independent of both deposition temperature and RF power, within the investigated regime. Compared to HCDS, PCDS demonstrated approximately 20–30% higher GPC under the same process condition while maintaining comparable WER.

In addition, it was found that the films with higher hydrogen content had a general tendency to have a higher WER while the films with a higher density or higher R.I. tended to have a lower WER. The oxygen content of the bulk SiN_x films determined by ex-situ X-ray photoelectron spectroscopy (XPS) was approximately 3~5 at. % and didn't have a direct correlation with the WER. Furthermore, MIM capacitors (Al/SiN_x/degenerated Si) using PEALD SiN_x films grown with PCDS were fabricated. The capacitors exhibited excellent electrical properties, such as a low leakage current density of 10^{-9}–10^{-10} A/cm^2 at 3 MV/cm, and a high breakdown electric field ~13 MV/cm.

[1]. Meng, X.; Byun, Y.-C.; Kim, H.; Lee, J.; Lucero, A.; Cheng, L.; Kim, J., "Atomic Layer Deposition of Silicon Nitride Thin Films: A Review of Recent Progress, Challenges, and Outlooks," Materials, 9 (12), 1007 (2016)

11:20am **TF+EM+MI-WeM11 Removal of Charge Centers in Hafnia Films by Remote Plasma Nitruration**, ***Orlando Cortazar-Martínez***, *J.A. Torres-Ochoa, C.L. Gomez-Muñoz, A. De Luna-Bugallo, A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

We investigated the effect of soft nitridation on the electrical properties of hafnia-based MOS capacitors. Starting from a cleaned Si (100) wafer a 2 nm of HfO_2 thin film is grown by ALD using tetrakis (dimethylamido) hafnium(IV) and water type I as precursors. The growth was performed at a temperature of 250 °C with a 20 sccm flow of ultra-high purity nitrogen (UHP-N). Hafnium oxide soft nitridation was performed by a remote plasma (Litmas) using a power of 2500 W, a substrate temperature of 500 °C, the ultra-high purity nitrogen flow was set at 140 sccm and the working pressure is fixed at $3.5x10^{-2}$ Torr. A 300 nm titanium nitride (TiN) layer is deposited in-situ after nitration in a sputtering system, avoiding undesired contamination. Finally, MOS capacitors were defined using photolitography and etching process.

Capacitance vs voltage measurements characterization was carrying out at different frequencies (1 kHz to 1 MHz). MOS capacitors before nitriding shows a decreasing value in their accumulation capacitance when the frequency is increased. This behavior is attributed to the defects states located inside the oxide layer[1]. In contrast, MOS capacitors measured after nitriding barely shows dispersion in their accumulation regime as the frequency was varied. Also, it can be noted that the threshold voltage remains unchanged.

Films thickness and composition were characterized by ARXPS[2]. The initial thickness and composition were 20.7 Å and $HfO_{2.09}$. After nitridation the thickness changed to 19.8 Å with a composition of $HfO_{1.4}N_{0.48}$. XPS spectra show that the N 1s peak observed at 396.8 eV is associated with the N-Hf bond[3], showing a robust evidence of a substitutional incorporation of nitrogen species into the HfO_2 with a saturation process like the one reported in silicon oxide nitridation[4]. Results can be correlated with the soft nitridation process used during fabrication with the remote plasma in which the substitutional nitrogen to oxygen interchange in the HfO_xN_y films keeping the tetrahedral structure from the ALD hafnium as the same as the original but decreasing the amount of the defect states inside the oxide layer.

[1] A. Herrera-Gómez, A. Hegedus, and P.L. Meissner, Appl. Phys. Lett. 81, 1014 (2002).

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[3] K.-S. Park, K.-H. Baek, D.P. Kim, J.-C. Woo, L.-M. Do, K.-S. No, Appl. Surface Science 257, 1347, 2010.

[4] A. Herrera-Gómez, A. Hegedus, and P.L. Meissner, Appl. Phys. Lett. 81, 1014 (2002).

11:40am **TF+EM+MI-WeM12 Seam-free Bottom-up Filling of Trenches with HfO_2 using Low Temperature CVD**, ***Tushar Talukdar***, *W.B. Wang, E. Mohimi, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

Filling a deep structure is always a transport-reaction problem, one that is sensitive to the geometry of the structure. For example, with parallel sidewalls, a conformal process can mostly fill the structure, but as film growth diminishes the width of the remaining opening, the AR rises towards infinity; under that condition, no process can eliminate the "seam" in the center. We have shown, using both diffusion and molecular transport models, that a V-shape with an outwards taper (e.g., 3° or more) is needed for conformal coating to work [1]. The other alternative is to develop a process in which film growth is faster at the bottom of the structure: a *superconformal* process in which the growth rate increases progressively with depth. We previously demonstrated a superconformal process for MgO based on (i) a competition for surface adsorption sites between precursor and water co-reactant, and (ii) a large ratio in diffusivity between the high-mass precursor and low-mass water [2].

Here, we attempt to develop superconformal growth of HfO_2 from tetrakis dimethylamido hafnium (TDMA-Hf) based on our previous method for MgO. We choose the TDMA-Hf precursor because it affords excellent film quality in ALD, e.g., HfO_2 for gate dielectrics. However, the reaction kinetics of this precursor with water as the co-reactant differ strongly from the competitive adsorption model that is the basis for superconformal MgO deposition. Instead, the film growth rate is nearly independent of precursor flux and increases almost linearly with water flux.

For HfO_2, we therefore introduce a new approach in which water is injected in a forward-directed flux through a tube aligned with the trench axis. Water is transported ballistically to the trench bottom, where it partially reflects and creates a *virtual source at the trench bottom*. At the same time, the coating conditions are nearly conformal. The combination of a virtual source at the bottom and nearly conformal growth affords a V-shaped profile and excellent filling characteristics. We also introduce a simple kinetic model that predicts the fill profile based on the measured growth rate kinetics.

A limitation to this method is that rapid film growth also occurs on the exposed top surfaces. For a structure with parallel sidewalls, this tends to narrow the opening such that pinch-off can occur prior to complete fill. One solution is to use a structure with an outwards taper to the sidewalls. Another potential solution is to suppress growth at the trench opening using an inhibitor, which we will demonstrate.

1. W. B. Wang and J. R. Abelson, JAP **116**, 194508 (2014)

2. W. B. Wang *et al.*, JVST A **32**, 051512 (2014)

12:00pm **TF+EM+MI-WeM13 Low-κ Organosilicon Thin Films Deposited by iCVD for Electrical Insulation of Through Silicon Vias**, ***Mélanie Lagrange***, *C. Ratin, M. Van-Straaten, C. Ribière, T. Mourier, V. Jousseaume*, CEA-Leti, France

3D integration is considered as an attractive technological route to fabricate cost-effective, high-performance products with reduced size.[1] This technology is based on the use of Through Silicon Vias (TSV), which are vertical connections between electronic components. One of the key steps in TSV fabrication is their electrical insulation from the Si substrate. Depending on the TSV integration scheme used, the allowed thermal budget is limited. For instance, via-middle and via-last integrations need process temperatures lower than 400°C and 200°C, respectively. Moreover, considering the high Aspect Ratio (AR $\geq$ 10) required by the TSV-middle integration, a highly conformal deposition technique is needed.

Initiated Chemical Vapor Deposition, iCVD, is a low-energy and solvent-free polymer film fabrication process. It is able to deposit solid materials with high step coverage of deep blind features on low-temperature substrates. In the last decade, this versatile method has enabled the deposition of numerous types of polymers, including organosilicons (OSi)[2]. OSi polymers are low-κ materials having shown to be useful in a broad range of applications, including insulation layers in electronic devices.[3]

In this study, dielectric thin films were deposited from vinyl-based OSi precursors using iCVD. The impact of different process conditions on deposition rate, chemical composition and electrical properties of the films have been investigated. Thin films deposited at low temperature, typically < 60°C, can present low dielectric constants (< 3) without the need of any post-deposition treatment. However the films have to face 400°C thermal budget from BEOL process in via-middle integration, therefore a need for sample stabilization emerged. The impact of thermal or UV-assisted annealing on the films properties was investigated in order to understand the thermal stability of the materials and extrapolate their behavior during TSV fabrication and its integration in a full device fabrication flow (BEOL and Back side process). A study of the step coverage achieved by iCVD-deposited thin films in 10*100 µm TSV was performed. It shows that iCVD is promising to deposit materials with high conformity in high AR TSV. Finally, the integration of these OSi polymers in functional TSV, using a standard metallization process on 300 mm wafers, is presented.

The OSi films depositions were processed in a vertical flow reactor, under a collaboration with Kazuya Ichiki, Bruce Altemus and Jacques Faguet, at TEL Technology Center, America.

[1] Gambino et al., *Micro. Eng.* **135** (2015)

[2] Wang et al., *Adv. Mater.* (2017)

[3] Chen et al., *Annu. Rev. Chem. Biomol. Eng.***7** (2016)

Thin Films Division
Room: 20 - Session TF-WeM

Thin Film for Photovoltaics

Moderators: Mariadriana Creatore, Eindhoven University of Technology, The Netherlands, Virginia Wheeler, U.S. Naval Research Laboratory

8:00am **TF-WeM1 Stable Perovskite Solar Cells by 2D/3D Interface Engineering**, ***Mohammad Khaja Nazeeruddin***, *G. Grancini, C. Roldán-Carmona, I. Zimmermann, Y. Lee*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Metal halide perovskite solar cells (PSCs) have received global attention because of their excellent photovoltaic performance and ease of fabrication. However, much of the focus in perovskite solar cell advance has been on improved device efficiency through trial and error recipe modification. Despite the impressive photovoltaic performances, perovskite solar cells are poorly stable under operation, failing by far the requirements for a widespread commercial uptake.[1-3] Various technological approaches have been proposed to overcome the instability problem, which, while delivering appreciable improvements, are still far from a market-proof solution.[4-5] In this talk we demonstrate stable perovskite devices by engineering an ultra-stable 2D/3D $HOOC(CH_2)_2NH_3)_2PbI_4/CH_3NH_3PbI_3$ perovskite junction. The 2D/3D composite delivers an exceptional gradually organized multidimensional structure that yields 13% photovoltaic efficiency in a low cost, hole-conductor free architecture and 20% in standard mesoporous solar cells. To demonstrate the up-scale potential of this technology we fabricate 10x10 cm^2 solar modules by a fully printable, industrial-scale process delivering 11% efficient devices which are stable for >10,000 hours with zero efficiency loss measured under controlled standard conditions. This innovative architecture will likely enable the timely commercialization of perovskite solar cells.

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3. X. Li et al., Improved performance and stability of perovskite solar cells by crystal crosslinking with alkylphosphonic acid ω-ammonium chlorides. *Nat. Chem.* 7, 703–711 (2015).

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5. K. Domanski et al., Not All That Glitters Is Gold: Metal-Migration-Induced Degradation in Perovskite Solar Cells. *ACS Nano.* 10, 6306–6314 (2016).

8:40am **TF-WeM3 Single-step, Atmospheric CVD of Methylammonium Bismuth Iodide Perovskite Thin Films**, *X. Chen*, Washington University in St. Louis, *Y. Myung*, Sejong University, Republic of Korea, *A. Thind, Z.N. Gao, B. Yin, B. Sadtler, R. Mishra*, ***Parag Banerjee***, Washington University in St. Louis

Synthesis of methylammonium bismuth iodide $(CH_3NH_3)_3Bi_2I_9$) is achieved through a single step, atmospheric pressure, chemical vapor deposition (CVD) process. The precursors used are powders of bismuth iodide (BiI_3) and methylammonium iodide (CH_3NH_3I). These precursors are sublimated inside a tube furnace reactor with a well-controlled and predetermined temperature profile. The sublimated vapors are transported via Ar carrier gas to the cooler parts of the tube furnace, where simultaneous condensation and reaction between the two precursors leads to the formation of high quality $(CH_3NH_3)_3Bi_2I_9$ films on the wafer surface.

Structural and compositional information is obtained via grazing incidence X-ray diffraction (GI-XRD), SEM, TEM and XPS which confirm the $(CH_3NH_3)_3Bi_2I_9$ phase. Band-edge information is obtained via a combination of cyclic voltammetry and UV-vis spectroscopy. The band gap is revealed to be 1.9 eV. Temperature-dependent Hall measurements detect the recently observed [1] ferrielectric phase transition at ~150K via changes to the slope in the concentration vs. temperature and mobility vs. temperature curves. A room temperature electron concentration of 1.48 x 10^{19} cm^{-3} and mobility of 7.13 cm^2/V.sec is obtained for $(CH_3NH_3)_3Bi_2I_9$ films with good crystallinity.

Reference:

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9:00am **TF-WeM4 Atomic Layer Deposition of TiO_2 Charge Recombination Blocking Layer and SnO_2 Electron Transport Layer for Perovskite Solar Cells**, *Y. Kuang*, Eindhoven University of Technology, Netherlands, *V. Zardetto*, Solliance Solar Research, Netherlands, *R.J. van Gils*, Eindhoven University of Technology, Netherlands, *F. di Giacomo*, Solliance Solar Research, Netherlands, *G. Lucarelli*, University of Rome Tor Vergata, Italy, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands, *T.M. Brown*, University of Rome Tor Vergata, Italy, ***Mariadriana Creatore***, Eindhoven University of Technology, Netherlands

Within the class of emerging photovoltaic technologies, 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 atomic layer deposition (ALD) offers to perovskite solar cells [1] by highlighting the following merits: control on charge carrier transport and recombination processes at complex interfaces [2,3] and compatibility with low-temperature processing [3]. Specifically, two case studies will be presented:

· Plasma-assisted ALD amorphous TiO_2 (cycles consisting of $Ti(Cp^{Me})(NMe_2)_3$ and O_2 plasma exposure steps) has been adopted in $MeNH_3PbI_3$ perovskite solar cells in a mesoscopic configuration [2], with the purpose of suppressing charge recombination processes at the ITO/mesoscopic scaffold/perovskite interface. The superior performance of 10 nm thick ALD TiO_2 layers (i.e. up to 16% cell efficiency under 1000/m^2 illumination and 24% under indoor illumination) with respect to conventionally adopted spray pyrolysis TiO_2, is explained by a lower reverse dark current measured for ALD TiO_2. This result points out the superior blocking character of the ALD TiO_2 layer toward electron-hole recombination, which is also confirmed by the evaluation of the electron lifetime from open circuit voltage decay analysis. Since ALD TiO_2 is carried out at temperatures below 150°C, flexible perovskite solar cells built on PET/iTO substrates are also tested, exhibiting a conversion efficiency of 10.8% under indoor illumination, comparable to the one of flexible dye-sensitized solar cells and exceeding the one of flexible a-Si:H solar cells.

· Ultra-thin (15 nm) plasma-assisted ALD amorphous SnO_2 (cycles consisting of $Sn(NMe_2)_4$ and O_2 plasma exposure steps) is adopted as electron transport layer in a $Cs_x(MA_yFA_{1-y})_{1-x}Pb(I_z,Br_{1-z})_3$ perovskite solar cell in an n-i-p thin film configuration. The solar cell efficiency reaches the value of 15.9±0.5%, while the same solar cell configuration with an electron-beam deposited TiO_2 electron transport layer reaches an efficiency of just 10 ±0.5%. UPS analysis shows that the higher efficiency achieved by SnO_2 (with respect to TiO_2) is due to a better energy level alignment between the SnO_2 and perovskite conduction bands, promoting electron transport. Hole transport, instead, is efficiently blocked because of the misalignment between the SnO_2 and perovskite valence bands.

References

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[2] F. Di Giacomo et al., Nano Energy 30, 460 (2016)

[3] V. Zardetto et al., Solar Energy, accepted (2017)

9:20am **TF-WeM5 The Reaction Between Pyridine and $CH_3NH_3PbI_3$ Surface-Confined Reaction or Bulk Transformation?**, ***XiaoZhou Yu***, *H.M. Yan, Q. Peng*, University of Alabama

Abstract

The Methyl amine lead iodide perovskite ($CH_3NH_3PbI_3$) shows great potential in solar cells, light-emitting diodes, lasers, and chemical sensors. Base on the surface chemical properties of $CH_3NH_3PbI_3$, many chemicals with Lewis base group, for instance: pyridine, tetra-ethyl ammonium, were used to enhance the photovoltaic, optoelectronics performance and the stability in ambient environment. However, people found contradict results that Pyridine molecules not only passivate the surface Pb^{2+} sites of $CH_3NH_3PbI_3$, but also to bleach and recrystallize $CH_3NH_3PbI_3$. Surface passivation demands the confinement of the reaction at the surface region but recrystallizing and bleaching require the transformation of bulk $CH_3NH_3PbI_3$. The underlying mechanism for these seemly contradicting results are not well-understood. Our results show, at 25 ºC, partial pressure of pyridine vapor is a determining factor for its reaction behaviors with $CH_3NH_3PbI_3$: one can modify just the surface of $CH_3NH_3PbI_3$ by using pyridine vapor of the pressure less than 1.15 torr, but can transform the whole bulk $CH_3NH_3PbI_3$ film with a pyridine vapor of 1.3 torr or higher. The results indicate, for the first time, that a small change of free energy of pyridine vapor (~ 0.3 kJ/mol) can cause the transition from surface-confined reaction to bulk transformation. It is interesting that in all pressure ranges, pyridinium ions is the main product from the reaction between pyridine and $CH_3NH_3PbI_3$. The bulk transformation is probably due to the formation of a liquid-like film, which increases the mobility of species to catalyze the reaction between pyridine and $CH_3NH_3PbI_3$. These findings provide a guidance for designing experiments in applying pyridine and probably other amines to functionalize and transform $CH_3NH_3PbI_3$ and other hybrid halide perovskites.

9:40am **TF-WeM6 GaN-stabilized Ta_3N_5 Thin Film as a Photoanode for Solar Water Splitting**, ***Taro Yamada***, *Y. Sasaki*, The University of Tokyo, Japan, *S. Suzuki*, Shinshu University, Japan, *M. Zhong*, The University of Tokyo, Japan, *K. Teshima*, Shinshu University, Japan, *K. Domen*, The University of Tokyo, Japan

Tritantalum pentanitride (Ta_3N_5), a visible-light absorbing material (<600 nm), was formed into a thin layer and tested as a photoelectrode in electrolytic solution under simulated solar light. By the aid of cobalt phosphate catalyst (CoPi), the electrode surface evolved O_2 at a substantial efficiency for photon energy conversion. By inserting a GaN layer between the catalyst and Ta_3N_5, the electrode exhibited an improved stability and durability for O_2 evolution in aqueous electrolytic solution.

The Ta_3N_5 film was prepared by high-temperature (1000-1300 K) nitridation of sputtered Ta film on Ta metallic substrate in NH_3 flow at the atmospheric pressure. Ta sputtering was performed in a RF magnetron setup with a Ta metal target at 4 Pa of purified Ar introduction pressure. The gas impurities were minimized and a trace amount of O_2 was introduced for sputtering. The formed Ta film is amorphous with a thickness approximately 500nm. After nitridation, the formed Ta_3N_5 is a transparent, orange-colored film with a visible light absorption cutoff at xxx nm. The CoPi catalyst was deposited by simulated solar irradiation in $Co(NO_3)_3$ solution in neutral phosphate buffer.

The O_2 evolution performance was examined in pH 13 K_3PO_4 buffer under potentiostatic control with a Pt counter electrode and a Ag/AgCl reference electrode. At 1.23 V vs RHE of the anodic potential, The photocurrent by a solar simulator at AM1.5G (1 kWm^{-2}) reached 7 $mAcm^{-2}$ or higher, however rapidly decay in 1 hour. This was due to Ta_3N_5 oxidation, and we introduced a GaN overlayer (thickness ~ 50 nm) by NH_3-nitridation of evaporated Ga_2O_3 layer (electron-beam heating, largely metallized). The same photoelectrochemical test exhibited a photocurrent higher than 8 $mAcm^{-2}$, lasting for more than 10 hours, with slow deactivation afterwards. Microscopic observation of the GaN layer showed fine grains (<50 nm in diameter) of GaN, blocking Ta_3N_5 oxidation. The faradaic O_2 evolution was confirmed by anther setup.

The semiconductive properties of Ta_3N_5 and the GaN/Ta_3N_5 junction are currently investigated. Both Ta_3N_5 and GaN in the present case are polycrystalline and contain influential amounts of impurities, reflecting in the resistivity and other transportation properties.

The photoelectrochemical performance of the present GaN/Ta_3N_5 electrode matches nearly 5 % of solar-to-H_2 energetic conversion as a free-run water photo-splitting device by assembling a with H_2 evolving photocathode. By improving the quality of the layers of Ta_3N_5 and the GaN in terms of crystallinity and purity, we can gain a good control for the performance of the photoelectrodes towards efficient solar energy recovery.

11:20am **TF-WeM11 A Viable Magnetron Sputtering Process for Thin Film CdTe Solar Cells**, ***John Walls***, *F. Bittau, R.C. Greenhalgh, A. Abbas, S. Yilmaz*, Loughborough University, UK

The exceptional uniformity of deposition provides magnetron sputtering with potentially important advantages for the production of thin film CdTe solar cells. For example, the thickness of the absorber layer could be reduced to ~1um saving on material cost. The uniformity is also essential for glazing applications such as power producing semi-transparent windows. Efforts to develop a viable process for the deposition of thin film CdTe solar cells by magnetron sputtering have been hampered for many years by the formation of surface blistering following the cadmium chloride activation process. Delamination of the films at the cadmium sulphide junction is often observed and catastrophic void formation within the CdTe layer and at the junction has also been reported. As a result, the conversion efficiency of sputtered devices has not matched that obtained using lower energy deposition techniques such as Close Space Sublimation or Vapour Transport Deposition. We have discovered that blistering is caused by argon trapped in the CdTe layer during the sputtering process. High Resolution Transmission Electron Microscopy reveals that argon gas bubbles are formed by diffusion during the high temperature device activation process. The bubbles then coalesce to cause surface blistering. Here we report on the development of a viable sputtering process by replacing argon with xenon as the magnetron working gas. Using xenon avoids gas bubble and blister formation. The microstructural integrity of the devices is retained resulting in increased performance of sputtered thin film CdTe photovoltaic devices.

11:40am **TF-WeM12 Hybrid Single Layer Organic Solar Cell Based on Polyvinyl Alcohol and Zinc Oxide Nanoparticles**, ***Monas Shahzad***, Forman Christian College (A Chartered University), Pakistan

Organic solar cell technology is very low cost, reliable and efficient technology. In this work, we have studied the performance of single layer hybrid organic solar cell, which is based on polyvinyl alcohol (PVA) doped with Camellia sinensis (Black Tea) solution and Zinc Oxide (ZnO) as plasmonics nanoparticles to scatter more light into active layer of solar cell. The broad absorption spectra of the composite material (PVA and tea solution) with various concentrations ranged from UV to visible region. Its energy gap was measured which allowed trapping a large portion of the incident solar light. The band gap is reduced upon the addition of Camellia sinensis (Black Tea) because the addition of Camellia sinensis (Black Tea) caused PVA to get more ordered structure. Characterization of ZnO nanoparticles using XRD and SEM confirmed the hexagonal wurtzite structure and spherical surface morphology of nanoparticles. Six solar cells were fabricated based on various concentrations of PVA doped with Camellia sinensis (Black Tea) solution using silver paste/graphite as counter electrodes, with and without ZnO nanoparticles thin film. The current-voltage (IV) characteristics curves of the fabricated organic solar cells were measured. The IV curves were studied of all soar cells that gave the following efficiencies 0.0216%, 0.0364%, 0.34%, 0.42%, 0.564 and 0.729%. The maximum energy conversion efficiency was calculated to be 0.7%, for an organic solar cell having high concentration of camellia sinensis, with ZnO nanoparticles thin film and silver paste as a counter electrode.

Key Words: Hybrid organic cell, polyvinyl alcohol, Camellia Sinensis, ZnO nanoparticles.

12:00pm **TF-WeM13 Phase Stability and Cation Site Distribution during Thermal Annealing of CZTS Nanoparticle-Coatings**, ***Stephen Exarhos***, *E. Palmes, R. Xu, L. Mangolini*, University of California, Riverside

Cu_2ZnSnS_4 (CZTS), a potential low-cost, earth-abundant absorber material, has been under intense investigation for prospective use in thin film photovoltaic (PV) devices. Its high optical absorption coefficient and variable band gap also have potential applications in other areas including photocatalysis, thermoelectrics, and energy storage. Theoretically predicted physical properties, however, have not been realized to date owing to the lack of control over chemical and microstructural heterogeneity and grain size and grain boundary chemistry. Using a modified aerosol spray pyrolysis technique, we have grown phase-pure 25 nm CZTS nanoparticles having no organic ligand contaminant. This is desirable in that grain boundary chemistry is known to degrade both optical and electrical response. Many applications demand that these nanoparticles be consolidated into relatively thick, large grain size films by means of a high temperature annealing treatment that drives impurities to interfaces thereby degrading properties. For PV applications, large grains are required to significantly reduce exciton recombination at grain boundaries. While the particles produced here do not sinter uniformly into polycrystalline thin films, we have shown that introducing a thin amorphous oxide to the surface of the particles does indeed promote uniform grain growth to create thin films with the optimal morphology for absorber layers in PV devices. The improvement is attributed to an increased retention of volatile SnS, a byproduct of CZTS decomposition, which occurs at high temperature. We have also controlled grain growth by incorporating Na_2S into the film prior to annealing by means of a facile dipping technique – sodium is known to enhance grain growth in this material, though its incorporation is generally uncontrolled. Additionally, we present data from *in situ* Raman spectroscopy measurements designed to simulate the standard CZTS thin film annealing process. Using this approach, we have characterized the time/temperature effects on the vibrational spectrum of annealed CZTS films at high temperature in static variable atmospheres of sulfur vapor with and without a thin surface oxide interfacial coating. This technique is also used to monitor the cation site exchange process (copper and zinc) in the lattice that appears to be dependent on the rate of cooling following high temperature annealing.

Plasma Science and Technology Division
Room: 22 - Session PS+SS+TF-WeA

Plasma Deposition
Moderators: Jeffrey Shearer, IBM Research Division, Albany, NY, Thorsten Lill, Lam Research Corporation

2:20pm **PS+SS+TF-WeA1 Correlation Between Ion Energies in CCRF Discharges and Film Characteristics of Titanium Oxides Fabricated via Plasma Enhanced Atomic Layer Deposition**, ***Shinya Iwashita***, *T. Moriya, T. Kikuchi, N. Noro, T. Hasegawa,* Tokyo Electron Limited, Japan, *A. Uedono*, University of Tsukuba, Japan

A plasma enhanced atomic layer deposition (PEALD) process for synthesizing titanium oxide (TiO_2) thin films, which allows to modify the film properties by tuning the ion energies of capacitively coupled radio frequency (CCRF) discharges, was performed. TiO_2 films were deposited via the oxidation of titanium tetrachloride using a typical CCRF discharge in argon/oxygen mixtures, and the energy distributions of ions hitting an electrode (wafer surface) during the deposition were adjusted by controlling the impedance of the electrode [1]. The wet etching rate of TiO_2 films shows a clear correlation with the mean ion energy; a higher mean ion energy realizes a higher value of the wet etching rate. The film characteristics are varied due to the balance between the oxidation and ion bombardment during the PEALD process. In a high mean energy condition, fine pores are formed in films due to the bombardment of high energetic ions, which was confirmed by the physical analyses such as positron annihilation spectroscopy. One can conclude that the energy control of ions in CCRF discharges is interpreted as tuning the oxidation and ion bombardment, both of which determine the film characteristics.

[1] K. Denpoh et al Proc.38th Int. Symp. Dry Process, 183 (2016).

2:40pm **PS+SS+TF-WeA2 Functionalized Titanium-Nitride Surfaces Formed by Femtosecond-Laser Processing**, ***David Ruzic***, *S. Hammouti, B.J. Holybee,* University of Illinois at Urbana-Champaign, *B.E. Jurczyk*, Starfire Industries

Thin films surfaces are playing an increasing role in the application of smart materials. This covers the improvement of surface properties like hardness, corrosion resistance, thermal, magnetic properties and so on depending on the application field. Many methods evolved for the preparation of thin films and coatings and among them the laser surface treatment. Since a decade, femtosecond laser micro-machining has been successfully introduced in industry for optic, surface wetting, biological or catalytic applications. The high precision achieved with femtosecond lasers for drilling or texturing purposes originates primarily from the limited heat affected zone which is greatly reduced compared to that of laser systems with longer pulse duration such as nano or picosecond. Moreover, ultrafast laser surface processing provides a simple way of nanostructuring and surface functionalization towards optical, mechanical or chemical properties. Indeed, irradiation of surfaces with short laser pulses of high intensity in a reactive atmosphere can result in a direct coating formation if the laser parameters are properly adjusted.

In this study, femtosecond laser processing of titanium surface in nitrogen (laser nitriding) has been investigated due to technological importance of nitrogen in metals and alloys for fusion applications. A two-step process consisting firstly to a femtosecond laser texturing of titanium surface under argon and then under nitrogen, both at atmospheric pressure, has been used. The laser treatment under argon has been proved to be efficient to remove most of the oxide layer which otherwise reduce the formation of titanium nitride. Several laser parameters for both laser treatments have been tested to obtain the best combination for the generation of titanium nitride. Beside chemical modifications of titanium surface, the formation of self-organized micro/nanostructures usually observed after irradiation in an ultrashort regime which result in topographic modifications are also of the high interest for wetting properties. Due to nonthermal effects involved in the ultrashort femtosecond processes the normal nitrogen diffusion process, as in the case of nanosecond laser nitriding. The titanium nitride layer produced by the femtosecond pulses most probably corresponds to nitride fall out from the recondensing plasma formed after the laser pulse above the irradiated surface, containing titanium and nitrogen ions and atoms.

3:00pm **PS+SS+TF-WeA3 Controlling the Thin Film Properties of Silica Synthesised by Atmospheric Pressure-Plasma Enhanced CVD**, ***Fiona Elam***, *A.S. Meshkova,* FOM institute DIFFER, Netherlands, *B.C.A.M. van der Velden-Schuermans, S.A. Starostin,* FUJIFILM Manufacturing Europe B.V., *M.C.M. van de Sanden, H.W. de Vries*, FOM Institute 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.

Industrially and commercially relevant roll-to-roll AP-PECVD has been used to deposit silica thin films onto flexible polyethylene 2,6 naphthalate substrates by means of a glow-like dielectric barrier discharge using an air-like gas mixture. Single and bilayer films were evaluated in terms of their encapsulation performance, their chemical structure, the nature of their porosity and their morphology, with respect to the deposition conditions.

It was found that by increasing the plasma residence time and reducing the precursor (tetraethyl orthosilicate (TEOS)) flux, the specific input energy per TEOS molecule could be enhanced, which in turn resulted in the deposition of films with a lower intrinsic porosity. However, an input E/TEOS greater than 9 keV was found to limit the encapsulating performance of single layer barrier films, due to the creation of ~1 μm diameter pinhole defects. This restriction was overcome by the deposition of a semi-porous silica ‘buffer’ layer between the polymer substrate and silica ‘barrier’ layer. The buffer layer within the bilayer architecture acted as a protective coating to prevent excessive plasma-surface interactions that can occur during the harsh processing conditions necessary to generate dense barrier films. As a result, the bilayer films demonstrated exceptionally low effective water vapour transmission rates in the region of 2×10^{-4} g m^{-2} day^{-1}, values so far unprecedented for silica encapsulation barriers deposited at atmospheric pressure on flexible polymer substrates. Finally, regarding process throughput for the manufacture of silica thin films capable of protecting flexible solar cells, a 140% increase in processing speed was achieved for bilayer films with respect to 100 nm single layer barriers of equivalent encapsulation performance.

3:20pm **PS+SS+TF-WeA4 Plasma Information Based Virtual Metrology for Nitride Thickness in Multi-Layer Plasma-Enhanced Chemical Vapor Deposition**, ***Hyun-Joon Roh****, *S. Ryu, Y. Jang, N.-K. Kim, Y. Jin, G.-H. Kim,* Seoul National University, Republic of Korea

Advanced process control (APC) is required to assure the quality and throughput of plasma-assisted process. For this purpose, the process result of all wafers should be measured. However, direct metrology can measure only 1~3 wafers within a lot due to slow time response. To improve the speed of metrology, virtual metrology (VM) is alternatively adopted to support APC. VM can predict the process results close to real-time, since it predicts the process results by using statistical methods based on equipment engineering systems (EES) and sensor variables. However, previously developed VMs face the degradation of prediction accuracy as the chamber wall condition drifts in long-term process. This robustness issue is originated from that the used input variables of VM cannot recognize the drift of chamber wall condition. To enhance the robustness even in a process with severe drift of chamber wall condition, we propose PI-VM that uses plasma information (PI) as input variables of statistical methods. Experimental application of PI-VM is performed to predict the nitride film thickness in multi-layer plasma-enhanced chemical vapor deposition (PECVD) for 3D NAND fabrication which has a severe drift of chamber wall condition. PI variables are composed of the chamber wall condition (PI_{Wall}) and property of bulk plasma (PI_{Plasma}) considering plasma-surface interaction. Each PI variable is decomposed from N_2 emissions in optical emission spectroscopy (OES) by analyzing them based on optics and plasma physics. Then, PI-VM is constructed by implementing PI and EES variables to partial least squares regression (PLSR). Compared to conventional VM, PI-VM improves the robustness more than twice in long-term variation by implementing PI_{Wall} on PLSR. Also, evaluation of the ranking of variables on PI-VM shows that the robustness is improved by decomposing PI_{Wall} and PI_{Plasma} from OES based on optics and plasma physics. This result showed that an effective VM model for plasma-assisted process can be constructed by making phenomenological-based, statistical-tuned VM model that recognizes the

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* **Coburn & Winters Student Award Finalist**

drift of chamber wall condition and property of plasma separately, based on optics and plasma physics.

4:20pm **PS+SS+TF-WeA7 Sidewall Effects in the Modulation of Deposition Rate Profiles of a Capacitively Coupled Plasma Reactor**, ***Hojun Kim***, Samsung Electronics Co. Ltd., Republic of Korea **INVITED**

In the recent semiconductor industry, plasma-enhanced chemical vapor deposition (PECVD) using capacitively coupled plasma (CCP) is often chosen to coat a thin uniform film with a high production efficiency. Since inside of a CCP reactor, a discharge volume is radially surrounded by a sidewall, the modulation of the sidewall surface can contribute to controlling distributions of plasma variables. In this study, we thus investigate the sidewall effects by varying the electrical condition of the sidewall from grounded to dielectric. In the cases with the dielectric sidewalls, a cylindrical insulator with a grounded exterior surface is adopted, and then its radial thickness is additionally varied from 2 mm to 45 mm. As an example for the particular case of PECVD, SiH_4/He discharge during deposition of an amorphous hydrogenated silicon (a-Si:H) film is simulated using a two-dimensional fluid model. The cases with the thick insulators have more uniform distributions of the plasma variables than the case with the grounded sidewall or the case with the thin insulator. An increase of the showerhead radius also improves a distribution uniformity because non-uniformity sources of the plasma distribution are set further away from the electrode edge.

5:20pm **PS+SS+TF-WeA10 Linear Magnetron Magnetic Field Optimization for HiPIMS Industrialization**, ***Ian Haehnlein****, J. McLain, B. Wu, I. Schelkanov,* University of Illinois at Urbana-Champaign, *B.E. Jurczyk,* Starfire Industries, *D.N. Ruzic,* University of Illinois at Urbana-Champaign

High power impulse magnetron sputtering (HiPIMS) has time and time again been proven to provide superior film qualities over direct current magnetron sputtering (DCMS) due to increased ion fraction at the substrate. Throughput however is decreased due to the increase in return of sputtered target material [1]. Work done previously at the Center for Plasma Material Interactions (CPMI) at the University of Illinois Urbana-Champaign by Raman et al. introduced the Tripack for a 4” circular magnetron. This magnet configuration features three distinct racetracks with magnet fields tuned to allow electron escape from the magnetron magnetic field during high power pulses [2]. This was used in a linear magnetron to increase the deposition rate of HiPIMS. McLain et al. has shown using a 5x11” linear magnetron a decrease in the confinement parameter of during DC from 6 using a conventional magnet pack to 3 using the Tripack designed for a linear magnetron. Deposition rates for HiPIMS using Tripack increased deposition rates over the conventional pack by ~25% for copper. In the 1.5kW case the HiPIMS discharge using the Tripack was ~1nm/s greater than that of DCMS using the conventional magnet pack. Triple Langmuir probe measurements at the substrate verified an increase of several orders of magnitude over the conventional pack, supporting the theory that a decreased electron confinement would increase deposition rate, further supported by an increase in ion-neutral fraction at the substrate from ~12% to 35% measured at the substrate surface. Due to non-uniform redeposition on the target surface the, preferentially towards the center, that the outer racetracks eroded faster and subsequentially had stronger magnetic fields at the target surface. The inner racetrack fails to ignite, causing uneven erosion of the target. It is proposed that by creating a serpentine magnet pack which utilizes the reduced confinement parameter seen in the Tripack with only one racetrack as to confine electrons evenly over the target surface. Deposition rates, electron densities, and ion-neutral fractions for the improved magnet pack are provided in this work. These values are presented with and without the use of a positive polarity modified waveform controlling ion deposition energy independent of the substrate for a better controlled deposition on insulators or temperature sensitive materials.

5:40pm **PS+SS+TF-WeA11 Investigating the Effect of the Substrate at Short Deposition Times for Plasma Polymerised Films**, ***Karyn Jarvis****, N.P. Reynolds,* Swinburne University of Technology, Australia*, L.D. Hyde,* Melbourne Centre for Nanofabrication, Australia*, S.L. McArthur*, Swinburne University of Technology and CSIRO, Australia

Plasma polymerization modifies surfaces via the deposition of a thin film containing specific functional groups. The organic monomer is introduced into the chamber as a vapour, fragmented via radio frequency and deposited onto all surfaces in contact with the plasma. Plasma polymerization is typically referred to as ‘substrate independent’, but is this true for short deposition times? Does the substrate conductivity, chemistry or roughness influence the early stage deposition of plasma polymer films? In this study, plasma polymerized acrylic acid (ppAAc) and allylamine (ppAA) were deposited onto glass, silicon, gold and fluorinated ethylene propylene (FEP) substrates for deposition times of 10 to 600 seconds. Surface chemistry was investigated using X-ray photoelectron spectroscopy while surface roughness was determined using atomic force microscopy. Film thickness measurements were made by spectroscopic ellipsometry and wettability determined via contact angle measurements. Different contact angle behaviours were observed between the deposition of ppAAc and ppAA films, while different substrates resulted in different contact angle trends for ppAA. For ppAAc films deposited for 10 seconds, all substrates became more hydrophobic (80-100°) and was proposed to be due to ‘island’ film formation, which would increase surface roughness and therefore increase hydrophobicity. For ppAA films deposited for 10 seconds, the contact angles of all substrates except FEP increase/decrease to 60-70° and do not significantly change as deposition time increase. Such behaviour suggests the ppAA films may deposit continuously from the start, unlike ppAAc which may initially form film islands. Unlike all the other substrates, FEP showed the same behaviour for both monomers, suggesting initial island formation for both monomers. These initial results suggest that for short deposition times, the underlying substrate does have some influence on the formation of plasma polymerized films.

Advanced Surface Engineering Division
Room: 11 - Session SE+2D+NS+SS+TF-WeA

Nanostructured Thin Films and Coatings
Moderators: Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

2:20pm **SE+2D+NS+SS+TF-WeA1 Plasma Process Development and Optimized Synthesis of TiB_2 Coatings from DC Magnetron Sputtering, High Power Impulse Magnetron Sputtering, and DC Vacuum Arc**, ***Johanna Rosen***, Linköping University, Sweden **INVITED**

The use of high power impulse magnetron sputtering (HiPIMS) or cathodic arc for the synthesis of TiB_2 coatings will drastically increase the amount of ionized species impinging on the substrate compared to regular DC magnetron sputtering. In particular for HiPIMS, it is possible to control the flux of ionized species by varying the pulse frequency, which allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant.

We show that the additional energy supplied during film growth in the HiPIMS process, compared to regular DC sputtering, results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to ≥ 42 GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Furthermore, we show that the energy supplied to the film surface is influenced by when the bias is applied relative to the HiPIMS pulse. Based on charge-state-resolved plasma analysis it is found that by applying the bias in synchronous with the HiPIMS pulse, a higher fraction of B^+ ions will constitute the total flux of bombarding ions. This results in a lower residual stress compared to coatings deposited under bombardment of mainly Ar^+ ions.

Finally, we also present results from TiB2 synthesis based on DC vacuum arc, and a route for attaining a stable, reproducible, and close to fully ionized plasma flux of Ti and B by removal of the external magnetic field. Plasma analysis shows increased ion charge states as well as ion energies compared to HiPIMS. Furthermore, while regular DC magnetron sputtering and HiPIMS typically give a B to Ti ratio above 2, the arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

3:00pm **SE+2D+NS+SS+TF-WeA3 Multi-technique Approach for Studying Co-sputtered M-Si-O Thin Films**, ***Lirong Sun***, General Dynamics Information Technology, *N.R. Murphy,* Air Force Research Laboratory, *J.T. Grant,* Azimuth Corporation

In this work, the M-Si-O thin films (M: Al and Ta) were prepared through reactive pulsed DC magnetron co-sputtering of M and Si targets in an O_2/Ar mixture. The M fraction [M/(M+Si)] of different chemical compositions ($M_xSi_yO_z$), as determined through X-ray photoelectron spectroscopy (XPS), was varied between 0 and 100% by changing sputtering power applied to the M targets. The film thickness, refractive index (n) and extinction coefficient (k) were determined by *in situ* spectroscopic ellipsometry (*i*SE). Concurrent with ellipsometry measurements, the *in situ* stress evolution of the films, as correlated to the M fraction, was investigated using a multi-beam optical sensor (MOS) system. The MOS system was used to measure both intrinsic stress resulting from the deposition process as well as thermal stress evolved during heating/cooling process. Data obtained through stress monitoring during heating and cooling was used to calculate the coefficient of thermal expansion (CTE). The density and crystallinity of the films were measured by X-ray diffraction and X-ray reflectivity, respectively. Transmission and reflectance of the films were carried out by UV-Vis-NIR spectroscopy. Finally, this study derives a process-property-microstructure relationship correlating the optical constants, CTE, intrinsic stress, and M fraction.

3:20pm **SE+2D+NS+SS+TF-WeA4 Ultra-high Vacuum Magnetron Sputter-deposition of Zr/Al_2O_3(0001): Effect of Substrate Temperature on Zr Thin Film Microstructure and Thermal Stability of Zr-Al_2O_3 Interfaces**, *K. Tanaka, J. Fankhauser,* University of California at Los Angeles, *M. Sato,* Nagoya University, Japan, *D. Yu, A. Aleman, A. Ebnonnasir, C. Li,* University of California at Los Angeles, *M. Kobashi,* Nagoya University, Japan, *M.S. Goorsky,* ***Suneel Kodambaka***, University of California at Los Angeles

Zr thin films are grown on Al_2O_3(0001) substrates in an ultra-high vacuum deposition system via dc magnetron sputtering of Zr target in Ar atmosphere at temperatures T_s between 600 ºC and 900 ºC. The as-deposited layer surface structure and composition are determined *in situ* using low-energy electron diffraction and Auger electron spectroscopy, respectively. Bulk crystallinity and microstructures of the samples are determined using x-ray diffraction, cross-sectional transmission electron microscopy along with energy dispersive spectroscopy. At $600\ ºC \leq T_s < 750\ ºC$, we obtain fully dense, hexagonal close-packed structured Zr(0001) thin films with smooth surfaces. At $T_s \geq 750\ ºC$, the Zr layers are porous, exhibit {0001} texture, and with rough surfaces. Energy dispersive x-ray spectra obtained from the Zr/Al_2O_3 interfaces reveal the formation of Zr-Al intermetallic compounds, whose thickness increases exponentially with increasing T_s. We attribute the formation of this interfacial layers to fast diffusion of Zr and reaction with the Al_2O_3 substrate.}

4:20pm **SE+2D+NS+SS+TF-WeA7 Structural, Mechanical, Optical Properties of Molybdenum Incorporated β-Ga_2O_3 Nanocrystalline Films for Extreme Environment Applications**, ***Anil Battu****, S. Manandhar, C.V. Ramana*, University of Texas at El Paso

Recently, gallium oxide (Ga_2O_3) has been attracting the attention of researchers as a suitable material for different extreme environment applications, such as high power electronics, optoelectronics, ultraviolet transparent conductive oxides, and gas sensors. β-Ga_2O_3 exhibits the highest thermal and chemical stability, which makes the material interesting for high-temperature oxygen sensor applications. However, the response time and sensitivity must be improved. In recent years, doping Ga_2O_3 with the suitable metal ions has been considered to alter the electronic properties and to improve sensor performance. In this context, the present work was performed on using a mechanically resilient metal (Mo) to incorporate into Ga-oxide (GMO) to provide excellent physical and thermo-mechanical characteristics. The GMO nanocomposite films with variable Mo contents (0-11.23 at%) were sputter-deposited onto Si(100) by varying the sputtering power in the range of 0-100 W. The effect of Mo on the crystal structure, mechanical properties and optical properties of GMO nanocomposite films is significant. While Mo content ≤ 4 at% reatins the β-Ga_2O_3 phase, higher Mo content induces amorphization. Molybdenum incorporation into β-Ga_2O_3, reduces the grain-size leading to amorphous nature of the entire film as well as surfaces. The nanoindentation studies indicate the remarkable effect of structural evolution and Mo content on the mechanical properties of the deposited GMO thin films. While Mo incorporation increases the hardness from 25 to 36 GPa, elesatic modulus decreases. Mo-induced red-shift in the band gap is significant in GMO films. Based on the results, a structure-property relationship in established in Mo incorporated Ga_2O_3 films.

4:40pm **SE+2D+NS+SS+TF-WeA8 Investigating Mass Transport and other Events underlying Rapid, Propagating Formation Reactions in Pt/Al Multilayer Films**, ***David Adams****, M.J. Abere, C. Sobczak, D.E. Kittell, C.D. Yarrington, C.B. Saltonstall, T.E. Beechem*, Sandia National Laboratories

Metallic thin film multilayers that undergo rapid, self-propagating exothermic reactions are of interest for several applications including advanced joining technology. Reactive multilayers, such as commercially available Ni-Al, have been developed as a heat source to locally solder or braze dissimilar materials. A local heating approach is of great benefit for joining temperature-sensitive components and metastable structures. The development of new materials for reactive joining requires an improved, detailed understanding of mass transport, chemical reactions, heat release and thermal transport processes. With this presentation, we describe recent studies of a more highly exothermic reactive multilayer system (Pt/Al). Thin Pt/Al multilayers exhibit rapid propagating reactions with flame speeds as high as 100 m/s and internal heating rates > $1\text{x}10^7$ K/s. Equimolar designs are characterized by a substantial heat of formation, ~100 kJ/mol. at., which is approximately twice that of Ni/Al. Our discussion of equimolar Pt/Al multilayers will focus on the thermal and mass transport characteristics which underly their self-propagating reactions. We have utilized advanced thin film characterization techniques to probe the thermal conductivity of different Pt/Al multilayers having various periodicities. This acquired information is used within the framework of an analytical method developed by Mann et al. (J. Appl. Phys. 1997) to estimate the mass transport properties of Pt/Al multilayers subjected to high heating rates. The analytical model accounts for layer thicknesses, compositional profiles near interfaces, flame temperatures, heats of reaction, and adiabatic temperatures in order to predict reaction wavefront velocity and its variation with multilayer design.

This work was supported by a Sandia Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

5:00pm **SE+2D+NS+SS+TF-WeA9 Adaptive Ceramic Coatings for Extreme Environments**, ***Samir Aouadi***, University of North Texas, *C. Muratore*, University of Dayton, *A.A. Voevodin*, University of North Texas **INVITED**

This talk will provide an overview of the latest research developments in the design and exploration of hard coatings with high temperature adaptive behavior in tribological contacts. The initial focus of the talk will be on understanding the major mechanisms that lead to a reduction in friction and/or wear in high temperature lubricious oxides. Adaptive mechanisms will also be discussed and will include metal diffusion and formation of lubricant phases at worn surfaces, thermally- and mechanically-induced phase transitions in hexagonal solids, contact surface tribo-chemical evolutions to form phases with low melting point, and formation of easy to shear solid oxides. All of these adaptive mechanisms are combined in nanocomposite coatings with synergistic self-adaptation of surface structure and chemistry to lubricate from ambient temperatures to 1000 °C and provide surface chemical and structural reversibility during temperature cycling to maintain low friction coefficients. Changes in the structural and chemical properties of these materials as a function of temperature will be correlated to their mechanical and tribological performance using a range of experimental tools in addition to simulations based on *ab initio* calculations and molecular dynamics simulation methods. This review also includes a discussion of the industrial applications of these coatings as well as of potential improvements to the coating design and other anticipated future developments.

5:40pm **SE+2D+NS+SS+TF-WeA11 Ultralow Wear of Stable Nanocrystalline Metals**, ***Nicolas Argibay****, T.A. Furnish, T.F. Babuska, C.J. O'Brien, J.F. Curry, B.L. Nation, A.B. Kustas, P. Lu, M. Chandross, D.P. Adams, M.A. Rodriguez, M.T. Dugger, B.L. Boyce, B.G. Clark*, Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been recently proposed and supported by demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of mechanical stress on this stability. In this presentation we discuss the results of an investigation on the stress and temperature dependent stability of a nanocrystalline noble-metal alloy (Pt-Au) in the form of sputtered thin films. We show that stabilization of nanocrystalline structure can impart low friction (μ ~ 0.2-0.3) and remarkable wear resistance, 100x lower than any previously reported metal.

6:00pm **SE+2D+NS+SS+TF-WeA12 From Ab-Initio Design to Synthesis of Multifunctional Coatings with Enhanced Hardness and Toughness**, ***Daniel Edström****, D. Sangiovanni, L. Hultman, I. Petrov, J. Greene, V. Chirita*, Linköping University, University of Illinois at Urbana-Champaign

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride (TMN) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. The essential feature in the disordered alloys, as reported for ordered alloys, is the increased occupancy of electronic d-t_{2g} metallic states, which allows the selective response to tensile/shearing stresses, and explains the enhanced toughness confirmed experimentally for VMoN films.

Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness > 50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack.

New DFT calculations suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC. A comprehensive

electronic structure analysis, as well as stress/strain curves DFT-based calculations, carried out for the newly formed ternary TMC alloys, reveal similar trends between shear-stressed TMN and TMC compounds, and predict VMoC as the best candidate alloy with enhanced ductility.

KEYWORDS: nitrides, carbides, toughness, hardness, ductility.

Plasma Science and Technology Division
Room: 23 - Session PS+NS+SS+TF-ThM

Atomic Layer Etching I

Moderators: Andrew Gibson, University of York, UK, Saravanapriyan Sriraman, Lam Research Corporation

8:00am **PS+NS+SS+TF-ThM1 Strategies to Control the Etch per Cycle During Atomic Layer Etching of SiO_2 and SiN_x**, ***Ryan Gasvoda***, Colorado School of Mines, *S. Wang, E.A. Hudson*, Lam Research Corporation, *S. Agarwal*, Colorado School of Mines

Decreasing device dimensions and the incorporation of increasingly complex 3D architectures place new constraints on conventional plasma processing techniques. One method to address the limitations of conventional etching is atomic layer etching (ALE) which can provide low damage and atomic-scale etch control. ALE has been extensively studied for a variety of materials, including Al_2O_3, HfO_2, Si, and Si-based dielectrics. In this study, we have explored the atomistic-level details of an SiO_2 and SiN_x ALE process consisting of a hydrocarbon-containing precursor dose, CF_x deposition from a C_4F_8/Ar plasma, and an Ar plasma activation step in which the CF_x film is activated and the underlying substrates are etched. In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions and film composition as well as the net film thickness during the deposition and etching steps.

Sequential cycles of ALE of SiO_2 show a drift in the etch per cycle (EPC) with increasing cycle number. We attribute the drift in EPC is from excess CF_x that is liberated from the reactor walls in the Ar plasma step. This increase in the EPC occurs even though the infrared spectra confirm that the CF_x deposition onto the SiO_2 film is reproducible from cycle to cycle. To minimize the drift in EPC, Ar plasma half-cycles of twice the length are employed, which allows for the removal of CF_x from the reactor walls during each cycle, thus creating more reproducible chamber wall conditions.

To further control the EPC, a hydrocarbon precursor prior to the start of ALE retards the EPC. A broad feature centered at ~1,400 cm^{-1} builds up on the surface with increasing hydrocarbon dose frequency and cycle number, which is assigned to a carbonaceous film of CH_xF_y. The film acts as a blocking layer which prevents the activation of CF_x at the CF_x/SiO_2 interface and thus limits SiO_2 etching. No graphitic carbon buildup is observed. However, increasing the Ar plasma half-cycle length limits the buildup of the CH_xF_y film and increases the EPC. Using the same baseline processing conditions as ALE of SiO_2, ALE of SiN_x leads to a carbonaceous film buildup of both CH_xF_y and nitrile species at ~2,225 cm^{-1} which accumulates over cycle number and eventually leads to an etch stop. A longer Ar plasma half-cycle limits the accumulation of the CH_xF_y film and the EPC drift. The addition of a hydrocarbon precursor retards the EPC in a similar fashion as observed on the SiO_2 film.

8:20am **PS+NS+SS+TF-ThM2 Enabling Atomic Layer Etching of Magnetic and Noble Metal Alloys**, ***Nicholas Altieri****, *E. Chen*, University of California, Los Angeles, *J.K. Chen*, Lam Research Corporation, *J.P. Chang*, University of California, Los Angeles

Etching of magnetic and noble metals alloys utilized in ferromagnetic thin films crucial to the operation of magnetic memory has created a processing bottleneck, due to their chemically resistant nature. Widely-used etch techniques, including noble ion sputtering, exhibit limited success at patterning high aspect ratio features as well as a lack of selectivity. Furthermore, as feature sizes shrink, the demand for atomic level precision in patterning increases. A generalized strategy has been developed to enable dry etch processes shown to be effective for patterning elemental and alloyed metal thin films through the use of surface modification. Controlling the thickness of the modified layer allowed for direct control of the amount of material removed, indicating that this process would be viable for achieving atomic layer etch.

The etch of Co and Pt, elements commonly used in the magnetic memory stack, as well as ferromagnetic alloys CoPt and $Co_{30}Fe_{45}B_{25}$ were studied in this work. Inductively coupled oxygen plasma was utilized for surface modification, and organics including oxalic acid, formic acid, acetylacetone, and hexafluoroacetylacetone were investigated as chemical etchants.

Pt, Co, CoPt, and CoFeB thin films were first studied using continuous exposure to organic solutions. Pt showed no etch beyond the removal of a thin layer of native oxide. CoPt and CoFeB were shown to etch at rates up to 10 nm/min in formic acid solutions without plasma modification. Upon translation to the gas phase, where the concentration of organics was substantially lower, no etch was observed across all materials when continuously exposed to organic acid vapor.

Plasma oxidation was then utilized to chemically modify the surface through generation of directional metal-oxide bonding prior to treatment with organics. Subsequent exposure to formic acid solution indicated preferential and complete removal of metal oxides. A dual-step dry etch process consisting of plasma oxidation and organic vapor dosing was then developed which exhibited etch rates of 0.5, 2.8, 1.1, and 1.8 nm/cycle for Pt, Co, CoPt and CoFeB, respectively, and removing metallic oxides.

In formic acid solution, PtO_2 exhibited infinite selectivity to Pt, while oxidized CoPt and CoFeB were observed to have selectivities of 6.4 and 3.1, respectively, compared to their unoxidized counterparts. In the vapor phase, each oxidized material exhibited nearly infinite selectivity to each corresponding metallic film. Coercivity values (H_c) of 20 and 3.5 Oe were measured for Co and CoFeB before processing conserved to up to 99% of their original pre-processing values.

8:40am **PS+NS+SS+TF-ThM3 Directional Atomic Layer Etching: First Principles, Modelling and Applications**, ***Thorsten Lill***, *K. Kanarik, I.L. Berry, S. Tan, Y. Pan, V. Vahedi, R.A. Gottscho*, Lam Research Corporation **INVITED**

Atomic layer etching (ALE) has recently been introduced into manufacturing to produce 10 nm logic devices. ALE is an etching technology that deploys time or space separated and self-limited steps. In directional ALE, at least one of the two steps has to be directional, i.e., has to transfer momentum to the surface and/or be sensitive to line of sight. Ion bombardment is most commonly used to realize directional ALE. ALE exhibits the same ion-neutral synergy as RIE but the removal amount is not flux dependent due to the separation of the neutral (chemical) and ion fluxes /1,2/. Flux independence gives ALE its most prominent property: inherent uniformity across all length scales – across wafer, loading, ARDE and surface smoothness.

As compared to conventional plasma etching, step separation in ALE also offers a simplified system in which to study the etching mechanisms based on first principles. For example, recently, the process window of ALE was shown to be predictable based on the energy barriers relevant to the substrate-reactant combination, such as the surface binding energies of the chemically modified and bulk material /3/. The separate and independent steps make it particularly suitable to modelling efforts. Here we present the latest results in feature scale modelling of new material systems amenable to the ALE approach as well as experimental results.

[1] H.F. Winters, J.W. Coburn, E. Kay, J. Appl. Phys. 48, 4973 (1977)

[2] K.J. Kanarik et al., J. Vac. Sci. Technol. A 33(2) (2015)

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9:20am **PS+NS+SS+TF-ThM5 Thermal Atomic Layer Etching of VO_2 Using Sequential Exposures of SF_4 and Either $Sn(acac)_2$ or BCl_3**, ***Jonas Gertsch***, *V.M. Bright, S.M. George*, University of Colorado Boulder

Thermal atomic layer etching (ALE) is based on sequential self-limiting thermal reactions [1]. Thermal ALE offers a precise and gentle etching procedure and has been demonstrated for many materials including Al_2O_3, HfO_2, ZnO, ZrO_2, SiO_2 and AlN [1,2]. This study developed thermal ALE processes for vanadium oxide (VO_2). VO_2 has a metal-insulator transition at ~68 °C and is useful for thermochromic films and heat-switching devices. The initial VO_2 films were deposited using VO_2 atomic layer deposition (ALD) with tetrakis(ethylmethylamino) vanadium(IV) (TEMAV) and H_2O as the co-reactants at 150 °C.

The VO_2 films were etched using sequential exposures of sulfur tetrafluoride (SF_4) and either tin(II) acetylacetonate ($Sn(acac)_2$) or boron trichloride (BCl_3) at temperatures ranging from 150-250 °C. *In situ* quartz crystal microbalance studies were used to monitor film growth and etching during the ALD and ALE reactions. The VO_2 etching mechanism using SF_4 and $Sn(acac)_2$ is observed to occur by fluorination and ligand-exchange reactions [1]. The SF_4 exposures yielded mass gains that were consistent with fluorination of VO_2 to VF_4. The $Sn(acac)_2$ exposures then led to mass losses that were attributed to ligand-exchange reactions that produced volatile acetylacetonate reaction products. VO_2 ALE etch rates increased with temperature from 0.04 Å/cycle at 150 °C to 0.27 Å/cycle at 225 °C.

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* **Coburn & Winters Student Award Finalist**

A different reaction mechanism was observed for VO_2 ALE using SF_4 and BCl_3. The SF_4 exposures yielded mass losses at all temperatures that were not consistent with simple fluorination of VO_2 to VF_4. The BCl_3 exposures produced mass losses at higher temperatures and slight mass gains at 150 °C. The etching of VO_2 by SF_4 and BCl_3 is believed to occur by a "conversion-etch" mechanism [2]. In the "conversion-etch" mechanism, BCl_3 converts the surface of VO_2 to a thin B_2O_3 layer. SF_4 can then remove the B_2O_3 layer to produce volatile BF_3 and SO_2. The VO_2 etch rates increased with temperature from 0.06 Å/cycle at 150 °C to 1.9 Å/cycle at 250 °C.

[1] Y. Lee, C. Huffman and S. M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem. Mater.* **28**, 7657 (2016).

[2] D. R. Zywotko and S. M. George, "Thermal Atomic Layer Etching of ZnO by a "Conversion-Etch" Mechanism Using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum", *Chem. Mater.* **29**, 1183-1191 (2017).

9:40am **PS+NS+SS+TF-ThM6 Atomic Layer Etching of MoS_2 for Nanodevices**, ***KiSeok Kim***, *K.H. Kim, Y.J. Ji, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Among the layered transition metal dichalcogenides (TMDs) that can form stable two-dimensional (2-D) crystal structures, molybdenum disulfide (MoS_2) has been intensively investigated due to its unique properties in various electronic and optoelectronic applications with different band gap energies from 1.29 to 1.9 eV as the number of layers is decreased. To control the MoS_2 layers, atomic layer etching (ALE) (which is a cyclic etching consisting of a radical-adsorption step such as Cl adsorption and a reacted-compound desorption step via a low-energy Ar^+-ion exposure) can be a highly effective technique to avoid inducing damage and contamination that occur during the cyclic steps. In this study, for the MoS_2 ALE, the Cl radical is used as the adsorption species and a low-energy Ar^+ ion is used as the desorption species. A MoS_2-ALE mechanism (by which the $S_{(top)}$, $Mo_{(mid)}$, and $S_{(bottom)}$ atoms are sequentially removed from the MoS_2 crystal structure due to the trapped Cl atoms between the $S_{(top)}$ layer and the $Mo_{(mid)}$ layer) is reported with the results of an experiment and a simulation. A monolayer MoS_2 field effect transistor (FET) fabricated after one-cycle of ALE of a bilayer MoS_2 FET exhibited electrical characteristics similar to a pristine monolayer MoS_2 FET indicating no electrical damage on the monolayer MoS_2 surface after the ALE.

11:00am **PS+NS+SS+TF-ThM10 Ge Atomic Layer Etching for High Performance FinFET**, *W. Mizubayashi*, AIST, Japan, *S. Noda*, Tohoku University, Japan, *Y. Ishikawa, T. Nishi*, AIST, Japan, *A. Kikuchi*, Tohoku University, Japan, *H. Ota*, AIST, Japan, *P.-H. Su, Y. Li*, National Chiao Tung University, Taiwan, *S. Samukawa*, Tohoku University, AIST, Japan, ***Kazuhiko Endo***, AIST, Japan **INVITED**

Ge is a promising material for use as high mobility channel in future CMOS. For 5-nm-node CMOS and smaller, to attain electrostatic controllability of the gate electrode, a multichannel fin structure is utilized. Fin structure formation in Ge FinFETs on GeOI substrates is mainly performed by ICP etchings. However, ICP etching causes plasma induced damages owing to the ultraviolet (UV) light generated from the ICP and charge up by ionized atoms. A concern is that such etching damage reduces the performance and reliability of Ge-channel CMOS. In this work, to break-through these plasma induced damages, we demonstrated defect-free and highly anisotropic Ge etching for Ge FinFET fabricated by Cl neutral beam etching.

There are two advantages in the neutral beam etching process. 1) The wafer is not exposed by the UV light generated from the plasma through the high-aspect-ratio carbon aperture plate. 2) Ions are efficiently neutralized by collision with the carbon aperture plate. Thus, in neutral beam etching, the influences of the UV light and charge-up can be perfectly eliminated and defect-free etching can be realized.

In the ICP etching, the Ge fin is formed but has a trapezoidal shape. On the other hand, the Ge fin in the case of neutral beam etching can be vertically formed as compared with that in the case of the ICP etching. A channel surface with atomic-level smoothness was confirmed in neutral beam etching while some roughness was observed in the ICP etching. In neutral beam etching without UV light irradiation, the Ge surface is not damaged, and a surface dangling bond is formed only on the atomic layer and it undergoes a chemical reaction with the reactive species [1]. Thus, atomic layer etching can be realized by neutral beam etching.

The $|I_d|–V_d$ and $|I_d|–V_g$ characteristics of the Ge FinFET fabricated by neutral beam etching are markedly improved as compared with those of the FinFETs fabricated by ICP etching, in n- and p-type FinFETs. $g_{m\,max}$ for the Ge FinFET fabricated by neutral beam etching is two times higher for the nFinFET and 10% higher for the pFinFET than those of the FinFETs fabricated by ICP etching, regardless of the fin thickness. In the case of neutral beam etching, since there is no etching damage in the Ge fin, the interface state and surface roughness are drastically lowered. This is the reason for the improved $g_{m\,max}$ for the n- and p-type Ge FinFETs fabricated by neutral beam etching. Thus, the atomic-level flatness and damage-free etching in the Ge fin formation are essential to high performance Ge FinFETs, which can be realized by neutral beam etching.

References

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11:40am **PS+NS+SS+TF-ThM12 Numerical Simulations of Atomic-Layer Etching (ALE) for SiO_2 and SiN**, ***Yuki Okada***, Osaka University, Japan, *R. Sugano*, Hitachi, Ltd., Japan, *M. Isobe, T. Ito, H. Li, K. Karahashi, S. Hamaguchi*, Osaka University, Japan

As the sizes of modern semiconductor devices approach near-atomic scales, processing to create such devices in mass production scale also requires atomic-scale precisions. Recent technological advancement for atomic-scale processing includes the development of atomic-layer deposition (ALD) and atomic-layer etching (ALE), in which deposition or etching processes take place layer by layer with each step having self-limiting chemical reactions. In such a process, self-limiting reactions result in not only atomic-scale accuracy of processed structures but also process uniformity over a large area regardless of structure densities. In this study we have examined mechanisms of ALE processes of SiO2 and SiN based on digital or pulsed application of fluorocarbon or hydrofluorocarbon plasmas, using molecular dynamics (MD) simulations. In MD simulations, chemically reactive species and low-energy incident ions are supplied to a SiO2 or SiN surface alternatively. A supply of a certain amount of chemically reactive species to the surface does not spontaneously induce etching reactions. However, when the surface with such reactive species is subject to ion bombardment, energy and momentum supplied to the surface by incident ions activate surface reactions and etching reactions take place. If the ion bombardment energy is sufficiently low, this etching process stops when reactive species are depleted from the surface. In this study, we have examined various combinations of reactive species and ion bombardment. For example, in the case of SiO2, reactive species and ions used in this study are fluorocarbon radicals and low-energy (e.g., 40 eV) Ar+ ions. In the case of SiN, reactive species and ions are hydrogen radicals and low-energy (e.g., 10 eV) Ar+ ions. Also in the case of SiN, we have used simultaneous injection of hydrogen radicals with low energy CF3+ ion bombardment as a radical supply process and low-energy (e.g., 50 eV) Ar+ ion injections as a process to remove excess fluorocarbon deposited on the surface. In the last case, etching self limit occurs because of accumulation of a fluorocarbon layer, rather than the removal of it. It has been found that, in most cases, the complete removal of reactive species from the surface is not easy and the control of remaining reactive species on the surface after each digital process step is the key for the success of ALE process development.

12:00pm **PS+NS+SS+TF-ThM13 Organometallic Etching Chemistry for Thermal Atomic Level Etching of Lanthanum Oxide**, ***Yoshihide Yamaguchi***, *K. Shinoda*, Hitachi, Japan, *Y. Kouzuma, S. Sakai, M. Izawa*, Hitachi High-Technologies Corp., Japan

The demand for thermal atomic level etching (ALEt) of a wide variety of materials including silicon-based materials, metals, and high-k materials is increasing as semiconductor device geometries continue to shrink. To meet the increased demand, remarkable progress into ALEt research has been made in the last few years. One example is the pioneering research on the thermal ALEt of hafnium oxide emerged [1], where hafnium oxide sequentially reacted with HF and a stannous organometallic compound (Sn(acac)2). Thermal ALEt of SiN is another example [2][3], where sequential reactions of a plasma-assisted self-limiting surface modification and a thermal desorption of the self-limiting layer was employed.

In this work, we present our challenge for the thermal ALEt of lanthanum oxide by using surface modification followed by thermal desorption. A key technology of this ALEt is the novel organometallic chemistry for the one-step surface modification of lanthanum oxide. A lanthanum oxide sample exposed to gas of fluorine-containing ketone together with a stabilizer led to the formation of volatile organic species on the sample surface, while a SiO2 sample remained unchanged under the same process condition. The gas-exposed lanthanum oxide sample was then annealed at elevated temperatures under vacuum to remove the volatile species from the surface. After these consecutive processes, the volatile organic species from the lanthanum oxide sample were collected and identified by nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectroscopy. These results indicated that the volatile species was an organo-lanthanum complex bearing the fluorine-containing ketone moiety as the ligand. On the basis of these results, a novel selective dry-chemical removal of lanthanum oxide was successfully demonstrated.

Several results on selective dry-chemical removal of lanthanum oxide with respect to TiN, metal oxide, and some other material will also be disclosed.

[1] Y. Lee et al., ECS J. Solid State Sci. Technol. 4. N5013 (2015).

[2] K. Shinoda et al., Appl. Phys. Express 9, 106201 (2016).

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

Thin Films Division
Room: 20 - Session TF+SE-ThM

Control, Characterization, and Modeling of Thin Films I
Moderators: Hilal Cansizoglu, University of California, Davis, Tansel Karabacak, University of Arkansas at Little Rock

8:00am **TF+SE-ThM1** ***In Situ* Synchrotron Characterization Techniques Enabled Nanostructured Materials using ALD**, ***Yu Lei***, University of Alabama in Huntsville

To achieve the goal of rational design of next generation of advanced materials, we have been working on developing atomic layer deposition (ALD) as a promising method to tailor size and composition of nanostructured materials for a wide range of applications. Benefiting from self-limiting surface reactions, ALD enables conformal coatings of materials on three-dimensional substrates. The atomic level control of depositions makes it attractive to precisely synthesize the size and composition of nanomaterials. The size and composition of nanomaterials play important roles in achieving high performance in many applications. In this talk, we will discuss nanomaterials synthesized using Pd ALD and their applications in catalysis and energy storage. We will also illustrate that *in situ* characterization techniques such as synchrotron X-ray based X-ray absorption spectroscopy (XAS), X-ray pair distribution function (PDF), and FT-IR significantly advance our understandings of ALD in terms of surface chemistry and surface dynamics.

8:20am **TF+SE-ThM2 Probing the Atomic Scale Structure of Polar Oxide Interfaces**, ***Sanaaz Koohfar***, *D.P. Kumah*, North Carolina State University

Complex oxide heterostructures possess a wide range of functional electronic and magnetic properties including metal-insulator transitions, superconductivity, ferroelectricity and colossal magnetoresistance effects. At epitaxial interfaces formed between atomically thin complex oxide films, electronic, chemical and structural interactions can be used to effectively tune the physical properties of these materials. Using a combination of atomic-scale controlled thin film synthesis and high resolution synchrotron diffraction based imaging, we show that structural distortions at the interfaces between polar $La_{1-x}Sr_xMnO_3$ films and non-polar substrates can be effectively tuned by chemical modifications at these interfaces to control ferromagnetism in [001]-oriented $La_{1-x}Sr_xMnO_3$ films with thickness less than 1 nm. We show that atomic-scale chemical control at polar/non polar oxide interfaces provides a powerful route to engineer novel electronic and magnetic phenomena at complex oxide interfaces.

8:40am **TF+SE-ThM3 CVD Chemistry of Trimethylboron - Gas Phase Reactions and Surface Poisoning Effects**, ***Henrik Pedersen***, *L. Souqui, M. Imam,* Linköping University, Sweden, *R. Tonner,* Philipps Universität Marburg, *H. Högberg*, Linköping University, Sweden

Organoborons with short alkyl groups; trimethylboron (TMB), $B(CH_3)_3$, triethylboron (TEB), $B(C_2H_5)_3$, and tributylboron (TBB), $B(C_4H_9)_3$, were suggested as alternative, highly reactive, less-poisonous, non-explosive B-precursors in the mid 1990's[1].TEB was found to exhibit the best properties for CVD of boron-carbon films, making it a popular CVD precursor[2]. TMB and TBB were deemed not suitable as CVD precursors as no boron was found in the films deposited from these molecules. Consequently, these molecules are less investigated in CVD.

We study the gas phase chemistry of TMB in a thermal CVD process, using a combination of B-C film deposition experiments at several temperatures in both hydrogen and argon atmosphere and quantum chemical calculations for a wide range of possible gas phase reactions. We suggest that without assistance from the carrier gas, i.e. in argon ambient, TMB most likely decomposes by α-H elimination of CH_4 to form H_2CBCH_3. Methane is not highly reactive in CVD at deposition temperatures below 1000 °C, meaning that the H_2CBCH_3 species is the major film forming species. This correlates well with the B/C ratio of about 0.5 observed for films deposited in Ar at 700-900 °C. At higher temperatures, the B/C ratio of films increases as attributed to further decomposition to H_2BCH_3.

With assistance from the hydrogen carrier gas, TMB can also decompose to $HB(CH_3)_2$ that can further decompose to H_2BCH_3 and finally to BH_3, all with negative Gibbs free energies, albeit with some high energy barriers. This in combination with the unimolecular α-H elimination with a somewhat lower energy barrier, can explain the higher B/C ratios of films deposited in H_2.

Furthermore, we note that the onset of film deposition from TMB is 700 °C and at then at a very low deposition rate. Interestingly the film thickness does not increase with longer deposition time at 700 °C, indicating a surface poisoning effect. As this is seen both in Ar and H_2, we speculate that this is caused by CH_4 or H_2CBCH_3, which is currently the subject of our further investigations.

[1] J. S. Lewis et al. Chemical vapor deposition of boron-carbon films using organometallic reagents. *Mater. Lett.* **1996**, *27*, 327.

[2] M. Imam et al. Gas phase chemical vapor deposition chemistry of triethylboron probed by boron–carbon thin film deposition and quantum chemical calculations. *J. Mater. Chem. C* **2015**, *3*, 10898.

9:20am **TF+SE-ThM5 *In Situ* Synchrotron-based Characterization of Noble Metal ALD Processes**, *J. Dendooven,* ***Eduardo Solano***, *R.K. Ramachandran, M.M. Minjauw,* Ghent University, Belgium, *A. Coati*, Synchrotron SOLEIL, France, *D. Hermida-Merino,* ESRF, France, *C. Detavernier*, Ghent University, Belgium **INVITED**

Supported noble metal nanoparticles (NPs) are widely used in heterogeneous catalysis because of their high resistance against chemical poisoning. Atomic Layer Deposition (ALD) can be used to synthesize noble metal NPs on different high surface area supports, and offers sub-monolayer control over the metal loading (atoms per cm^2 of support) [1]. However, an improved understanding of how the deposition parameters influence the formation and growth of noble metal NPs is required to fully exploit the tuning potential of ALD.

We developed a synchrotron-compatible high-vacuum setup that enables in-situ monitoring during ALD [2]. Using this setup and focusing on ALD of Pt with the $MeCpPtMe_3$ precursor at 300 °C [3], we present an in-situ investigation of Pt NP growth on planar SiO_2 substrates by means of X-ray fluorescence (XRF) and grazing incidence small-angle X-ray scattering (GISAXS). The surface density of Pt atoms was determined by XRF. Analysis of the GISAXS patterns [4] yielded dynamic information on average real space parameters such as Pt cluster shape, size and spacing. The results indicate a diffusion-mediated particle growth regime for the standard O_2-based Pt ALD process, marked by a decreasing average areal density and formation of laterally elongated Pt clusters. Growth of the Pt NPs is thus not only governed by the adsorption of Pt precursor molecules from the gas-phase and subsequent combustion of the ligands, but is largely determined by adsorption of migrating Pt species on the surface and diffusion-driven particle coalescence [5].

Next, we have studied the influence of the reactant type (O_2 gas, O_2 plasma, N_2 plasma, NH_3 plasma [6]) on the Pt NP growth. Surprisingly, a clear difference in island growth behavior was found for the oxygen- vs. nitrogen-based processes. The latter processes were marked by a constant average particle distance during the growth process. Particle dimension analysis furthermore revealed vertically elongated NPs for the N_2 and NH_3 plasma-based Pt ALD processes. Therefore, it is concluded that atom and cluster surface diffusion phenomena are suppressed during the nitrogen-based processes. Finally, this insight provided the ground for the development of a tuning strategy that is based on combining the O_2-based and N_2 plasma-based ALD processes and offers independent control over NP size and coverage.

[1] Lu et al., Surf. Sci. Rep. 71 (2016) 410. [2] Dendooven et al., Rev. Sci. Instrum. 87 (2016) 113905. [3] Aaltonen et al., Chem. Mater. 15 (2003) 1924. [4] Schwartzkopf et al., Nanoscale 5 (2013) 5053. [5] Mackus et al., Chem. Mater. 25 (2013) 1905. [6] Longrie et al., ECS J. Solid State Sci. Technol. 1 (2012) Q123.

11:00am **TF+SE-ThM10 *In-situ* FTIR Study of the Atomic Layer Deposition of Scandium Oxide Films using Bis(methylcyclopentadienyl)3,5-dimethylpyrazolatoscandium with Ozone and with Water**, ***Rezwanur Rahman***, *J.P. Klesko, A. Dangerfield,* University of Texas at Dallas, *J.-S. Lehn, C.L. Dezelah, R. Kanjolia,* EMD Performance Materials, *Y.J. Chabal*, University of Texas at Dallas

Scandium oxide (Sc_2O_3) thin films have been thoroughly studied for their use in microelectronic devices.[1–2] However, processes for the atomic layer deposition (ALD) of Sc_2O_3 films are scarce, and have mostly involved $Sc(thd)_3$,[1] $ScCp_3$,[1] $Sc(MeCp)_3$,[2] and $Sc(amd)_3$[3] precursors. To date, the only mechanistic investigation has focused on the $Sc(MeCp)_3/H_2O$ process using *in-situ* time-resolved quadrupole mass spectrometry to probe the Sc_2O_3 ALD chemistry.[2]

Herein, we have explored the Sc_2O_3 ALD using bis(methylcyclopentadienyl)3,5-dimethyl pyrazolatoscandium ($Sc(MeCp)_2(Me_2pz)$) with ozone and with D_2O. This precursor reacts with hydroxyl-terminated silicon, Si(111)– SiO_2–OH, at 150 °C and appears to remain thermally stable to 450 °C. Between 225 and 275 °C, there is a clear ligand exchange with ozone observed in the differential IR absorption spectra involving the formation of intermediate formate and carbonate species (1400–1600 cm^{-1}) after each ozone pulse. A short incubation period (≤ 5 ALD cycles) is observed at 225 °C prior to the onset of steady-state ligand exchange. The signature for the formation of Si–O–Sc bonds (1240 cm^{-1}) is clearly present after cycles 1–2 for the ozone process at 275 °C. The Sc_2O_3 growth is quantified by X-ray photoelectron spectroscopy (XPS) and by spectroscopic ellipsometry (SE), from which a growth rate of ~0.3–0.9 Å/cycle is extracted over the 225–275 °C temperature range.

In contrast, there is no ligand exchange observed for the D_2O process within the same temperature range, although some deposition occurs. The deposition rate for the D_2O process calculated by XPS and SE, is ~1.3 Å/cycle within the 225–275 °C window, which is higher than the non-uniform growth rate measured for the ozone process within that temperature range. The higher growth rate and lack of ligand exchange observed with D_2O is tentatively attributed to a CVD component that dominates the film growth process.

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11:20am **TF+SE-ThM11 Ultra Fast Compositional Depth Profile Analysis for Microelectronics Applications**, ***Agnès Tempez***, Horiba France S.a.s., France, *Y. Mazel, J.-P. Barnes, E. Nolot*, CEA/LETI-University Grenoble Alpes, France, *S. Legendre*, Horiba France S.a.s., France, *M. Chausseau*, HORIBA Instruments Incorporated

Wouldn't it be a considerable gain of time to be able to check the stoichiometry of just deposited thin films in a few minutes? A recently commercially available sputter-based technique called plasma profiling time-of-flight mass spectrometry (PP-TOFMS) is capable to produce, in a few minutes, nm-scale depth resolved profiles of all elements (including light elements) of the periodic table, over a wide dynamic range (from 100% down to ppm)[1]. A simple ratio of the amount of ions detected from a given layer provides a calibration free semi-quantification.

For such fast feedback purposes a PP-TOFMS instrument (Horiba Scientific, Horiba FRANCE SAS, France) has been installed in the clean room of the CEA-LETI in close proximity to process tools.

In this paper we will present data obtained from microelectronics and nanotechnology thin films to demonstrate the performance of the technique. It will be shown that PP-TOFMS can be used for determining composition, detecting contamination, measuring doping level, and characterizing diffusion mechanisms.

For example we will show the ease of detecting, identifying, and locating in depth the presence of unexpected contamination in magnetic Iron Cobalt Boron multi-layers. Another example will show the depth profile of a Germanium Antimony Tellurium alloy deposited on silicon oxide used for phase change memories, a type of non-volatile random access memory. PP-TOFMS depth profiles agree with TOF-SIMS and STEM-EDX analyses for both the first nanometers and the in-depth composition.

[1] A. Tempez et al., J. Vac. Sci. Technol. B (2016) 34

11:40am **TF+SE-ThM12 Surface Termination of Fe_3O_4(111) Films Studied by CO Adsorption**, ***Francesca Mirabella***, *E. Zaki, F. Ivars, S. Shaikhutdinov, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *X. Li, J. Paier, J. Sauer*, Humboldt Universität zu Berlin, Germany

Although the (111) surface of Fe3O4 (magnetite) has been investigated for more than twenty years, substantial controversy remains in the literature regarding the surface termination [1, 2]. To shed more light on this issue, we performed CO adsorption studies on (111) and (001) oriented thin films, using in-situ infrared reflection absorption spectroscopy, temperature programmed desorption, and scanning tunneling microscopy. The experimental results were rationalized on the basis of theoretical calculations, thus leading to a unified picture in which the Fe_3O_4(111) surface is terminated by 1/4 monolayer of tetrahedrally coordinated Fe^{3+} ions on top of a close-packed oxygen layer as previously determined by low energy electron diffraction. However, surface defects play a crucial role in adsorption properties and most likely dominate chemical reactions on Fe_3O_4(111) when exposed to the ambient.

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Thin Films Division
Room: 21 - Session TF-ThM

Area-selective Deposition and Infiltration Growth Methods
Moderator: James Fitz-Gerald, University of Virginia

8:00am **TF-ThM1 Thin-Film Encapsulation Based on ALD Technology for Organic Light-Emitting Diodes**, ***Tony Maindron***, CEA-Leti, France **INVITED**

Thin-film encapsulation of organic electronic circuits like Organic Light-Emitting Diodes (OLED) consists in the addition of vacuum deposited thin mineral barrier directly onto the organic circuit. The main challenge today is to achieve high encapsulation levels with WVTR ~ 10^{-6} g/m^2/day. The ALD technology is well-suited to reach that goal because the technology allows the deposition of defect-free thin barrier films, mainly of Al_xO_y. However, the main limitation of the ALD technology is the relative stability of the Al_xO_y layer when it is exposed to hot humid atmospheres. Due to its high C and H atoms content, resulting from the low temperature deposition used to deposit onto the fragile circuits (maximum process temperature allowed for OLED ~ 100 °C), the Al_xO_y layer corrodes very quickly and loses its barrier properties prematurely. An additional passivation is therefore mandatory in order to protect the Al_xO_y from water condensation onto its surface. Different works have illustrated the benefits of depositing an additional ALD layer on top of the Al_xO_y, an additional PECVD or PVD layer on top of the Al_xO_y or using hybrid ALD/MLD (Al_xO_y/metalcone) nanocomposites. In each case, the stability of the aluminum oxide is improved because it is not exposed directly to moisture condensation. Alternatively for thin-film encapsulation purposes, other materials of interest can be deposited by low-temperature ALD: ZrO_2, TiO_2, SnO_2, SiN_x, ZnO, or ZnO:Al (AZO). After a review of solutions to stabilize Al_xO_y films, performances of new single barrier materials will be described in this work and compare to Al_xO_y. It is well-known also that the quality of the encapsulation relies also on the cleanliness of processes. Defects can be described as exogenous particles but they can be seen also as the circuit's surface topography, as well as its surface nature. Getting rid of defects is an important feature for thin-film encapsulation. ALD can provide high surface conformity and can be deposited almost onto every surface. However, as thin-film barriers deposited by ALD remain very thin (dozens of nm), it is mandatory to grow them onto a particle-free surface to ensure a reliable encapsulation. Otherwise, particles can create pinholes that act as a pathway for moisture to reach the fragile device underneath. In the case of OLEDs, black spot features then appear. Other encapsulation processes, based on other deposition technologies like PECVD or PVD, described the use of thick planarization layers to fix the particle issue. Similar strategies can be applied with ALD. The technology developed at CEA-Leti will be presented in the second part of this work.

8:40am **TF-ThM3 Vapor Phase Infiltration: Unifying the Research Community Around Processing Science Fundamentals**, ***Mark Losego***, Georgia Institute of Technology

Vapor phase infiltration (VPI) and its sister processing routes—sequential vapor infiltration (SVI), multiple pulse infiltration (MPI), and sequential infiltration synthesis (SIS)—are exciting, new chemical vapor processing technologies for synthesizing unique organic-inorganic hybrid materials. Because each of these processes were developed independently at various laboratories around the globe and designed to solve different technological problems, a common language has yet to emerge. This lack of a common lexicon introduces unnecessary complexity to the literature and slows the cohesive advancement of the science. This talk seeks to unify the research community around the fundamental science of these processes and demonstrate its uniqueness amongst other chemical vapor processing routes. While VPI/SVI/MPI/SIS emerged from the atomic layer deposition (ALD) research community, its kinetics is substantially different from ALD and truly unique amongst all chemical vapor processes. Unlike ALD and CVD, VPI/SVI/MPI/SIS is not a deposition process but rather an infiltration process composed of three distinct steps: (1) sorption (dissolution) of the gaseous precursor into an organic (polymeric) material, (2) diffusion of that precursor within this host material, (3) entrapment (reaction) of the precursor within the host material (Fig. 1). These unique processing kinetics are similar (identical?) for all of these infiltration processes and rich in fundamental science that intersects with a surprising number of disparate fields including gas membrane separations and solvent vapor annealing. For decades, understanding the fundamental kinetics of ALD and CVD has been the driver for advancing these technologies' processing capabilities; it is now time to do the same for these chemical infiltration processes, such that rationale design physics can be established to devise processing schemes that precisely control the depth and quantity of inorganic infiltration. To guide this unification, this talk will introduce (1) a kinetics-based taxonomy scheme for classifying chemical vapor processes, (2) a basic framework for a common kinetics theory, and (3) a series of common, fundamental scientific questions that, if solved, could significantly advance the utility and expand the use of VPI processing technology.

9:00am **TF-ThM4 Vapor Phase Infiltration (VPI) of Polymers with Intrinsic Microporosity**, ***Emily McGuinness***, *F. Zhang, R.P. Lively, M.D. Losego*, Georgia Institute of Technology

PIM-1, a polymer with intrinsic microporosity, is commonly used for membrane-based chemical separations. However, PIM-1 undergoes detrimental microstructural changes over time and after exposure to certain solvents. In this talk, we will discuss our efforts to use vapor phase infiltration of inorganic components as a means to maintain the microstructure of PIM-1. Vapor phase infiltration (VPI) is a process by which metalorganic precursors are diffused into organic polymer materials to transform them into organic-inorganic hybrids. In this work, we investigate how utilizing VPI can increase PIM-1 durability. We examine VPI of several metal-organic precursors including diethylzinc, trimethylaluminum, and titantium tetrachloride. VPI has been effective in diffusing and trapping inorganic species to a depth of more than 10 microns in PIM-1 material (Figure 1). Gas sorption measurements (BET) indicate that the infiltration process does not significantly decrease the surface area nor the permeability of these PIM-1 membranes (Figure 2). These treatments are also found to improve the chemical stability of PIM-1 when exposed to organic solvents. The kinetics of the VPI process on PIM-1 materials will also be discussed.

9:20am **TF-ThM5 Organic Solvent Resistance of Hybrid Organic-Inorganic Films Synthesized via Vapor Phase Infiltration**, ***Collen Leng***, *M.D. Losego*, Georgia Institute of Technology

We have observed that poly(methyl methacrylate) (PMMA) films infiltrated with trimethylaluminum (TMA) precursors no longer dissolve in toluene, a PMMA solvent. TMA chemically reacting with carbonyl groups in PMMA could be the reason for this solubility resistance. However, films with only a small amount of TMA infiltration will swell significantly inside toluene (over 20% of pre-immersion thickness) and buckle. Interestingly, PMMA films can swell over 50% when infiltrated by TMA at 60 °C without buckling. We attribute this difference to potential crosslinking of PMMA chains during TMA reactions, resulting in a more rigid film and less polymer chain mobility.

For our experiments, the films are spun-cast on silicon and have thicknesses ranging from around 200 nm to 2 microns. The samples are then treated using VPI, with processing temperatures ranging from 60 to 120 °C and exposure times ranging from 1 second to full infiltration (on the scale of hours). Spectroscopic ellipsometry is used to track film thickness changes as the treated films are immersed in toluene for times up to several days.

At a processing temperature of 90 °C, films exposed to TMA for more than 10 minutes no longer dissolve entirely in toluene, but significant film swelling has caused the films to buckle and create micro-folds. Partial delamination of the films from the silicon substrates are also observed due to the buckling actions as well as from small scratches and holes in the films that allow toluene to penetrate and remove the bottom section of the film, where not enough TMA has reacted with PMMA. We find delamination, swelling, and buckling to not be issues for films that are fully treated, which we define as having enough precursor exposure to allow TMA to interact with the entire bulk of the PMMA film. Films that are fully infiltrated remain stable when immersed in toluene for over 10 days.

The results of this study will provide a better understanding of new properties for these polymer films treated by metalorganic precursors. The findings on solubility may be applicable in coatings for various applications.

9:40am **TF-ThM6 Surface Selective CVD of Metallic Thin Films Using Inhibitor Molecules**, ***Elham Mohimi***, *Z. Zhang, S. Liu, B.B. Trinh*, University of Illinois at Urbana-Champaign, *J.L. Mallek*, MIT Lincoln Laboratory, *G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

In the fabrication of nanoscale devices, the top-down process of lithography and etching is time consuming and expensive. A proposed bottom-up approach – area selective growth – would enable device fabrication beyond conventional patterning limits: thin films would preferentially deposit onto pre-existing portions of a structure with no nucleation and growth on other surfaces. However, a selective process is subject to statistical failure – the nucleation of unwanted material – when it relies on the initial characteristics of the non-growth surface, either the inherent chemical properties or passivation pre-treatments. A robust process requires dynamic control of selectivity to ensure that no stray nucleation occurs on the intended non-growth surfaces for the total time required to deposit film on the device areas.

Here, we present a perfectly selective CVD method which involves adding a neutral molecule “inhibitor” to the process gas mixture: the inhibitor dynamically populates oxide surfaces and prevents nucleation while permitting the deposition of film on metal surfaces, where the inhibitor effect is weaker. Because the inhibitor concentration on the oxide surfaces is continuously replenished, it completely eliminates film nucleation on defects or impurity sites.

We previously demonstrated perfectly selective copper CVD using the Cu(hfac)VTMS precursor with additional VTMS as the inhibitor: no nucleation occurs on thermal SiO_2 or on porous, carbon doped oxide, while copper growth occurs on areas covered with a ruthenium seed layer [1]. The excess VTMS scours Cu(hfac) intermediates off the dielectric surface prior to the disproportionation (growth) reaction. Here, we extend the method by using a different class of inhibitor molecules to afford the selective CVD of transition metals and their compounds on a wide variety of oxide substrates; and we explain the mechanism of selectivity .

1. S. Babar, E. Mohimi, B. Trinh, G. S. Girolami and J. R. Abelson, "Surface-selective chemical vapor deposition of copper films through the use of a molecular inhibitor," ECS J. Solid State Sci. Tech. 4(7), N60-63 (2015)

11:00am **TF-ThM10 Toward Area Selective Atomic Layer Deposition on Co, W and Ru Metal/Silicon Patterns**, ***Dara Bobb-Semple***, *S.F. Bent*, Stanford University

Modern electronic devices have achieved significantly smaller sizes and increased structural complexity in recent years. Device fabrication today is based on ‘top-down’ processes with multiple lithography and etching steps which serve as a bottleneck as well as a source of errors for device miniaturization. Area-selective atomic layer deposition (AS-ALD), which combines a surface modification technique and atomic layer deposition (ALD) in a ‘bottom-up’ approach to nanopatterning,shows great promise in addressing these issues. Most work on AS-ALD typically uses tightly-packed, self-assembled monolayers (SAMs) to modify the substrate surface and block ALD. Past studies have demonstrated AS-ALD on Si/SiO_2 substrates patterned with SAMs and, more recently, our group has demonstrated AS-ALD using octadecylphosphonic acid SAMs and alkanethiol SAMs on Cu/SiO_2 substrates.

Incorporating the AS-ALD process into any fabrication scheme requires understanding how SAMs interact with different materials. In this work, we have extended our previous studies on Cu substrates to perform comparative studies on the formation of octadecylphosphonic acid and alkanethiol SAMs on three metal substrates: Co, W and Ru. After SAM deposition, model metal (Pt) and metal oxide (ZnO) ALD processes were performed to assess the quality and blocking ability of the SAM layer on the different substrates. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, X-ray reflectivity, water contact angle (WCA) goniometry, and atomic force microscopy were used to characterize modified samples before and after ALD.

Overall, we observed that the most passivating SAMs of both alkylphosphonic acids and alkanethiols are consistently formed on Co and Ru; SAMs formed on W are less well-packed and hence less reliable in blocking ALD. In fact, XPS results did not show evidence that a SAM was formed on the W substrate following deposition of ODPA in t-butanol, even though increased WCA was observed. Moreover, the solvent was found to play an important role. We found that after a 48h deposition, the Co and Ru substrates passivated using ODPA in t-butanol showed WCA 5° higher on average than when passivated in a toluene solution. Conversely, W substrates showed WCAs < 90° when t-butanol was used as a solvent, but >100° when toluene was used. These results may be explained in terms of the poor Lewis acid character of the W substrate and may indicate a larger role of solvent-substrate interactions in SAM deposition. These studies provide insights that are important for consideration in the development of fabrication processes which incorporate SAMs for AS-ALD.

11:20am **TF-ThM11 Area-selective ALD of Ru by Combining an ABC-type ALD Process and O_2 Plasma Etching**, *S.N. Chopra, M.F.J. Vos*, Eindhoven University of Technology, The Netherlands, *J.G. Ekerdt*, The University of Texas at Austin, *W.M.M. Kessels*, ***Adrie Mackus***, Eindhoven University of Technology, The Netherlands

Area-selective atomic layer deposition (ALD) is expected to be an enabling technology for the fabrication of future nanoelectronics with sub-10 nm dimensions. In practice it is extremely difficult to achieve high selectivity for area-selective ALD because of undesirable growth initiation on defects and impurities. Given that many processes exist for etching materials, novel combinations of area-selective ALD and etching are currently being considered to eliminate this unwanted growth.[1] In this work, the selectivity of area-selective ALD of Ru on Pt patterns (metal-on-metal deposition) is improved by etching Ru using an O_2 plasma after or during the deposition.

ALD of Ru was carried out using an ABC-type process consisting of ethylbenzene-cyclohexadiene Ru(0) precursor, O_2 gas, and H_2 gas steps. The additional H_2 dosing step ensures that metallic Ru is deposited by reducing the RuO_2 top layer every cycle. This ABC-type ALD process allows for Ru deposition at low temperatures to exploit the larger differences in growth rates on SiO_2 versus Ru or Pt for achieving area-selective ALD. However, even at the low temperature of 150 ºC, for which 500 Ru ALD cycles on Ru resulted in 17.5 nm growth, undesirable Ru islands were observed on the SiO_2 non-growth substrate.

When Ru is exposed to O_3 or to an O_2 plasma, RuO_4 is formed as a volatile reaction product. Because O_2 plasma has a high selectivity toward Ru etching, it can be used in a post-deposition treatment to eliminate residual Ru islands from the SiO_2 non-growth substrate. Area-selective ALD with an almost perfect selectivity was obtained when performing supercycles consisting of Ru ABC cycles and an O_2 plasma etch step every 100 cycles. The selectivity of the growth was investigated by performing Ru ALD on Pt-containing seed layers patterned by electron beam induced deposition (EBID) on SiO_2 substrates.[2] The O_2 plasma etch does not significantly influence the properties of the Ru on the seed layer patterns as will be shown in the presentation.

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

2. A.J.M. Mackus, S.A.F. Dielissen, J.J.L. Mulders, and W.M.M. Kessels, *Nanoscale* **4**, 4477 (2012).

11:40am **TF-ThM12 Enhancing the Inherent Area-selective ALD of TiO_2 using BCl_3**, ***Seung Keun Song***, *P.C. Lemarie, G.N. Parsons*, North Carolina State University

Area selective deposition of thin film becomes increasingly important as semiconductor industries require shorter node than 10nm scale to alleviate trade-offs between performance and power consumption. Since inherent substrate-dependent selectivity shows relatively narrow selective window, enhancing procedure is required. TiO_2 atomic layer deposition (ALD) using titanium tetrachloride ($TiCl_4$) and water has been observed to selectivity deposit TiO_2 on Si-OH preferentially over Si-H surfaces. However, the selectivity is lost after initial incubation cycles. In an attempt to better understand selectivity loss mechanisms, we studied the role of surface hydrophobicity and found that the incubation period increased as the contact angle of the initial substrate surface also increased. Furthermore, we incorporated BCl_3 into our TiO_2 ALD sequence to further enhance the overall selectivity. Through the ellipsometry thickness measurement, TiO_2 ALD with BCl_3 shows more delayed TiO_2 growing on Si-H without delaying on Si-OH. Using quartz crystal microbalance (QCM) we show that BCl_3 appears to impede TiO_2 growth, rather than significantly etching TiO_2. Finally, we provide evidence that the ability to effectively impede TiO_2 deposition on Si-H without significantly reducing deposition on the Si-OH surface depends on the amount and frequency of BCl_3 dosing. This work ensures better selectivity than previous result.

12:00pm **TF-ThM13 Selective ALD by Intercalation of Etching Cycles in PEALD Process**, ***Rémi Vallat***, *R. Gassilloud*, CEA/LETI-University Grenoble Alpes, France, *C. Vallée*, Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France

Therefore complementary techniques are needed to continue extreme scaling and extend Moore's law. Selective deposition processes can be used to increase and enhance patterning capabilities at very low cost. In our lab, a new selective Plasma Enhanced ALD process has been developed by adding etching steps in the PEALD flow. To be effective, 3 conditions must be satisfied (Figure 1):

- A different nucleation delay on different substrates
- A nm scale etching of the thin film
- The etching step must add a new nucleation delay

We used this process for the selective deposition of Ta_2O_5 with TBTDET (TertButylimido Tris(DiEthylamino Tantalum) precursor and a plasma gas mixture of O_2/Ar/NF_3 for deposition and etching steps. Ta_2O_5 has been selectively deposited on a metal substrate (TiN) versus SiO_2 and Si substrates (no deposition on these substrates). For this process, the different substrates have been patched onto a Si wafer and introduced simultaneous into the PEALD reactor. [1]

For this presentation we will present the selective process developed for TiO_2 with TDEAT (Tetrakis DiEthylAmido Titanium) precursor. The ALD selective process has been successfully developed for the deposition of TiO_2 on three different metallic substrates (TiN, NiPt and W). As for Ta_2O_5 deposition, a thin TiO_2 film is deposited on the different metal substrates but not on Si and SiO_2 substrates although all substrates are introduced simultaneously in the deposited chamber. Details on the process will be given during the presentation with a focus study on precursors and radicals interactions with the different surfaces after each step of the process. In this study, quasi in situ XPS was used. Figure 2 shows Ti*2p* peak for one titanium pulse on silicon substrate with or without etching step. Fluorine treatment lead to thinner layer. This difference is explained by Si-F and Si-O-F bonds presence at the surface. This fluorine bonds blocks the titanium growth.

The thin oxide films selectively deposited will be used in 3D nonvolatile memory devices. Our objective is to realize a crosspoint memory in backend level from a pattern area or a trench area without the photolithography step. Therefore, electrical properties of the Ta_2O_5 and TiO_2 oxides deposited with the standard PEALD process are compared to those of thin films selectively deposited thanks to C(V), C(f) and I(V) measurements. We will show that the selective ALD process does not degrade the dielectric properties of the films in terms of leakage current and electrical field breakdown. Resistive memories cycles are also compared and discussed. Finally, 3D structures with the selective deposition process will be shown.

Tribology Focus Topic
Room: 10 - Session TR+AC+TF+VT-ThM

Lubricant, Coatings, and Biotribology
Moderator: J. David Schall, Oakland University

8:00am **TR+AC+TF+VT-ThM1 Superlubricity of Hard Compliant Carbon Coatings with Green Lubricants: Role of Surface Chemistry and Structural Changes**, ***Maria-Isabel De Barros Bouchet***, Ecole Centrale de Lyon - LTDS, France **INVITED**

Reduction of energy loss by mechanical friction has been strongly required in recent years for improving fuel efficiency especially for automotive engine. Even at a modest rate, it is of primary importance to reduce parasitic energy losses and provide environmental sustainability. An approach to achieve this target is the development of new lubrication technologies, combining new lubricant formulations and cutting-edge coatings transferable to industrial applications. Since superhard carbon material like tetrahedral amorphous carbon (ta-C) and Nano-Crystalline Diamond (NCD) coatings combine both crucial properties, high hardness with an ultra-smooth surface roughness, they have attracted a growing interest in the last decade. While the friction coefficient is generally extremely high under ultra high vacuum conditions, in the earlier years we have discovered the ability of these coatings to be lubricated by selected biodegradables green molecules like fatty acids, glycerol mono-oleate GMO and polyols, as well as their mixture with synthetic base oil such as Poly-Alpha Olefines (PAO). Some of these compounds are able to lubricate ta-C and NCD coatings with a friction coefficient below 0.01 (so-called superlubricity) in thin-film EHL/mixed regime and below 0.03 in severe boundary regime without significant wear1. As this case of superlow friction is extremely promising for many applications fields, the related mechanism has been investigated and a special attention has been paid to the surface chemistry and structural changes of the carbon coatings. By coupling advanced extreme surface analyses (PES and XANES), we show that the mechanism of friction reduction is related to the tribo-formation of quasi-2D planar graphene-like structures at the top of the colliding asperities (thickness about 1 nm). Eventually, the graphene can be slightly oxidized by the OH-groups coming from the tribo-decomposition of the lubricant molecules trapped between asperities. Moreover, the rubbed sub-surface is enriched with sp2-hybridized carbon, such as in a soft a-C material, during the friction2. These strong structural changes certainly ease the tribochemical-formation of the carbon rings present in the graphene-like structure as pointed out by atomistic computer simulations.

1. M. Kano, J. M. Martin, K. Yoshida, M.I. De Barros Bouchet, Friction J., 2 (2) (2014) 156.

2. M.I. De Barros Bouchet, J.M. Martin, J. Avila, M. Kano, K. Yoshida, T. Tsuruda, S. Bai, Y. Higuchi, N.i Ozawa, M. Kubo and M. C. Asensio, Scientific Reports, 2017 (DOI: 10.1038/srep46394).

8:40am **TR+AC+TF+VT-ThM3 Role of Deuterium and Hydrogen in the Physical Understanding of Nano-friction in a-C:H/D Thin Films**, *F.G. Echeverrigaray, S.R. Sales de Mello, A.F. Michels*, UCS, Brazil, *F. Alvarez*, UNICAMP, Brazil, ***Carlos Figueroa***, UCS, Brazil

The friction phenomenon is a complex manifestation of the nature. In spite of phenomenological laws can describe the friction force at different scales, the fundamental physical understandings of such a phenomenon do not have consensus. Phenomena such as phononic, electronic, magnetic, and also electrostatic effects and models were developed in order to explain the meta- and nano-friction behavior of materials. In this work, we report the friction behavior of a diamond spherical dome sliding on different amorphous carbon thin films containing different amounts of hydrogen and/or deuterium inspecting at the meta-nanoscale indentation. Two important situation are reported. Firstly, for samples where hydrogen was replaced by deuterium in the thin film bulk, the friction coefficient decreases for increasing *deuterium* included in the carbon underneath structure. Secondly, for samples where hydrogen content is increased on the surface, the friction coefficient decreases with the increasing of the ratio H/C at the surface. In this paper, we discuss two different physical mechanisms describing these peculiar experimental results: dissipation effects associated with phonon coupling and van der Waals forces contributions coexisting and determining the friction behaviour of a-C:H/D for the cited studied situations.

9:00am **TR+AC+TF+VT-ThM4 Imaging X-Ray Absorption Spectroscopic Investigation of the Mechanisms Behind the Environmental Dependence of the Tribological Properties of Amorphous Carbon Surfaces**, ***Filippo Mangolini***, University of Leeds, UK, *M. Koshigan,* Ecole Polytechnique Montréal, Canada, *M.H. Van Benthem, J.A. Ohlhausen,* Sandia National Laboratories, *J.B. McClimon, J. Hilbert,* University of Pennsylvania, *J. Fontaine,* Ecole Centrale de Lyon, France, *R.W. Carpick,* University of Pennsylvania

Among the variants of diamond-like carbon films developed for the ever-increasing performance and durability requirements of tribo-mechanical applications, silicon oxide-containing hydrogenated amorphous carbon (a-C:H:Si:O) is of interest as it exhibits good tribological performance across a broader range of environments compared to hydrogenated amorphous carbon, and higher thermo-oxidative stability. However, the scientific basis for this improved behavior is not established. In this work, we develop a fundamental understanding of the structural transformations occurring in a-C:H:Si:O when sliding against steel in different environments (from high vacuum to controlled hydrogen and oxygen pressures). The results of tribological experiments revealed that upon increasing the oxygen pressure in the experimental chamber from 10 mbar to 1000 mbar, the coefficient of friction increased from 0.02±0.01 to 0.06±0.01, whereas upon increasing the hydrogen pressure from 50 mbar to 2000 mbar, the coefficient of friction decreased from 0.08±0.01 to 0.02±0.01.The subsequent near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements and X-ray photoelectron spectroscopy (XPS) analyses provided insights into the structural transformations and chemical reactions occurring in a-C:H:Si:O upon sliding. Independently of the gas, a stress-induced conversion from sp^3-to sp^2-bonded (disordered) C-C bonds occurs. When sliding in hydrogen, the newly-generated, strained sp^2 carbon layer reacts with hydrogen molecules to form a hydrogenated amorphous carbon interfacial material. Upon increasing the hydrogen pressure, the fraction of C-H bonds increases in the near-surface region of the wear tracks formed on a-C:H:Si:O. This is proposed to progressively lower the shear strength of the material at the sliding interface, thus resulting in a decrease of friction with hydrogen pressure. When sliding in oxygen, the dissociative reaction of oxygen molecules with strained sp^2 C-C bonds leads to the formation of C=O groups. Additionally, increasing the oxygen pressure during tribological testing leads to an increase in oxygen concentration in the near-surface region of a-C:H:Si:O together with an increase in the fraction of Si atoms in high oxidation states. These surface chemical changes and structural transformations are proposed to increase friction with oxygen pressure by progressively increasing the shear strength of the material generated at the sliding interface.

9:20am **TR+AC+TF+VT-ThM5 Structure Evolution in Tribological Interfaces Studied by Multilayer Model Alloys**, ***Martin Dienwiebel***, *E. Cihan,* Karlsruhe Institute for Technology (KIT), Germany **INVITED**

During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called “third body” or “tribomaterial” forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-stady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS.During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called “third body” or “tribomaterial” forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-stady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS.

11:00am **TR+AC+TF+VT-ThM10 Carbon, Carbon Everywhere, from Catalysts to Hip Implants**, ***Laurence Marks***, Northwestern University **INVITED**

Friction is a pervasive problem, by some estimates consuming about 5% of the GDP of the economies of the developed world, and a recent analysis has indicated that about one third of the fuel energy in automobiles goes to overcoming frictional losses. While the importance of minimizing friction can be traced back at least as far as the tomb of Tehuti-Hetep, circa 1880 B.C, where a man can be seen pouring a lubricant to assist moving a statue, there are still many unknowns in the field of tribology which encompasses friction as well as other critical processes such as wear and lubrication. For many of the phenomena in tribology there are still numerous unknowns. When it comes to biological systems most work to date has assumed that different mechanisms are taking place than occur for inorganic systems. While there are differences, there are also significant similarities particularly in implants when inorganic and biological meet. We have recently shown that for metal implants in-vivo the same type of graphitic materials that appear in many areas ranging from heterogeneous catalysis to oil lubrication are present. Beyond just lubrication, corrosion of these materials is not special to biological systems, but has strong similarities to established factors such as grain boundary precipitation and a significant role for molybdenum as reducing the occurence of breakdown of the protective oxide film via complex processes involving solute trapping. These and related recent results will be described.

11:40am **TR+AC+TF+VT-ThM12 Tribology of Cellular Interfaces**, ***Angela Pitenis***, *J.M. Urueña, S.M. Hart, T.T. Hormel, C.S. O'Bryan, S.L. Marshall, K.D. Schulze, P.P. Levings, T.E. Angelini, W.G. Sawyer*, University of Florida **INVITED**

Human health, mobility, and quality of life critically hinge on the body’s ability to provide adequate lubrication between most contacting and sliding biological interfaces. Soft, aqueous, and mucinated biopolymer networks lining all moist epithelia enable the body to provide lubricity over a wide range of contact pressures and sliding speeds. The exquisite slipperiness and softness of biological sliding interfaces present significant experimental challenges for fundamental studies on their tribological performance. Physiological contact pressure conditions must be matched in in vivo, ex vivo, and in vitro studies that aim to acquire physiologically-relevant friction measurements. While biotribological investigations using living cells, cell layers, and tissues necessitate low contact pressure measurements, such studies frequently rely on the application of low forces to achieve accomodating contact pressures (kPa range), and traditional methods can decrease the contact area below a physiologically-relevant threshold. The softness of a cell layer (E ~ 10 kPa) provides an order-of-magnitude estimate for the amount of mechanical pressure that may be applied to cells during tribological testing; contact pressures about 5 kPa and shear stresses in excess of 200 Pa are sufficient to wreak significant damage to a cell layer. Recently, direct contact tribological experiments on a living cell layer without incurring any measurable cell death in the sliding path has become possible through the application of a soft, thin, spherically-capped membrane hydrogel probe. With this experimental configuration, in vitro tribological experiments were performed against a monolayer of mucin-producing human corneal epithelial cells (hTCEpi) for 10,000 reciprocating cycles at physiologically-relevant contact pressures and challenging sliding speeds. The gel-cell sliding interface under applied normal loads of ~ 200 μN resulted in measured friction coefficients of $\mu \sim 0.06$ and achieved shear stresses on the order of 60 Pa, which is below the critical shear stress for inducing cell death; excellent cell survival rates (~99.8%) were measured after extended duration tribological experimentation.

Plasma Science and Technology Division
Room: 23 - Session PS+TF-ThA

Plasma Enhanced ALD
Moderators: Steven George, University of Colorado at Boulder, Mingmei Wang, TEL Technology Center, America, LLC

2:20pm **PS+TF-ThA1 Mechanical, Physical, and Electrical Properties of Plasma-Enhanced Atomic Layer Deposition of Vanadium Nitride using Tetrakis(Dimethylamido)Vanadium and Nitrogen Plasma**, ***Mark Sowa***, Ultratech, Inc., *L. Ju, N.C. Strandwitz*, Lehigh University, *A.C. Kozen*, US Naval Research Laboratory, *G. Zeng, B.A. Krick*, Lehigh University

Vanadium nitride (VN) has been proposed for a variety of thin film electronics applications including interconnect diffusion barrier and supercapacitor electrodes. As with other transition metal nitrides, VN exhibits excellent mechanical properties and has been studied for its self-lubricating coating performance. VN thin films have been created primarily through PVD methods. Recently, atomic layer deposition of VN has been reported with tetrakis(diethylamido)vanadium (TDEAV) with NH_3 gas and tetrakis(ethylmethylamino)vanadium (TEMAV) with NH_3 gas and NH_3 plasma.

We report plasma enhanced atomic layer deposition results for VN using tetrakis(dimethylamido)vanadium (TDMAV) with N_2 plasma. Optimized TDMAV pulsing and N_2 plasma conditions have been established. Analyses include spectroscopic ellipsometry(thickness and optical properties), four point probe(resistivity), XPS(stoichiometry and impurities), XRD(crystallinity), XRR(density and thickness), and sliding wear testing(tribological properties). Depositions were investigated over 150 - 300 °C. Sub-100 μΩ-cm resistivities have been realized at 300 °C.

2:40pm **PS+TF-ThA2 Optimizing Process Parameters for Plasma Assisted Atomic Layer Deposition**, ***David Boris***, *V.D. Wheeler*, Naval Research Laboratory, *V.R. Anderson*, ASEE (residing at NRL), *N. Nepal*, Naval Research Laboratory, *S.G. Rosenberg*, ASEE Postdoctoral Fellow, *A.C. Kozen*, ASEE (residing at NRL), *J.K. Hite, S.G. Walton*, Naval Research Laboratory, *C.R. Eddy, Jr.*, U.S. Naval Research Laboratory

Plasma assisted atomic layer deposition (PA-ALD) is a low temperature conformal layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.

In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PA-ALD systems. In this work we employ optical emission spectroscopy and charged particle collectors to characterize a Fiji 200 (Ultratech/CNT) PA-ALD tool. In particular, we assess the total ion flux reaching the substrate surface and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions in context of PA-ALD of AlN and Ga_2O_3 films. Changes in plasma parameters are then linked with changes in film characteristics.

3:00pm **PS+TF-ThA3 Tuning of Optical and Structural Properties of ZnO Deposited by Room Temperature-plasma Assisted Atomic Layer deposition**, ***Alberto Perrotta***, *J. Pilz, A.M. Coclite*, Graz University of Technology, Austria

Wurtzite-structured ZnO thin films have been extensively investigated because of their unique optical, electrical, and piezoelectric properties, making it the material of choice in various applications such as transparent conducting electrodes, surface acoustic wave devices, and as sensors. In engineering ZnO-based devices, the material characteristics have to meet specific requirements in terms of opto-chemical and electrical properties and crystalline structure, together with very high conformality and thickness control. Plasma-assisted atomic layer deposition (PA-ALD) has been shown able to deposit very high quality ZnO thin films, combining the low process temperature with the exceptional atomic-thickness control. Furthermore, the properties of the material can be tuned by varying the plasma characteristics, making it suitable to adapt the material to specific applications.

In this contribution, high quality ZnO thin films have been deposited by PA-ALD optimized at room temperature, adopting diethyl zinc (DEZ) and oxygen plasma. The properties of the material have been investigated as a function of the radio frequency plasma power and plasma exposure time, and characterized by X-ray diffraction (XRD), gracing incidence XRD with synchrotron radiation, spectroscopic ellipsometry (SE), and X-ray photoelectron spectroscopy (XPS). The X-ray diffraction patterns of polycrystalline ZnO thin films showed rather preferred (100) orientation and XPS analysis showed the complete removal of the DEZ carbon ligands, confirming the possibility to obtain high quality crystalline ZnO at room temperature. Furthermore, the effect of the plasma power on the opto-chemical properties, growth, and crystalline structure has been investigated. Finely tuning of the optical properties of the PA-ALD ZnO layers has been achieved, with refractive index ranging between 1.82 and 1.89 at 633 nm. Moreover, the absorption has been found to increase and shift in the visible range at low plasma power. In addition, XRD showed a distortion of the (100) peak at low and high plasma power, indicating the possibility to vary the crystallite size as a function of the plasma parameters.

As an outlook, the optimized PA-ALD process at room temperature allows the deposition of ZnO on thermo-sensitive nanostructured templates, inferring the possibility to adopt it in engineering (flexible) structured devices.

3:20pm **PS+TF-ThA4 Influence of Plasma Power on the Si Solar Cell Passivation Properties of Al_2O_3 Thin Films deposited by Atomic Layer Deposition at 90 °C**, *Z. Zhu*, Beneq Oy, Finland, *P. Sippola*, Aalto University, Finland, ***Emma Salmi***, Beneq Oy, Finland

In the recent years ALD Al_2O_3 surface passivation for Si solar cells has gained increasing popularity. The excellent passivation properties of ALD Al_2O_3 are based on a combined effect of chemical passivation and fixed high negative charge density. A bulk of the work has concentrated on thermal ALD, but also plasma enhanced ALD (PEALD) has been considered. However, the effect of plasma parameters, particularly plasma power, on the passivation properties remain uncharted.

In this work, we have studied the effect of plasma power on the properties of PEALD Al_2O_3 deposited at low temperatures with focus on the Si solar cell passivation. The Al_2O_3 was grown from TMA and O_2 plasma. All depositions were done with a Beneq TFS 200 ALD reactor at 90 °C. The lifetime was studied for as deposited and post-annealed samples.

The plasma power significantly affected the film properties. Low plasma power appeared to lead to the lowest film quality in regards of purity, density and refractive index. When the power was increased from 50 to 100–300 W the density increased from 2.6 to 2.8 g/cm^{-3}. Similarly, the refractive index increased from 1.61 to 1.62 (at 628 nm). The higher plasma power appeared to increase the amount of available O radicals, leading to more efficient reaction completion and improved film optical and structural properties. The same trend was also clear for the passivation properties for Si solar cells. For a 25 nm Al_2O_3 deposited with 50 W plasma power and annealed at 400 °C the lifetime at 10^{15} cm^{-3} injection level was 1.1 ms, while for Al_2O_3 deposited with 100 or 180 W it was 2.0 ms. The interface properties were also influenced. The 50 W sample had the lowest density of negative charge and the highest interface defect density, which agreed with the lower lifetime of the sample. Interestingly, the 100 W sample had the lowest level of defect density. This can be related to the more moderate level of ultraviolet radiation from the O_2 plasma that the 100 W sample was exposed to as compared to the 180 W sample. Nevertheless, the 180 W sample had the best passivation properties due to its highest negative charge density. In fact, the negative charge density plays a major role in surface passivation when the magnitude of the negative charge density is much greater than that of the defect density.

High quality surface passivation of Si solar cells was achieved with PEALD Al_2O_3 grown at 90 °C. The passivation properties were shown to significantly improve with increasing plasma power.

4:00pm **PS+TF-ThA6 Optimizing MoO_3 Plasma-enhanced ALD Thin Films for use in Controllable 2D Material Synthesis**, ***Brittney Burant***, MIT Lincoln Laboratory

Monolayer MoS_2 is a direct bandgap semiconductor with promising properties for novel devices. It has been shown that valley polarization can be achieved in MoS_2 monolayers with circularly polarized light, which would allow the realization of novel information processing architectures through manipulation of the valley pseudo-spin. However, current production methods of MoS_2 monolayers are either low yielding, or of relatively poor quality for valleytronic applications. To control the layer number, defectivity, and crystallinity of MoS_2, a novel method for limiting growth through the sulfurization of wafer-scale MoO_3 thin films has been developed.

Thorough characterization of the MoO_3 plasma-enhanced ALD process was performed to understand the effect of MoO_3 process parameters on the resultant MoS_2. MoO_3 films of 20-35 nm were deposited utilizing $(NtBu)_2(NMe_2)_2Mo$ as the organometallic precursor and O_2 plasma for the oxygen source. Variations in Mo precursor dose time and O_2 plasma exposure time show the expected trends, but substrate temperature effects are more significant. Growth per cycle increases with substrate temperature, from 0.88 Å/cycle at 100 ºC, to 1.32 Å/cycle at 350 ºC, with the highest GPC of 1.4 Å/cycle at 300 ºC. Raman spectroscopy shows that films grown at low temperature are amorphous, while polycrystalline film growth occurs above 250 ºC. These results are consistent with previously demonstrated MoO_3 growth utilizing the same process and precursor[1]. Surface roughness, as measured by AFM, also increases with temperature, which is consistent with a transition to polycrystalline film growth. Through XPS analysis, the deposited films were determined to be sub-stoichiometric in all deposits, averaging an O/Mo ratio of 2.6, regardless of substrate temperature.

MoS_2 films were grown on bare sapphire wafers by placing MoO_3 source wafers face-to-face with growth wafers. The wafers were oriented horizontally and enclosed in a graphite susceptor to enable inductive heating. Spacing between the MoO_3 source wafer and sapphire growth wafer was varied from 0 to 1 mm, and wafers were reacted at 700 ºC in H_2S gas. Initial reactions have shown increasing film deposition with decreased spacing between growth and source wafers. These results suggest that MoS_2 film growth by this method is vapor-phase transport limited. XPS data confirms the formation of MoS_2 on the growth wafer, however several layers of growth are observed. The effect of MoO_3 source wafer crystallinity on MoS_2 film quality is under investigation and will be presented.

[1] Vos, M., Macco, B., Thissen, N., Bol, A., Kessels, W. *JVST A*, **2015**, 34(1), 01A103-1-7.

4:20pm **PS+TF-ThA7 Plasma ALD of Fluorides: Process Characterization and *In Situ* Study of AlF_3 ALD**

Harm Knoops, Oxford Instruments Plasma Technology, UK, *M.F.J. Vos, W.M.M. Kessels, A.J.M. Mackus*, Eindhoven University of Technology, The Netherlands

In this work we used TMA ($AlMe_3$) and SF_6 plasma for atomic layer deposition (ALD) of aluminum fluoride (AlF_3) films. SF_6 plasma is a novel co-reactant for ALD and we employed quadruple mass spectrometry (QMS) and optical emission spectroscopy (OES) to study the film growth. AlF_3 as well as other metal fluorides such as MgF_2 and CaF_2 generally have a wide bandgap (>10eV) and low refractive index (1.3-1.6). Due to these interesting properties they find use in many applications, including passivation layers in Li-ion batteries, electron transport layers in photovoltaics and protective coatings for optical devices. Previously, ALD of fluorides has been demonstrated using TiF_4 and TaF_5 as the fluorine source for the deposition of MgF_2, CaF_2 and LaF_3 and more recently using HF for AlF_3, ZrF_4, MnF_2, HfF_2, MgF_2 and ZnF_2.[1,2] The novel approach of using SF_6 plasma as a fluorine source is a promising alternative to HF, because of the ease of handling that SF_6 offers. Furthermore, SF_6 plasma provides increased reactivity at lower temperatures and allows for reduced purge times, similar to the benefits of using an O_2 plasma instead of H_2O for metal oxide ALD.

AlF_3 films were prepared on Si samples over a temperature window of 50°C to 300°C. Since SF_6 plasma etches Si and SiO_2, a thin Al_2O_3 layer was deposited prior to AlF_3 growth. Using *in situ* spectroscopic ellipsometry (SE) the growth per cycle (GPC) was determined to decrease from 1.5Å at 50°C to 0.5Å at 300°C. Interestingly, no significant impurity levels of S, C and O were detected in the bulk of the AlF_3 films using X-ray photo-electron spectroscopy (XPS), even for low deposition temperatures. Furthermore, XPS measurements showed a F/Al ratio of 3.0±0.2. The low impurity content and the stoichiometric F/Al ratio are in line with a refractive index of 1.35 at 633nm as determined by SE.

The reaction mechanism of the ALD process was addressed based on a combination of OES and QMS. These measurements suggest that CH_4 is released during the TMA dosing, and that CH_4, C_2H_2, HF, and CH_xF_y–species are formed during the plasma exposure. Furthermore, the reaction products during the plasma exposure show different trends in their release (e.g., mostly directly after striking the plasma or peaking after a few seconds of plasma exposure), which will be used to suggest a possible reaction mechanism. In addition, consumption of F can be observed similar to what is found in etching using SF_6 plasma. Overall this work shows that SF_6 plasma is a promising co-reactant which can inspire the ALD of a wide range of metal fluorides.

[1] Pilvi *et al.*, Chem. Mater. **20** (2008)

[2] Lee *et al.*, Chem. Mater. **28** (2016)

4:40pm **PS+TF-ThA8 Ion Energy Control During Remote Plasma ALD for Tuning Material Properties of Transition Metal Nitrides**

Tahsin Faraz, Eindhoven University of Technology, Netherlands, *H.C.M. Knoops*, Oxford Instruments Plasma Technology, UK, *S. Karwal, M.A. Verheijen, A.A. van Helvoirt*, Eindhoven University of Technology, Netherlands, *D.M. Hausmann, J. Henri*, Lam Research Corporation, *M. Creatore, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, it has been shown that the ion energy can play a significant role on the physical and chemical properties of thin films grown using plasma-enhanced atomic layer deposition (PEALD).[1] In this work, we demonstrate the impact of ion energy control during PEALD of transition metal nitrides (e.g., TiN_x, HfN_x, etc.) which are of great interest for nanoelectronic device applications owing to their low electrical resistivity and excellent diffusion barrier properties.[2] Ion energy control during plasma exposure was carried out in a commercial 200 mm remote plasma ALD system (Oxford Instruments FlexAL) equipped with radio-frequency (RF) substrate biasing (13.56 MHz, up to 100 W power, -350 V resulting DC bias voltage). In such low pressure, remote inductively-coupled-plasma reactors, the ion energy can be controlled independently of the ion flux by applying an RF bias signal on the substrate table during the plasma exposure step.

Depositions performed under no bias conditions for TiN_x (at 200°C) and HfN_x (at 450°C) films using a 10 s H_2 (+Ar) plasma yielded electrical resistivities of 1960±60 and $(900\pm0.7)\mathrm{x}10^3$ μΩcm and mass densities of 3.8±0.2 and 10.1±0.2 g/cm^3, respectively. Enhancing ion energies with substrate biasing during PEALD was observed to have pronounced effects on the chemical composition, microstructure and material properties of these transition metal nitrides. Energetic ion bombardment through application of bias voltages lowered film resistivity by one order of magnitude for TiN_x (139±10 μΩcm at -187V bias) and by two orders of magnitude for HfN_x ($(330\pm70)\mathrm{x}10^1$ μΩcm at -130V bias) while also increasing their respective mass densities (4.9±0.2 and 10.5±0.2 g/cm^3). The residual stress of these films were also observed to change from tensile under no bias to compressive under bias conditions. The oxygen impurity content for films deposited without substrate biasing (~20 to 30%) was observed to be significantly reduced (≤ 4%) in films grown with bias voltages applied during plasma exposure. Furthermore, it will be discussed how the use of substrate biasing enhances PEALD process capability by providing several additional knobs (magnitude, duration and duty-cycle of bias, etc.) for tuning a wide range of material properties.

[1] Profijt et al., *J. Vac. Sci. Technol. A*, **31**, 01A106 (2013)

[2] Karwal et al., *J. Vac. Sci. Technol. A*, **35**, 01B129 (2017)

5:00pm **PS+TF-ThA9 Understanding the Challenges in Atomic Layer Deposition of SiN_x through Identification of the Surface Reaction Mechanisms**

Rafaiel Ovanesyan*, Colorado School of Mines, *D.M. Hausmann*, Lam Research Corporation, *S. Agarwal*, Colorado School of Mines

The rapid shrinking of semiconductor devices has created a need for the low-temperature (≤400 °C) atomic layer deposition (ALD) of highly-conformal silicon nitride (SiN_x) and C-containing SiN_x films. However, to date, the ALD of these films remains challenging. In this work, we report the surface reaction mechanisms during the ALD of SiN_x and C-containing SiN_x for several ALD processes. Initially, our research focused on a baseline SiN_x ALD process that used alternating exposures of Si_2Cl_6 and NH_3 plasma. This process was subsequently modified by replacing the NH_3 plasma half-cycle with a CH_3NH_2 plasma to simultaneously incorporate both C and N. Finally, to overcome the limitations of SiN_x films deposited using H-containing plasmas, a three-step ALD process was developed that used Si_2Cl_6, CH_3NH_2, and N_2 plasma. The film composition, reactive surface sites, and adsorbed surface species were monitored using in situ attenuated total reflection Fourier transform infrared spectroscopy, which allowed us to elucidate the surface reaction mechanisms. In addition, in situ four-wavelength ellipsometry was used to obtain the growth per cycle (GPC). Ex situ analysis was used to obtain the conformality and elemental composition.

For the baseline Si_2Cl_6 and NH_3 plasma ALD process, our infrared spectra show that on a post-NH_3-plasma-treated SiN_x growth surface, Si_2Cl_6 reacts with surface $–NH_2$ species to form $–NH$ and $–Si_xCl_{2x-1}$ (x = 1, 2) surface species. In the subsequent NH_3 plasma step, the $–Si_xCl_{2x-1}$ surface species are removed and the $–NH_2$ surface species are restored, allowing for the continuation of the ALD process. Film growth during the Si_2Cl_6 and CH_3NH_2 plasma ALD process occurs via an almost identical reaction mechanism, with the exception that C is incorporated in the form of -N=C=N- species during the CH_3NH_2 plasma step. In the three-step ALD process, Si_2Cl_6 again reacts with surface $–NH_2$ species, while in the CH_3NH_2 step, the CH_3NH_2 reacts with $–Si_xCl_{2x-1}$ surface species via the formation of Si-N linkages to form $Si_2N\text{-}CH_3$ surface species. During the N_2 plasma step, the $Si_2N\text{-}CH_3$ surface

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* **TFD James Harper Award Finalist**

species are removed and the $–NH_2$ species are restored. When we compare the GPC and conformality (see Fig. 1) of the three-step ALD process to an aminosilane and N_2 plasma ALD process, we observe that the three-step ALD process has a higher conformality (~90%) and a higher GPC (~0.9 Å). However, these values are less than those reported for NH_3- or CH_3NH_2-plasma-based ALD processes. This suggests that the three-step ALD process behaves as an intermediate between an NH_3- or CH_3NH_2-plasma-based ALD process and an aminosilane and N_2 plasma ALD process.

5:20pm **PS+TF-ThA10 First-Principles Understanding and Kinetic Monte Carlo Analysis of Reaction Mechanisms in Plasma Enhanced Atomic Layer Deposition of Silicon Nitride**, *G. Hartmann*, University of Texas at Austin, ***Peter Ventzek***, *J.P. Zhao*, Tokyo Electron America, *T. Iwao, K. Ishibashi*, Tokyo Electron Tohoku Limited, *G. Hwang*, University of Texas at Austin

Plasma enhanced ALD (PEALD) allows fabrication of high quality and ultra-conformal SiN deposition at low temperature. The PEALD of SiN films involves a repetitive two-step process of i) silicon-containing precursor adsorption/decomposition and ii) nitridation. Halogenated silanes such as hexachlorodisilane, bis(tertiary-butyl-amino)- silane, and dicholorosilane (DCS, SiH_2Cl_2) have been utilized as Si precursors and nitrogen, hydrogen or ammonia have been used as nitrogen precursors. Despite previous studies, the underlying reaction mechanisms of these Si precursors with a nitrogen containing surface during PEALD still remain uncertain. First-principles density-functional theory (DFT) calculations have been used to identify a novel mechanism for the adsorption and decomposition of DCS on a hydrogenated SiN surface. Our study predicts that the DCS adsorption and dissociation can occur by overcoming a relatively low barrier (< 0.3 eV), far lower than the prohibitively large barriers predicted for previously proposed mechanisms. Through a detailed electronic structure analysis of the reaction intermediates, we have also elucidated the principles underlying the DCS adsorption and dissociation, notably the hypervalent nature of Si which permits chlorosilanes to adsorb prior to dissociation. A proper model of the interactions between the SiN surface are necessary to explain the ALD process and also indicate the mechanism for the formation of side products, which has a considerable contribution to the thermodynamic favorability of the proposed mechanism. Insights from the first principles calculations are incorporated into a Kinetic Monet Carlo Model (KMC) to illustrate different process scenarios. Understanding these principles allows us to develop guidelines for processing conditions, such as the importance of maintaining the proper surface composition to support Si precursor adsorption and dissociation.

5:40pm **PS+TF-ThA11 *High Quality Crystalline AlN Films Produced by PEALD with Microwave ECR Plasma below 200 ºC***, ***Jesse Kalliomäki***, *V. Kilpi, T. Malinen*, Picosun Oy, Finland, *H. Enami, N. Mise*, Hitachi High-Technologies Corp., Japan, *H. Hamamura, T. Usui*, Hitachi R&D Group, Japan

Due to continuous feature size scaling down and change to the 3D structures new process innovations are now required more than ever. Conformal film formation of Al compounds such as AlN is one of the key technologies. AlN is widely used in thermal management applications and due to its compatibility with III–V compounds it has shown growing interest e.g. as interface material. There is also huge potential for AlN in MEMS manufacturing. PEALD at low temperature is one of the suitable solutions for these applications.

We have earlier reported the superiority of low pressure microwave ECR(M-ECR) plasma for Si substrate nitridation at low temperature [1]. In present study, AlN film properties were evaluated for demonstrating the advantage of the newly combined tool with the M-ECR plasma and the leading ALD system from Picosun. TMA (Trimethylaluminum) was used as Al precursor while nitrogen plasma was generated with M-ECR plasma generator to form AlN. Film properties such as density, crystallinity and conformality were studied. Composition of film was analyzed by XPS with Ar sputter.

AlN film properties were investigated as a function of deposition temperature as shown in **Fig. 1.** The film density increases with deposition temperature and at 200°C the density is 3.09g/cm^3, which is consistent for literature values for bulk AlN [2]. It was shown that longer N_2 plasma exposure time improved film density. The temperature series in **Fig. 1** shows that the growth rate was 0.57Å/c and 0.54Å/c at 100 and 250ºC, respectively. Interestingly, it was found a thickness dependent crystallization. For 20nm films deposited between 100 and 250ºC showed an amorphous structure, whereas 30nm film thickness and above show crystalline structure (verified by XRD) and higher roughness, see **Fig. 2**. Good quality films with conformality of < 0.5% (1σ non-uniformity) for 300mm wafer and high purity (C<1%, O<3%) were achieved. Efficient generation of the radicals and ions by M-ECR plasma at low pressure [3] is supposed to improve the film properties.

The step coverage obtained in this study at AR 1:20 is >90% as shown in **Fig. 3.** This is promising for 3D device fabrication where conformal coating of high aspect ratios is crucial. From these results, PEALD with M-ECR plasma can be one of the most advantageous solutions for next generation devices and opens the possibilities for beyond-silicon CMOS devices.

[1] H.Hamamura *et al.*, 16th International Conference on Atomic Layer Deposition (ALD2016)

[2] JCPDF 00-003-1144 (AlN)

[3] H.Enami *et al.*, submitted to ALD2017

Thin Films Division
Room: 21 - Session TF+MI+NS-ThA

ALD and Nanostructures
Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Richard Vanfleet, Brigham Young University

2:20pm **TF+MI+NS-ThA1 Coating and Infilling 3D Geometries by Low-T CVD : HfB_2 throughout 0.5 mm Thick CNT Forests**, ***John Abelson***, University of Illinois at Urbana-Champaign **INVITED**

We describe the use of extremely conformal chemical vapor deposition to coat carbon nanotube forests throughout their depth with a film of HfB_2, a mechanically hard, electrically conductive and highly refractory alloy. CVD uses the precursor $Hf(BH_4)_4$ at partial pressures ≤ 15 Torr at substrate temperatures ≤ 200°C. The CNT forests are up to 500 µm thick and can be shaped by pre-depositing patterns of seed metal on the underlying substrate prior to their synthesis.

Coating CNT forests affords a new class of composite foams with adjustable mechanical properties : the HfB_2 coating both stiffens individual tubes and “welds” them together wherever they touch, whereas in the uncoated forest the tubes can slide relative to one another. We fabricate cylindrical pillar structures with HfB_2 thicknesses from 3-50 nm. As measured by nanoindentation using a flat punch, the Young’s modulus varies over three orders of magnitude as $E \sim \rho^{1.7}$, where the mass density ρ is dominated by the HfB_2 coating. The maximum stiffness and strength are 56 and 1.9 GPa, respectively.

A major question is how CVD can achieve a nearly uniform coating in such a deep structure. The challenge is inherent in the diffusion-reaction kinetics : the transport of reactants occurs by molecular diffusion, which is slow in narrow cross-sections; while at the same time the reaction (consumption) rate must be high enough to be useful. In combination, these factors imply that the partial pressure (flux) of reactants must diminish with depth; if the film growth rate varies monotonically with flux, then the coating thickness must decline with depth in the structure.

The solution is to (i) employ a precursor that exhibits a hard saturation in the growth rate vs. partial pressure, (ii) use a high partial pressure above the sample, and (iii) grow at low temperature to limit the reaction rate. Under these conditions, even though the partial pressure of precursor drops considerably from the top to the bottom of the sample, the growth rate remains almost constant. To achieve the high precursor pressure, we employ a static (unpumped) reaction tube apparatus. We previously derived a master relationship [1] that predicts the precursor pressure (p) necessary to achieve a desired step coverage (SC) and growth rate (GR) in a given aspect ratio (AR) given knowledge of the atomic density (r), growth rate coefficient (K) and molecular diffusivity (D_0): $p = (GR\ AR) * ((c\ r\ kT) / (2\ D\ K) * (1 - SC))$^0.5

We will discuss extension of this method to other thin film systems and substrate geometries.

1. A. Yanguas-Gil, Y. Yang, N. Kumar, and J. R. Abelson, JVST A **27,** 1235 (2009) [DOI: 10.1116/1.3207745]

3:00pm **TF+MI+NS-ThA3 Varying Penetration Depths in ALD on High Aspect Ratio Carbon Nanotube Forests**, ***David Kane***, *RC. Kane, R.R. Vanfleet*, Brigham Young University

We have observed steps in the penetration depth in atomic layer deposition on tall vertically aligned multiwall carbon nanotube (MWCNT) forests. The deposition thickness at the top of the forest is greater than that at the bottom and varies in distinct steps. The MWCNT forests used were 200 µm tall with an aspect ratio of about 2000. In the thermal TMA/water process on MWCNTs, precursor pulse times ranged from 0.5s to 2s. We propose a model for banding where Al2O3 nuclei grow in each cycle, thus the number of TMA adsorption sites increases. Due to the confined geometry, Knudsen diffusion and adsorption site density determine the relationship between precursor penetration depth and exposure time. The penetration depth is inversely proportional to the square root of the precursor adsorption site density and proportional to the square root of the exposure time. We have measured the penetration depth for different bands and a good fit to our model is shown.

3:20pm **TF+MI+NS-ThA4 NiOx Decorated Platinum Nanoparticles Via Atomic Layer Deposition for Enhanced Sintering Resistance**, ***Jiaming Cai***, *K. Cao, M. Gong, B. Shan, R. Chen*, Huazhong University of Science and Technology, PR China

Platinum nanoparticles (NPs) play an important role in the catalytic applications such as conversion of automotive exhaust, fuel cells, nano sensing and so on. For most catalytic applications, sintering of Pt NPs is undesired since the coalescence decreases the number of active sites of the catalyst. Herein we report the utilization of active oxide layers to encapsulate Pt NPs to enhance sintering resistance at high working temperature. The active oxide coated catalysts have additional metal-oxide interfaces which may further improve the catalytic activity besides good sintering resistance. Nickel oxide coating layer is prepared via atomic layer deposition (ALD) method. The effect of layer thickness towards catalytic properties and thermal stability for CO oxidation are investigated. The thickness of nickel oxide coating layer was controlled accurately by varying the ALD cycles. Characterizations including TEM, XPS, FTIR and XAFS were undertaken to explore the origin of the CO oxidation catalytic activity enhancement. *In-situ* AFM test is carried out to explore the mechanism of nanoparticles migration and sintering phenomenon in different environment by controlling the calcination temperature and oxygen partial pressure. Nickel oxide anchors Pt NPs with a strong metal oxide interaction, and coating structure around Pt NPs provide physical blocking that suppresses NP particle migration and coalescence. The catalysts show both enhanced CO conversion activity and improved sintering resistance up to 700 °C under oxidative atmospheric conditions.

4:00pm **TF+MI+NS-ThA6 Atomic Layer Deposition of HfO_2/Al_2O_3 Nanolaminates on Single-crystal GaN and Ga_2O_3: Investigation of Device Degradation in Power Semiconductor Devices**, ***David Mandia***, *A. Yanguas-Gil, J.A. Libera, J.W. Elam*, Argonne National Laboratory

The search for adequate binary metal oxide dielectric nanolaminates (NLs) to prevent degradation of power semiconductor devices is ongoing and involves the atomic layer deposition (ALD)-growth of a variety of binary metal oxide combinations. In the present work, we explore the ALD growth of amorphous (x)HfO_2/(y)Al_2O_3 NLs on Si (with native SiO_2 layer) substrates and then on both GaN and Ga_2O_3 single crystals. A variety of samples ranging from their homogeneous mixtures to HfO_2 or Al_2O_3-rich NLs are assessed before and after a thermal annealing by spectroscopic ellipsometry (SE), X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS) and 4-point probe resistivity measurements in order to elucidate the structural evolution of the NL at the GaN (or Ga_2O_3)-NL interface. By quantifying the HfO_2 incorporation throughout the Al_2O_3 layer and using the programmable nature of ALD to alternate layers of the HfO_2 and Al_2O_3 in an $(AB)_x$-$(CD)_y$ fashion, the influence of HfO_2 mobility within Al_2O_3 layer on the NL dielectric constant can be verified unequivocally. Moreover, combined X-ray absorption near-edge (XANES) and X-ray absorption fine structure (XAFS) spectroscopy data obtained at the Advanced Photon Source will confirm the local coordination environment of the Ga at the GaN (or Ga_2O_3)-HfO_2 interface and, at low super-cycle numbers (sub-nm scale), the ultimate stability of the NLs can be probed and optimized such that the bulk material properties are retained.

4:20pm **TF+MI+NS-ThA7 Atomic Layer Deposition Enabled Synthesis of Multiferroic Composite Nanostructures**, ***Jeffrey Chang****, University of California at Los Angeles, *A. Rosenberg,* Stanford University, *A. Buditama,* University of California at Los Angeles, *E. Jin, L. Kornblum, C. Ahn,* Yale University, *S.H. Tolbert,* University of California at Los Angeles, *K.A. Moler,* Stanford University, *J.P. Chang*, University of California at Los Angeles

Multiferroic materials, which exhibit the coexistence and coupling between ferroelectricity and magnetism, are of great interest due to their potential for enabling next-generation memories. To overcome the scarcity and weak responses of single-phase multiferroics, composite strategies were proposed for a robust multiferroic behavior by coupling the functional properties through the interface. By interfacing magnetostrictive and piezoelectric materials, the strain-mediated coupling strategy holds great promise, while both the interfacial-area-per-volume and the quality of interfaces play important roles in attainable functional properties. To obtain applicable magnetoelectric (ME) coupling under such scheme, lead-free multiferroic $BiFeO_3$ (BFO) and ferrimagnetic $CoFe_2O_4$ (CFO) were used in this study due to their robust functionality.

With the aim of enhancing the coupling by nanostructuring, atomic layer deposition (ALD), with its high quality and conformal film growth, was employed to achieve BFO/CFO composites with closely coupled interfaces and industrial scalability. BFO and CFO with were synthesized by radical enhanced ALD on $SrTiO_3$ (001) substrates using tmhd-based organometallic precursors(tmhd=2,2,6,6-tetramethylheptane-3,5 dione). The use of oxygen radicals as the oxidant provides a low temperature processing capability at 200°C. Post-deposition thermal treatments promotes the crystallization of both the BFO and CFO films and thus comparable functional properties were obtained. 2D-2D BFO/CFO composites were then synthesized by combining the ALD processes, with an optimized functionality obtained by nanolayering. ME behaviors comparable to previously studied multiferroic composites were observed, and the scaling of materials leads to an enhancement in the coupling coefficient (≈64 Oe cm/kV). The change in magnetic domains upon electrical poling was characterized using scanning SQUID. The 2D-2D BFO/CFO on $SrTiO_3$-buffered Si substrates exhibited comparable ME behaviors to the case on $SrTiO_3$, illustrating a path to integrate multiferroic materials into current industrial processes by ALD.

0D-3D BFO/CFO was realized by incorporating ALD-grown $BiFeO_3$ and mesoporous CFO substrates. Composite functionality as well as ME coupling were studied as a function of residual porosity after ALD filling. Higher BFO incorporation increases the overall ferroelectricity but limits the strain interaction due to a decreased mechanical flexibility. The strain interaction was verified by the change in lattice parameters observed using high-resolution XRD measurements. The results showed that the residual porosity is the key for ME coupling in a strain-mediated scheme.

4:40pm **TF+MI+NS-ThA8 Recent Developments in the Analysis of ALD/CVD Thin Film Conformality**, ***Riikka Puurunen***, Aalto University, School of Chemical Engineering, Finland **INVITED**

The downscaling of future semiconductor devices with increasing 3D character has lead to increasing demand of highly conformal thin films. Atomic layer deposition (ALD), based on the use of repeated, self-terminating reactions of typically at least two compatible reactants on a solid substrate, is often the only technique that can meet the conformality specifications. Conformal films made by ALD are also needed in other fields with intrinsic three-dimensionality requirements such as microelectromechanical systems (MEMS) and porous particle based applications (e.g., catalysis).

This work overviews recent progress in thin film conformality analysis made with the microscopic lateral high-aspect-ratio (LHAR), especially the “PillarHall” structures developed at VTT. Significant progress has taken place during the past year in the design and fabrication of the structures, conformality testing by academic and industrial partners, as well as modelling. The key feature of VTT’s PillarHall structures is the existence in silicon of a lateral gap of controlled height, typically 500 nm (can be varied from wafer to wafer, 100 to 2000 nm demonstrated), and controlled length up to 5 mm (several variations inside one chip, starting from 1 µm). Test structures with aspect ratio (AR) up to 50 000 : 1 ("hole-equivalent AR (EAR)" up to 25 000 : 1) have been fabricated this way. Growth of thin film inside the controlled 3-D gap and analysis of the film thereafter, often after removing the top part of the test structure by applying an adhesive, reveals the film thickness and composition profile. As compared to conventional vertical trenches etched into silicon, with VTT’s lateral PillarHall test structures, one can in a significantly shorter time obtain more detailed information on the conformality, which can be used for optimising processes, designing new processes, and investigating the fundamental mechanisms behind the deposition processes. Three scientific publications [1-3] report on the use of PillarHall 1st generation prototypes. At the time of writing this abstract, we work with 3rd generation prototypes and design the 4th generation.

Acknowledgements: Funding for the development of the conformality test structures has come from the Academy of Finland’s Finnish Centre of Excellence in Atomic Layer Deposition and the Tekes PillarHall project.

[1] Gao et al., J. Vac. Sci. Technol. A, 33 (2015) 010601 (5 pages). http://dx.doi.org/10.1116/1.4903941

[2] Mattinen et al., Langmuir 32 (2016) 10559-10569. http://dx.doi.org/10.1021/acs.langmuir.6b03007

[3] Puurunen & Gao, IEEE Xplore 2017, http://ieeexplore.ieee.org/document/7886526/

5:20pm **TF+MI+NS-ThA10 Spatial Atomic Layer Deposition Reactor Design for Nano-laminates**, *X.L. Wang,* ***Yun Li***, *J.L. Lin, J.M. Cai, R. Chen*, Huazhong University of Science and Technology, PR China

Atomic layer deposition (ALD) is commonly a vacuum based technique for ultrathin film fabrication with precise control of film thickness, uniformity and conformity. In contrast to conventional temporal ALD (T-ALD) that

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*** TFD James Harper Award Finalist**

precursors and purging gases are introduced into reactor sequentially, the separation mode of spatially-separately ALD (S-ALD) between reactive precursors is in space instead of in time, thus the process is continuous. In S-ALD process, the inert gas serves as a flow gas barrier to separate the precursors' zones, which prevents the cross contamination and atmosphere perturbation. With the alternating arrangements of oxidizer gas channels, metal source channels, and gas barriers of inert gas, the deposition rate of S-ALD could reach 1-3 order of magnitude higher than T-ALD. Moreover, the atmospheric pressure in S-ALD system enables this technique in a continuous form without vacuum. As the continuing development of S-ALD, it has found many potential high through-put and large scale applications. Here we present an S-ALD system design for fabricating binary oxides and their nano-laminates. The design of S-ALD reactor is based on motion structure of linear track and injector with a multiple slit gas source channel. By optimizing the structure of precursor channel based on the flow field simulation, a tree-branch-like gas feed structure is obtained, and the uniformity of the precursor distribution is enhanced significantly. The T-curve motion profile is replaced by the S-curve t o control the movement of substrate which can avoid abrupt change of acceleration and jerk in the acceleration and deceleration process, stabilizing the distance between injector and substrate precisely. The growth of thin film at different moving speeds has good linearity and uniformity. By integrating different reaction units, nano-laminates with tunable optical and electrical properties can be obtained.

Thin Films Division
Room: 20 - Session TF+MI-ThA

Control, Characterization, and Modeling of Thin Films II

Moderators: Subhadra Gupta, University of Alabama, Angel Yanguas, Argonne National Laboratory

2:20pm **TF+MI-ThA1** ***In Situ* Monitoring of the Growth of Metallic, Nitride and Oxide Thin Films Prepared by Pulsed Laser Deposition**, ***Michal Novotny***, *J. Bulir*, *E. Maresova*, Institute of Physics ASCR, Czech Republic, *P. Fitl*, *J. Vlcek*, University of Chemistry and Technology Prague, Czech Republic, *M. Vondracek*, *L. Fekete*, *J. Lancok*, Institute of Physics ASCR, Czech Republic, *N. Abdellaoui*, *A. Pereira*, University of Lyon, Université Claude Bernard Lyon, France

Pulsed laser deposition (PLD) is a well-established technique in fabrication of thin films. PLD profits from its simplicity, modesty, versatility and flexibility. Varying deposition conditions, ie. fluence, laser repetition rate, ambient pressure, substrate and its temperature, one can easily influence nucleation and the growth of thin film and consequently its properties. The in-situ monitoring of electrical properties allows sophistically control such processes. We demonstrated the in-situ monitoring possibilities for aluminium and silver as metallic materials examples, titanium nitride and zirconium nitride as nitride materials examples, and zinc oxide and tin oxide as oxide materials examples. The films attract attention in eg. photonics, plasmonics, electronics, sensors and biophysics. Particular application requires the film of special morphology, ie. isolated nanoparticles, arrays, or smooth surface.

The targets of Al, Ag, TiN, ZrN, ZnO and SnO_2 were ablated by a Nd:YAG laser operating at wavelength of 266 nm and pulse length of 4 ns. The laser repetition rate was varied from 0.1 Hz to 10 Hz. Electrical conductivity and I-V curve were measured by four-wire technique.

The results of the in-situ monitoring are correlated with the AFM and SEM analyses of the surface morphology, optical properties characterized by spectral ellipsometry and composition studied by XPS. We are able to distinguish the growth mode in the real-time, estimate the point of coalescence as well as the subsequent evolution of the surface roughness and control it. The obtained results provide knowledge toward synthesis of novel functional materials for optoelectronics and sensors.

2:40pm **TF+MI-ThA2 Perpendicular Magnetic Anisotropy in CoxPd100-x Alloys for Perpendicular Magnetic Tunnel Junctions and Bit Patterned Media**, ***Subhadra Gupta***, *B.D. Clark*, *A.G. Owen*, University of Alabama

Materials with high Perpendicular Magnetic Anisotropy (PMA) have drawn intensive research interest in recent years. This is because they have applications in perpendicular magnetic tunnel junctions (p-MTJ) and perpendicular magnetic recording media. Often solutions to these problems require overly complicated multilayer structure or high temperature grown $L1_0$ alloy. We demonstrate a simple room temperature grown CoPd alloy that is characterized by Alternating Gradient Magnetometry (AGM), Energy-Dispersive X-ray Spectroscopy (EDS), and X-ray Diffraction (XRD). We have found that the PMA and coercivity is tunable based off thickness, composition, annealing, and seed layer. Current in-plane tunneling (CIPT) measurements were performed on the stack Si/ SiO_2 / MgO (13)/ CoxPd100-x (50) / Ta (0.3) / CoFeB (1) / MgO (1.6) / CoFeB (1) / Ta (5) / Ru (10), with the numbers in parenthesis being the layer thickness in nm. CIPT data shows the highest magnetoresistance measurements correlates with the samples with the highest PMA. The stack Si / SiO_2 / Ta (5) / Pd (5) / $Co_{25}Pd_{75}$ (20) / Ta (5), with the numbers in parenthesis being the layer thickness in nm, were patterned using block copolymer templating and show an increase in coercivity from 3.3 kOe to 3.6 kOe with a nanopillar diameter approaching 10 nm, indicating that it may be suitable for bit pattern media (BPM) development.

3:00pm **TF+MI-ThA3 Combining Dynamic Shadowing Growth and Colloidal Monolayer to Design Plasmonic Metamaterials**, ***Yiping Zhao***, University of Georgia **INVITED**

The past decade has witnessed a rapid development of plasmonic metamaterials, which have unique optical properties and promising applications. Here, we report a simple, versatile, and scalable method for plasmonic metamaterial fabrication, which combines dynamic shadowing growth and self-assembled nanosphere monolayers, referred to as nanosphere shadowing lithography. In this method, a physical vapor deposition creates regular nanostructure arrays on modified nanosphere monolayers due to shadowing effect. The nanostructure morphology can be controlled by tuning the vapor flux direction with respect to the monolayers. Benefited from its control in nanostructure morphology, we have designed and fabricated a series of plasmonic nanostructures, including discrete nanoparticle arrays, nanoholes, nanoparticle networks, graded nanostructures, and chiral metamaterials such as patchy particles, helically stacked plasmonic layers, and Swiss roll structures. These well designed plasmonic nanostructures show tunable localized plasmonic resonance property and large circular dichroism response. In addition, by combining a co-deposition growth method, alloy or mixed phase plasmonic structures can be designed and investigated systematically. Such a simple but scalable fabrication method has a great potential for plasmonic metamaterial and meta-device development.

4:00pm **TF+MI-ThA6 Physical Vapor Deposition of Emerging Resistive Memories**, *M. Pakala*, ***Lin Xue***, Applied Materials, Inc. **INVITED**

We are getting deeper into the memory centric computing era, with emerging non-volatile memories being rapidly developed to fill gaps in latency, density and functionality. Various types of resistive memories such as STT MRAM, ReRAM and PCRAM are being developed to augment characteristics of available charge based memories. This is driving new deposition process / equipment requirements for these materials, since many of these materials are non-standard materials for an existing semiconductor fab. In my presentation, I will cover the requirements for depositing such materials as well as factors that drive these requirements. Particular focus will be on depositing magnetic tunnel junction stacks for STT MRAM as well as other semiconductor/oxide materials for resistive memories and selectors that can enable high density cross point memory.

4:40pm **TF+MI-ThA8 Metal Oxide Nanostructure Growth by a Simple Hot Water Deposition (HWD) Method**, ***Nawzat Saadi***, *T. Karabacak*, University of Arkansas at Little Rock

We are presenting a new hot water deposition (HWD) method to grow metal oxide nanostructures (MONSTRs). The technique is simple, low cost, low temperature, scalable, high-throughput, and does not involve any chemical agents or surface activators. Moreover, HWD can be used to deposit a large variety MONSTR materials on almost any type of substrate material or geometry. The process simply involves a source metal and a target substrate that are both immersed into hot water. The water temperature during HWD is typically between 50-95 ºC. In this work, we demonstrate that zinc oxide (ZnO) MONSTRs can be deposited on different substrates including copper (Cu) plate, Cu mesh, Cu foam, and ITO coated glass. We used Zn plate and powder as the source. Temperature of the water was set to 75 ºC. We observed that ZnO nanowires with lengths of few hundreds of nanometers and hexagonal cross-sections of about 50-100 nm grew within about 3 hours. ZnO MONSTRs covered the target substrates uniformly including the 3D foam surface. Smooth facets observed in SEM images and XRD results indicate that ZnO nanostructures have a well-developed crystal structure. In addition, we present a growth mechanism that includes the main processes of "plugging" and surface diffusion. The plugging involves the steps of metal oxide formation on metal-source surface, release of metal oxide molecules from the source, migration trough water, and deposition on the target surface. This is followed by surface diffusion of metal oxide molecules that help forming MONSTRs with smooth crystal facets. We also claim that "shadowing" effect can play an important role and promotes MONSTR growth on taller hills of the target surface vs valleys. We performed experiments such as HWD at different substrate-target distances, target roughness, and deposition time in order to better understand the contribution of each step listed above.

5:00pm **TF+MI-ThA9 Microsphere-Based Disordered Coatings for Effective Radiative Cooling**, ***Sarun Atiganyanun***, *J. Plumley, K. Hsu,* University of New Mexico, *J. Cytrynbaum,* Williams College, *T. Peng,* Air Force Research Laboratory, *S.M. Han, S.E. Han*, University of New Mexico

Being able to cool the buildings below the ambient temperature under the sun in the middle of a summer without having to use air conditioning would result in tremendous energy savings. As a step towards this goal, we have investigated a facile application of coatings made of silica microspheres in disordered structures, using evaporation as well as spray-coating. For the evaporation coating, silica microspheres are dispersed in water, and the colloidal stability is disrupted by dissolving ionic salt into the solution. The colloidal solution is confined onto a substrate and is allowed to evaporate. For the spray-coating, much like commercial painting, the aqueous colloidal solution is forced through a spray nozzle and deposited onto a substrate. Scanning electron microscopy images and autocorrelation analyses show that the resulting structures are disordered without short- or long-range order. Optical measurements also indicate that the coatings produced under optimal conditions have a short transport photon mean free path of approximately 4-8 μm in the solar spectral region. These coatings exhibit high emissivity above 95% in the atmospheric transparency window. These results suggest strong photon scattering properties in the visible region, while providing a strong thermal emission. Such films would enable effective radiative cooling. To estimate the theoretical limit, a computational model is first used to calculate the cooling power of the coatings under direct sunlight. The model predicts that the disordered coating with 200 μm thickness has a cooling power of ~250 W/m^2 at 27ºC and could reduce the temperature of the sample under the direct sunlight by approximately 37ºC below the ambient temperature. Our experimental measurements under direct sunlight show that our coatings perform better than commercial sunlight and heat reflective paints. We will further discuss how coatings of disordered, random, inverse structures can enhance the durability of our coating in a paint format, while maintaining radiative cooling properties.

5:20pm **TF+MI-ThA10 Sputter Beam Epitaxy: Innovation towards Spin Control in Intermetallic Thin Films**, ***Adam Hauser***, The University of Alabama **INVITED**

The vast array of interesting crystal structures and the wealth of elemental choices guarantee that we are never lacking for new opportunities in designing and making "custom-built" materials, if a method can be devised to build these complex materials systems. This talk will highlight our progress in thin film growth via Sputter Beam Epitaxy, an approach combining the fabrication strengths of off-axis magnetron sputtering and molecular beam epitaxy. We will focus on highly-ordered B2 alloys (including the Heusler sub-class) with an eye towards determination of the true properties of ideally ordered materials and tuning towards ideal spin damping properties.

Thin Films Division
Room: Central Hall - Session TF-ThP

Thin Films Poster Session

TF-ThP1 Hydrogen Bond Mediated Supramolecular Self-Assembly To Direct Thin Film Morphology For Organic Electronic Applications, ***Daken Starkenburg***, University of Florida

Phthalhydrazide, barbiturate, guanine, and diaminotriazine hydrogen bonding units have been integrated into pi-conjuagated oligomers. The addition of hydrogen bonding units on to one or both ends of the oligomers may be used to guide their self-assembly into optimized 2D and 3D morphologies for efficient charge separation and extraction in OPV devices. Scanning tunneling microscopy revealed several possible 2D ordered structures for vacuum deposited ditopic oligomers with diaminotriazine units dependent on processing conditions. Methyl and octyl chains were also added to the hydrogen bonding oligomers which led to easier film processing and the capability for designed modifications of the 2D structure. Furthermore, previously reported small molecules are currently being modified to integrate hydrogen bonding into a monotopic design in an effort to optimize 3D morphology and demonstrate high power conversion efficiencies for organic solar cells.

TF-ThP5 Indium Doped ZnO Nanopowders Synthesized by MW-HTS and their Physical Characterization, ***Mujdat Caglar***, Anadolu University, Turkey, *K. Gorgun*, Eskisehir Osmangazi University, Turkey, *S. Aksoy*, Sinop University, Turkey, *S. Ilican*, *Y. Caglar*, Anadolu University, Turkey

Zinc oxide (ZnO) are currently of great importance mainly as, transparent conductive electrodes, in solar cells devices, inorganic light emitting diodes, such as UV light emitting diodes, UV lasers and blue luminescent devices, photodetectors, gas sensors etc. The microwave synthesis is a synthesis method which is entirely different from the other methods. In the microwave method, a microwave diffuses to the material being heated volumetrically. In this study, Indium (In) doped ZnO nanopowders were synthesized via microwave assisted hydrothermal synthesis (MW-HTS) using zinc acetate dihydrate, indium acetate hydrate and sodium hydroxide. The effect of In dopant on the structural and morphological properties of ZnO nanopowders was investigated. To investigate the crystalline structure and the orientation of the doped ZnO nanopowders, XRD patterns were used. The lattice parameters and texture coefficient values of these nanopowders were determined. Field emission scanning electron microscope (FESEM) was used to analyze the surface morphology of the In doped ZnO. The presence of functional groups and the chemical bonding due to In doping are confirmed by Fourier transform infrared spectra (FTIR). **Acknowledgements:** This work was supported by Anadolu University Commission of Scientific Research Projects under Grant No. 1402F055 and 1705F259.

TF-ThP6 Effect of Erbium on the Structural and Morphological Properties of ZnO Films by MW-CBD and its Application in Heterojunction, ***Yasemin Caglar***, Anadolu University, Turkey, *K. Gorgun*, Eskisehir Osmangazi University, Turkey, *S. Aksoy*, Sinop University, Turkey, *M. Caglar*, *S. Ilican*, Anadolu University, Turkey

The doped zinc oxide (ZnO) films have attracted much attention because of their great potential for application to transparent conducting electrodes and insulating or ferroelectric layers in optoelectronic devices. Since ZnO has a wide bandgap energy of 3.37 eV at room temperature, its nanocrystals are suitable host materials for doping elements such as rare-earth (RE) and transition metal (TM) ions which are optically and magnetically active. RE doped ZnO nanocrystals are a potential candidate material for flat panel display phosphors due to efficient emission in the visible range, and different activators can be used to modify the color of luminescence. In this study, Erbium (Er) doped ZnO (ZnO:Er) films were deposited by microwave-assisted chemical bath deposition (MW-CBD). The structural and morphological properties of the films were investigated. Zinc nitrate hexahydrate was used as starting materials. The dopant source is Erbium (III) nitrat pentahydrate. The crystal structure and orientation of the films were investigated by X-ray diffraction (XRD) method. The films have the polycrystalline structure. Surface morphology of the films was also investigated by a scanning electron microscope (SEM). The *p-Si/n-ZnO:Er* heterojunctions were fabricated and their electrical properties were carried out in dark at room temperature. They were exhibited rectifying behavior by using thermionic emission theory. The important junction parameters such as ideality factor, barrier height and series resistance were systematically analyzed by the current-voltage (*I-V*) curves. **Acknowledgements:** This work was supported by Anadolu University Commission of Scientific Research Projects under Grant No. 1402F055 and 1705F283.

TF-ThP7 Influence of Fluorine Incorporation on Structural and Optical Properties of ZnS Films, ***Tulay Hurma***, Anadolu University, Turkey

ZnS has a wider band gap than other conventional II–VI semiconductors. Fluorine has a smaller atomic radius than both sulfide and zinc. ZnS and fluorine doped ZnS films were produced my means of ultrasonic spray pyrolysis (USP) method by spraying on glass substrates heated up to 340±5 ◦C. XRD and Raman spectroscopy were used to determine the crystalline formation and phase contents of these films and investigated the effect of fluorine having smaller atomic radius on both the structural and optical properties of the ZnS film. In addition to Raman spectroscopy, FTIR spectroscopy was used to detect the vibrations of atoms in the molecule. In the scope of morphological properties, SEM analysis was used and these images showed that the incorporation of fluorine in ZnS lattice caused important effects on the surface morphology and particle size. Optical absorption and reflectance spectra of the films that taken between 200 and 900 nm wavelengths were used to calculate the extinction coefficient, refractive index, dielectric constant and average refractive index values. The optical band gap and Urbach energy values of these films were determined depending on the fluorine incorporation.

TF-ThP8 WO_3/Ag Electrochromic Multilayer Film by RF Magnetron Sputtering, ***Chao-Te Lee***, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China, *P.K. Chiu, D. Chiang*, Instrument Technology Research Center, National Applied Research Laboratories, *W.-C. Chen*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China, *J.-H. Xie, C.-C. Jaing*, Department of Optoelectronic System Engineering, Minghsin University of Science and Technology

In this work, the novel electrochromic WO_3/Ag multilayer film on ITO glass were designed and made by RF magnetron sputtering at room temperature. The effects of Ag film on the microstructure and optical properties of the WO_3/Ag multilayers were examined by field emission scanning electron microscopy, X-ray diffraction (XRD) and spectrometer. The average transmittance in the range from 400 to 700 nm of WO_3/Ag multilayer films was slight increased from 81.13 (WO_3/ITO glass) to 84.74%. The electrochromic characteristics of WO_3/Ag multilayer films were investigated by the bleaching and colored WO_3/Ag multilayer film. The variation of average transmittance in the visible range of bleaching and colored WO_3/Ag multilayer film is above 65%. Particularly, the average transmittance in the range from 800 to 1000 nm of WO_3/Ag multilayer film was greatly decreased from 74.21(WO_3/ITO glass) to 1.59%. We found that novel WO_3/Ag multilayer film is suitable or electrochromic and hot mirror application.

TF-ThP9 Crystalline Quality and Surface Roughness Optimization of Hetero-Epitaxial Titanium Nitride on Sapphire, ***Hadley Smith***, University of Dayton, *A.N. Reed*, Air Force Research Laboratory, *S. Elhamri*, University of Dayton, *B.M. Howe*, *L. Grazulis*, *M.J. Hill*, Air Force Research Laboratory

In this project we optimized the growth of hetero-epitaxial titanium nitride (TiN) on sapphire using controllably unbalanced reactive magnetron sputtering. TiN is a mechanically-robust, high-temperature stable metallic material; these properties make TiN a material of interest for robust electrodes and resilient plasmonics. We adjusted deposition parameters such as external coil current, temperature, growth time and magnetron power to optimize the crystalline quality and surface morphology of TiN. Post-growth, we measured crystallinity using X-ray diffraction, and surface morphology using atomic force microscopy. X-ray diffraction showed a single TiN peak with pendellösung fringes; from these fringes we obtained a film thickness of ~55 nm. Atomic force microscopy showed a surface roughness of ~111 pm. Based on this characterization, we determined that the deposition parameters outlined in this presentation yielded (111)-oriented hetero-epitaxial TiN with minimal surface roughness. This optimization is a crucial first step in maximizing the usefulness of TiN for plasmonic applications.

TF-ThP11 Water Repellency or Hydrophilicity of the PTFE Irradiated by an Ar^+Ion Beam, ***Yuki Yamashita***, *I. Takano*, Kogakuin University, Japan

Recently, the application of polytetrafluoroethylene (PTFE) has spread to various fields. PTFE is a macromolecular material that has repetition of two fluorine atoms combined to a carbon atom. Because these atoms are strongly combined, PTFE has various excellent characteristics such as heat-resistant, chemical stability, low friction, etc. The significant characteristic among them is the high water-repellency which is well known as the coating of a cookware. The improvement of the water-repellency or hydrophilicity has been carried out by using the ion beam or the plasma treatment. In the case of the ion beam, the both properties of PTFE are able to be controlled by suitable ion beam energy.

Higher water-repellency of PTFE is required in a field such as a medical equipment, while higher hydrophilicity is anticipated to adhere between PTFE and the different material. Improvement of water-repellency and hydrophilicity are caused by the physical change of the surface morphology and by the chemical change of the molecular structure respectively.

In this study, the PTFE substrates of two types were used. Those are the adhesive tape type with 0.1mm in a thickness (T-PTFE: Chukoh Chemical Industries, Ltd.) and the sheet type with 1mm in a thickness (N-PTFE: NICHIAS Co.). Water-repellency or hydrophilicity of PTFE irradiated by an Ar^+ ion beam was investigated by the $\theta/2$ method. The irradiated ion species were Ar^+ ions with 10kV in an acceleration voltage at 40 $\mu A/cm^2$ in a current density. Dependence of the PTFE substrate temperature was investigated at a range from -50 to 50 degrees using the control system of the liquid nitrogen cooling and the heater heating. Dependence of the irradiation time was changed from 0 s to 30 s in a room temperature. The surface morphology was observed by the laser microscope (OLS4500: Shimadzu Co.) and the SEM (JSM5310: JEOL Ltd.). The surface chemical state was measured using an X-ray photoelectron spectrometer (ESCA-K1s: Shimadzu Co.) .

In the case of the T-PTFE temperature dependence, the surface morphology changed hardly at -50 degrees, while the needle-like structure was clearly observed in the substrate temperature of 50 degrees. It was considered that the surface morphology was strongly influenced by the substrate temperature than by sputtering of the ion beam. From the XPS measurement, it was confirmed that F atoms were selectively sputtered at -50 degrees as showing the low contact angle, while the low contact angle was showed in the lower irradiation time of T-PTFE. It was considered that water-repellency and hydrophilicity of PTFE were influenced by the PTFE substrate temperature during the ion beam irradiation.

TF-ThP12 Optical Chemical Sensors for the Detection of Taggants in Explosives

Sarka Havlova, *P. Fitl, M. Vrnata, E. Maresova, J. Vlcek, D. Tomecek, J. Herbst*, University of Chemistry and Technology Prague, Czech Republic

In this work, we present optical gas sensors with thin film of polymer as an active layer for the detection of taggants in explosives. The thin films of polymeric active layers based on poly(methyl methacrylate) (PMMA), polystyrene (PS) and low density polyethylene (LDPE) were prepared on lapped silicon substrates by spin coating with thicknesses in a range of hundreds nanometers (100 - 500 nm). These films were exposed to taggants' vapors such as 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT) and 2,3-dimethyl-2,3-dinitrobutane (DMNB) and measured in a range of their concentration 1 - 1000 ppm. Changes of refractive index were observed compared to reference atmosphere - synthetic air. The change of refractive index and layer thickness appears due to a swelling of the polymeric film in present of analyte vapors.

Thin films of polymers were subsequently doped with organic luminescent agents (metal phthalocyanines) and inorganic nanoparticles of rare earths (holmium oxide) and prepared with similar thicknesses. Soluble sulphonated metal phthalocyanines were dissolved and mixed with polymer solution, thin films were then prepared by spin coating. Insoluble phthalocyanines were evaporated under high vacuum conditions on the top of polymeric layer and localized laser melting of polymer was used for submerging of phthalocyanine molecules into the polymer matrix. These luminescent films were also exposed to vapors of taggants and changes in UV-VIS absorption spectra and luminescence spectra were detected. The influence of toluene was also evaluated for a comparison of detection properties with a substance similar to selected taggants.

The results suggest that gas sensors with these sensitive layers and based on connected optical techniques such as a measurement of luminescence, absorption and refractive index are very promising for the detection of taggants in explosives.

TF-ThP13 The Effect of e-gun Deposition Process Variables on the Film Characteristics of the Chromium Oxide

Po-Kai Chiu, National Applied Research Laboratories, Taiwan, Republic of China, *Y.T. Liao, H.Y. Tasi,* National Tsing Hua University, Taiwan, Republic of China, *D. Chiang*, National Applied Research Laboratories, Taiwan, Republic of China

The film characteristics and optical properties of the CrOx films prepared by the e-gun deposition with the different process variables are investigated. The process variables include the various oxygen flow rates, applied substrate temperatures to 200ºC, and with or without Ar and O_2 ion-assisted deposition. The optical constants of the deposited films with different process variables are determined from the reflectance and transmittance measurements obtained using spectrophotometer ranged from 350 nm to 2000 nm. The microstructures of the films are examined by the XRD, SEM, and XPS. The electrical conductivity is measured by four-point probe instrument. All the prepared films are amorphous without the significant pillar structure. The optical and electrical properties are illustrated by the analyzed XPS results with the ratio of the contribution of the free electrons to ion bonds in the deposited CrOx films. The major process variable to possess high extinction coefficient and low reflectance is the oxygen flow rate during the CrOx film deposition without ion-assisted deposition in the study.

TF-ThP14 Fabrication of High-period-number Resonant Transition Radiation Emitters for Generation of Femto-second Hard X-rays

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Femtosecond resonant transition radiation (RTR) in x-ray region can be generated from alternatingly stacked multilayer structures when they are driven by relativistic ultrashort electron beams. In contrast to large-scale facility like x-ray free electron lasers (XFELs), compact x-ray sources of moderate peak brightness can be developed by using this method for some ultrafast scientific research. These structures can be fabricated by coating layer pairs of high and low density materials. Narrow-bandwidth x-rays can be generated by increasing the number of periods (i.e. the number of layer pairs). Thanks to the high transmittance of hard x-ray in most materials, the radiation bandwidth is not limited by x-ray absorption up to dozens or even hundreds of layers. In this report, we present our efforts on the development of a femtosecond narrow-band 12 keV x-ray source by driving high-period-number RTR emitters with the NSRRC photoinjector linac system which is operating in short bunch mode. Since the optimum thickness for one emitter period is of several hundred nanometers, total thickness of an emitter can be as thick as few tens of μm. Sputtering is considered as an appropriate process to fabricate these structures with reliable quality in reasonable time. The fabrication process of making such emitters that are composed of Mo/Si multilayers is under test. Structures of 60 periods (120 layers) have been fabricated. The estimated photon yield is about $3x10^4$ for a 100 pC drive beam. A portion of x-ray generated from multi-layer structure would be absorbed by the Si substrate of the emitter, so removing the substrate would be helpful to enhance photon flux. The process to remove the substrate is also discussed.

Acknowledgement

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TF-ThP16 Materials and Methods for Bottom-Up Semiconductor Device Manufacturing by Selective Surface Modification

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In order to extend Moore's Law, device makers are looking at bottom-up approaches as an alternative for semiconductor device manufacturing. Recently, the variation in photoresist component distribution that is seen when scaling to sub-20-nm features has highlighted the need for very controlled and uniform distribution of materials. Bottom-up approaches to lithography patterning are able to address these stochastic issues, along with also addressing pattern roughness, excessive lithography steps, and others. We present novel materials and processes that enable selective surface modification with semiconductor device manufacturing as the end application. These materials are able to selectively deposit on various substrates, such as oxide, nitrides, metals, or even organic films. Properties such as selective deposition, catalysis, selective handles for further modification, ALD modifiers, and etch modifiers are reported.

TF-ThP17 Effects of the Electric Field Application for the Photocatalytic Property of TiO_2/Nithin Films

Taishi Segawa, *I. Takano*, Kogakuin University, Japan

In recent years, titanium oxide has attracted attention for its various properties and has been studied in a wide application field such as solar cells or medical instruments. Particularly the photocatalytic effect of TiO_2 produces antifouling, antibacterial action or decomposing environmental pollutants such as nitrogen oxide because the photocatalytic reaction of TiO_2 generates the active species of superoxide anion or hydroxyl radical by using the energy of ultraviolet rays. One of the reasons why TiO_2 is the superior material as a photocatalyst is that the photo-excited state is very stable and does not cause autolysis. Therefore TiO_2 irradiated with ultraviolet rays can make the electrolysis of water stably proceed. On the other hand, the weak point of TiO_2 is that the absorption wavelength is limited to the ultraviolet region under 380 nm. Therefore, many researchers have studied to improve the efficiency of the light reaction of TiO_2. The distinctive point of our study is the energy supply of electricity during the light irradiation.

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

200 degrees by an infrared heater. The film thicknesses of TiO_2 and Ni were changed with 0 - 100 nm to investigate the suitable condition.

The crystal structure of each thin film was analyzed by X-ray diffraction. Optical properties were measured using a UV-Visible spectrophotometer. The photocatalytic properties were measured by the methylene-blue immersion test under irradiation of the artificial sunlight (visible light) and the sterilizing lamp. The change of the methylene-blue transmittance was measured with a spectrophotometer at leaguer intervals.

In the case of the artificial sunlight irradiation, the methylene-blue transmittance of the TiO_2/Ni (100/50 nm) film without the electric field application was 7 %, while that with the electric field application showed 45 %. Also in the case of irradiation with sterilizing lamp, the transmittance of the sample with the electric field application was 1.6 times as compared with that without the electric field application. The photocatalytic effect was improved by the electric field application during the light irradiation. The mechanism of effects by the electric field application to the sample will be examined in future.

TF-ThP18 Investigations of Temperature and Humidity Sensors Constructed by Oxide Thin Films, ***Takahisa Kawaguchi***, *I. Takano*, Kogakuin University, Japan

Currently commercial temperature and humidity sensors have a low sensitivity for both sides of a high and a low humidity. On the other hand, because the main parts of these sensors are manufactured using polymer materials, there is the problem of a short life in environments such as a high temperature or a high humidity. Therefore, the next-generation type sensors are required in a longer life and a higher sensitivity.

As a material satisfying some of the above-mentioned functions, TiO_2 was adopted in our study. TiO_2 is an n-type oxide semiconductor and has the stable photo-excited state as the material without autolysis. In addition, TiO_2 shows the hydrophilicity under ultraviolet light irradiation. The next-generation type sensor with a higher sensitivity is promised by constructing some oxide layers such as a TiO_2 layer or a Cu_2O (p-type oxide semiconductor) layer.

In this study, basic investigations of TiO_2 and Cu_2O thin films prepared by reactive magnetron sputtering were carried out about those physical properties and the multi-layer thin films were constructed to improve the sensitivity of temperature and humidity on sensor characteristics. The TiO_2/Cu_2O thin film with each layer of 100 nm in a thickness and the $TiO_2/Cu_2O/TiO_2/Cu_2O$ thin film with each layer of 50 nm in a thickness were prepared by reactive magnetron sputtering.

The electric resistance of each sample was measured by changing the voltage from 0 V to 10 V. The resistance changes for temperature and humidity were measured about a range of the temperature from 25 degrees to 60 degrees and about a range of the humidity from 30 % to 60 %. Furthermore the water contact angle was measured by the q/2 method to investigate the relationship to humidity. In these experiments, the photoreaction on a semiconductor characteristic was examined by irradiating the White-LED light or UV-LED light to the sample surface.

The photo-excitation reaction of the TiO_2/Cu_2O thin film was not confirmed by the light irradiation, because Cu atoms diffused to the TiO_2 layer. The temperature coefficient of resistance (TCR) of the TiO_2/Cu_2O thin film and the $TiO_2/Cu_2O/TiO_2/Cu_2O$ thin film were -16820×10^{-6} [/K] and -18400×10^{-6} [/K], respectively. The resistance of the $TiO_2/Cu_2O/TiO_2/Cu_2O$ thin film was higher than that of the TiO_2/Cu_2O thin film, because the number of an interface between a TiO_2 layer and a Cu_2O layer influenced the bulk resistance of the thin film.

TF-ThP19 Analysis of Surface Species and Film Structure of Thin Films from Atomic Layer Deposition using Surface-Enhanced Raman Spectroscopy, ***Ryan Hackler***, *P. Stair*, *R.P. Van Duyne*, Northwestern University

In-situ surface-enhanced Raman spectroscopy (SERS) was used to identify dimeric methylalumina surface species during Al_2O_3 atomic layer deposition (ALD) on a silver surface. Vibrational modes associated with the bridging moieties of both trimethylaluminum (TMA) and dimethylaluminum chloride (DMACl) surface species were found during ALD. Density functional theory (DFT) calculations were also performed to locate and identify the expected vibrational modes. DMACl surface species were unable to be measured after multiple ALD cycles as a result of a loss in SERS enhancement and shift in LSPR. Currently, this work is being extended towards other ALD processes (such as TiO_2), as well as expanded to identify other characteristics of the thin films produced using adsorbate vibrational spectroscopy. This work highlights how *in-situ* optical spectroscopy by SERS and LSPR scattering are useful for probing the identity and structure of the surface species involved in ALD, as well as the structure of the resulting film.

TF-ThP20 Carbon Thin Films Prepared by the Ion Assistance the Mass Spectrometric Analysis Type, ***Kenji Iwasaki***, *I. Takano*, Kogakuin University, Japan

Recently, single-layer graphene sheets, diamond thin films, carbon nitride (C_3N_4) have attracted attention as a functional carbon thin film. Among them, DLC (Diamond-Like Carbon) is an amorphous carbon film showing characteristics which are close to that of diamond. Since those characteristics are high hardness, low friction coefficient, etc., DLC is used in a mechanical field such as sliding machine parts or engine parts.Practical application progresses rapidly in which tribology field, life expectancy has increased, maintainers

Contributing to Reducing Frequency In recent years, as a new characteristic of DLC gas barrier

Biocompatibility, etc. are recognized and it is expected to be applied to food containers, medical instruments, etc.

In our experiment, Ar^+, N_2^+, He^+ ion beam was used with evaporation to DLC films. This deposition method has some independent parameters from the film formation condition in comparison with other dry process methods. Therefore this method is anticipated in appearance of superior characteristics such as a high adhesion. In our previous research,

In our laboratory, we used Ar^+, $N_2{}^+$, He^+ as the ion species so far,

DLC film formation was carried out by an ion beam assist method in which toluene (C_7H_8) was introduced.

As a result of the investigation, by setting the ion species to Ar^+, the sp^3 ratio of the structure is maximized.

Although improvement of mechanical properties was expected, high-energy Ar^+ion irradiation turned out to be a factor of the increasing graphite structure. Therefore, further structural control is considered necessary to deposit DLC by low energy ions. In this study, we investigate various characteristics of DLC thin film by mass spectrometry type ion beam and compare it with DLC thin film with straight type ion beam.

TF-ThP21 Supramolecular Heterostructures - Engineering Organic Layered Materials with Tuneable Fluorescent Properties, *V.V. Korolkov*, The University of Nottingham, UK, *K. Watanabe*, *T. Taniguchi*, National Institute for Materials Science, Japan, ***Nicholas Besley***, *P.H. Beton*, The University of Nottingham, UK

For a long time the molecular self-assembly has been limited to engineering 2D molecular structures on surfaces. Here we demonstrate a successful approach that extends self-assembly into 3D by creating supramolecular heterostructures[1]. Essentially, these are layered organic materials that are stabilized by hydrogen bonds in plane and by van der Waals interactions between layers. Supramolecular heterostructures are formed by growing sequential layers of bi- and mono-component two-dimensional supramolecular arrays stabilized by hydrogen bonding. The heterostructures are formed on layered materials, hexagonal boron nitride (hBN) and graphite, by depositing layers of cyanuric acid/melamine (CA.M), 5,10,15,20-tetrakis(4-carboxylphenyl) porphyrin (TCPP), trimesic acid (TMA) and terephthalyc acid (TPhA).

We analyzed this heterostructures with ambient Atomic Force Microscopy that routinely achieve 0.1 nm resolution with conventional silicon probes. We have developed several approaches to characterize them. These include 'through-the-layer' imaging and scratching experiments to reveal the underlying layer structure.

AFM has confirmed that there is a clear epitaxial arrangement between these layers which intrinsically exhibit hexagonal (CA.M) and TMA, square (TCPP), linear (TPhA) symmetry. We demonstrate that heterostructure formation may be used to control the functional properties of supramolecular layers through a shift of the fluorescence peak position and a suppression of quenching for TCPP epitaxial layers.

The work will present outstanding examples of single molecule and submolecular resolution achieved in the ambient on standard atomic force microscopes. It is also possible to identify the registry between molecules in different layers and we include theoretical models which support our structural assignments and the observed shifts of fluorescent peaks.

[1] - *Korolkov et al.* **Nature Chemistry**, 2017, in press.

TF-ThP22 Predicting Feature Size of AZ 9260 Positive Photoresist Processed by Two-photon Lithography, ***Shelby Maddox***, *M. Zou*, University of Arkansas

Two-photon photolithography (TPP) is a promising fabrication method which allows very fine control over complex shapes in maskless lithography and is promising for creating 3D nanostructures. In this process, a high-fluence laser is focused into a photoresist in a discrete volume called a voxel. In the case of a negative photoresist, this volume is polymerized. In the case of a positive photoresist, the volume is monomerized. This size of this voxel depends on process parameters such as the focusing objective, the laser power, and the laser scanning speed across the photoresist surface. It is desirable to be able to precisely predict the feature width based on these process parameters. In this work, we present a mathematical model for predicting feature width created by a single-voxel using AZ 9260 positive photoresist with TPP. AZ 9260 is a high aspect ratio positive photoresist used in maskless lithography. The mathematical models are created which describe the resultant feature width as a function of the focusing objective, laser power, and the laser scanning speed. The features can be used as masks in a subsequent metal deposition to create conductive nanostructures for micro-electrode design, for use in biological research and multifunctional surfaces.

TF-ThP24 ALD of Titanium Oxide using Cyclopetadienyl Titanium Alkylamide and Ozone, ***Seongyoon Kim***, *J. Kim, T.R. Mayangsari, J.-M. Park,* Sejong University, Republic of Korea, *J.W. Park,* Hansol Chemical Co., Ltd., Republic of Korea, *W.-J. Lee*, Sejong University, Republic of Korea

Titanium-containing thin films are widely used in microelectronic device structures such as high-permittivity capacitors, barrier metals, and metal gate structures. ALD technology has replaced PVD and CVD to provide excellent step coverage, accurate film thickness control, and high film quality. Many organic titanium compounds such as alkylamido titanium compounds and cyclopentadienyl titanium alkoxides have been used as precursors. The preferred properties of such precursors include good thermal stability, high reactivity and sufficient volatility. In the present study, we investigated the ALD of titanium oxide by using cyclopentadienyl titanium alkylamide compound and ozone. Density functional theory calculation was used to predict the properties of precursors, and in-situ QCM and FTIR were used to investigate deposition rates and reaction mechanisms. The physical and electrical properties of the deposited films were also characterized.

TF-ThP25 Characteristics of Ge-Sb-Te Film Prepared by Atomic Layer Deposition and Tellurization of Ge-Sb Film, ***Yewon Kim***, *S. Kim, J. Gu, J.-M. Park,* Sejong University, Republic of Korea, *W. Koh,* UP Chemical Co., Ltd., Republic of Korea, *W.-J. Lee*, Sejong University, Republic of Korea

The phase change random access memory device is the next generation non-volatile memory device in the spotlight, especially storage class memory applications. Ge-Sb-Te (GST) compounds have been extensively studied due to their fast switching properties among the phase change materials. In particular, the pseudo-binary compositions between GeTe and Sb_2Te_3 attracted much attention. The GST thin films were prepared by physical vapor deposition, chemical vapor deposition and atomic layer deposition (ALD) techniques. Recent studies have focused on ALD of $Ge_2Sb_2Te_5$ film that combine ALD of GeTe with ALD of Sb_2Te_3, which is relatively complex. In this study, we prepared GST films by ALD and tellurization annealing of Ge-Sb film as an alternative manufacturing method of GST film. This method simplifies the deposition sequence and allows easy control of the film composition. The composition profile, crystal structure and phase transition temperature were investigated by Auger electron spectroscopy, Raman spectroscopy and resistance change before and after tellurium annealing. Changes in resistance were discussed in terms of composition and crystal structure. Gapfilling of the deposited film was also observed before and after tellurization.

TF-ThP26 Molecular Layer Deposition of Boron Carbide from Carboranes, ***Michelle Paquette***, *L. Dorsett, S. Malik, T.D. Nguyen, D. Bailey, K. Rimpson,* University of Missouri-Kansas City, *J.D. Bielefeld, S.W. King,* Intel Corporation

Atomic layer deposition (ALD) research has exploded in this era of electronic miniaturization, smart materials, and nanomanufacturing. To live up to its potential, however, ALD must be adaptable to many types of materials growth. To extend the reach of this layer-by-layer deposition framework, researchers have begun to explore molecular based processes. Still relatively rare, existing molecular layer deposition (MLD) processes are typically based on the condensation of “linear” 2D or “brush-type” organic polymer chains. To move toward a 3D MLD growth model, precursors with multiple reaction sites would be desirable. To this end, icosahedral carborane ($C_2B_{10}H_{12}$) molecules provide an interesting target. Carboranes have been used in the plasma-enhanced chemical vapor deposition of boron carbide films for low-*k* interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules, wherein the terminal H atoms at each vertex are known to be labile in the presence of plasma, heat, or a number of chemical reagents. The carborane molecule is very stable and can be derivatized with a range of functional groups; dozens of these derivatives are available commercially, many of which have relatively high vapor pressures. As such, the carborane molecule is particularly intriguing as a novel MLD precursor for 3D growth, possessing unique symmetry, chemical reactivity, and volatility properties not commonly encountered in traditional organic molecules. In this contribution, we describe early work in our group toward developing a novel MLD process for the growth of boron carbide films using a number of different carborane precursors and substrates.

TF-ThP27 Comparative Study of the Optical and Structural Properties of Single and Stacked SRO Thin Films Obtained by RF Sputtering, ***Karim Monfil Leyva***, *A.S.L. Salazar Valdez,* Benemérita Universidad Autónoma de Puebla, Mexico, *A. Morales Sánchez, F. Morales Morales,* CIMAV-Monterrey, Mexico, *J.A. Luna López,* Benemérita Universidad Autónoma de Puebla, Mexico, *A.L. Muñoz Zurita,* Universidad Politécnica Metropolitana de Puebla, Mexico

Silicon rich oxide (SRO) has proved to be a cheap and interesting alternative to develop ultraviolet absorbers or silicon-based light emitters. New electronic and optoelectronic devices based on SRO material may require of single or stacked films with different silicon excess to improve optical and electrical properties. SRO films can be deposited by several deposition techniques but they can be obtained at Room Temperature by RF Sputtering deposition technique and its thickness can be well controlled. Silicon excess can be changed by fixing the RF-Power density on the SiO_2 target and changing the RF-Power on the Silicon target (P_{Si}).

In this work, we report a comparative study and analysis of the optical and structural properties of single and stacked SRO thin films obtained by RF Sputtering. Single SRO films were obtained by changing the P_{Si} = 30, 40 and 50 W. Two different stacked SRO films, like a Bilayer (BL) structure, were obtained by changing the P_{Si} = 50/30 W and 30/50 W. All samples were deposited on *n*-type silicon (Si) substrates with low resistivity (1~5 W•cm). A thermal annealing of 1100°C for 3 hours in N_2 ambient was applied to all SRO films. Step measurements were applied to calculate thickness of SRO samples. X-ray photoelectron spectroscopy (XPS) measurements were obtained from all samples to calculate and compare the Silicon excess. XPS results revealed the non-stoichiometric nature of our single SRO films and a change of Silicon excess in the BL structure. SEM images showed clear clusters on surface possible due to Si-nanocrystals (Si-nc) on bulk; also, surface roughness was calculated for all SRO films. Both BL structures showed Photoluminescence emission (PL) at Room Temperature (RT) before and after thermal annealing but the intensity was clearly increased after annealing. BL structures showed higher PL than single SRO films. All SRO samples showed two bands, a low blue band from 400 to 550 nm and a strong red band from 575 nm to 875 nm. Blue and red emission bands were related to Si-nc and defects in the SRO samples.

TF-ThP28 Dependence of the Corrosion Behavior of Transition Metal Nitride Films on the Sputtering Power Mode, ***Yuri Chipatecua***, CINVESTAV-Unidad Queretaro, Mexico, *O. Tengstrand,* Linköping University, Sweden, *J.J. Olaya-Florez,* Universidad Nacional de Colombia, *G. Greczynski,* Linköping University, Sweden, *I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign, *A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

Transition metal nitrides (TMN) are valuable coatings because they provide desirable properties of practical use. Their physical and chemical properties are also interesting from the fundamental perspective . Through the combination of sputtering power modes (HIPIMS and DCMS), it is possible to control, at least partially, harmful structures such as porosity, defects among grains, vacancies and dislocations.

We employed a hybrid high-power pulsed and dc magnetron co-sputtering with synchronized substrate bias to grow TMN films. Ti and Al were deposited in DCMS and Ta in HIPIMS mode. The bias was applied in synchronous with the Ta-ion portion of each HIPIMS pulse to minimize Ar^+ bombardment. TiN coatings were deposited in the modes of direct current (TiN_DC) and direct current pulsed (TiN_P) with a constant substrate bias. TiTaN, TiTaAlN, TiN_DC and TiN_P coatings were grown onto stainless steel AISI 304 with thickness ~ 300 nm. Corrosion studies were carried out in a NaCl solution at room temperature by electrochemical impedance spectroscopy and potentiodynamic polarization. By Tafel extrapolarization from the potentiodynamic curves, corrosion current density values (I_{corr}) were three orders of magnitude lower than substrate AISI 304. While TiN (DC and P) coatings showed degradation or products of corrosion accumulation, TiTaN and TiTaAlN coatings proved to be efficient as corrosion protection barrier. Their integrity was not affected (there was no evidence of microcracks, delamination or failure). This is probably associated to a more intense ion bombardment due to higher applied potential in the range of 4 to 6 kW. These coatings showed lower oxygen content than TiN_DC and TiN_P. The chemical composition of all coatings was evaluated by XPS sputter resulting in $Ti_{0.82}Ta_{0.35}N$ and $Ti_{0.30}Ta_{0.12}Al_{0.78}N$, respectively, both with a small amount of oxygen contamination (4%). In the case of titanium nitride, the composition was $Ti_{1.09}N\ O_{0.53}$ for DC mode and $TiN\ O_{0.24}$ for DC pulsed mode. The background associated to the Ti 2p spectra show an interesting behavior with composition. In this paper we will also discuss the relationship between corrosion and sputtering power mode.

TF-ThP29 Laser Microstructuring of Gas Sensing Thin Films, ***Premysl Fitl***, *J. Vlcek, D. Tomecek, E. Maresova, S. Havlova*, University of Chemistry and Technology Prague, Czech Republic, *M. Novotny, J. Lancok*, Institute of Physics ASCR, Czech Republic, *M. Vrnata*, University of Chemistry and Technology Prague, Czech Republic

Focused Laser beam is a widely used for deposition, localized annealing and patterning of various materials (eg. Metals, oxides, organic substances). Our work is focused to possibilities of usage of continuous wave (CW) lasers for local deposition and patterning of inorganic and organic semiconductors.

The source substrates were prepared as follows: Thin glass slides with sputtered metal layer (gold - thickness ~ 100 nm) were cleaned and dried. Side with sputtered metal was then covered with a thin layer of purified organic semiconductors – Zn, Pb and Fe Phthalocyanines, deposited by organic molecular evaporation in high vacuum chamber (10-5 Pa, dep. Rate ~ 0.1-3nm/min, substrate temp. 20 – 300 °C). The temperature of deposition source and substrate was selected for each substance so as to achieve optimal growth rate and to avoid thermal decomposition of materials. In the next step CW laser depositions were carried out from these substrates. The deposition apparatus include micro CNC machine (minimal step adjustable to 300 nm) equipped with the semiconductor laser (405 nm, 10 - 50 mW, spot 6 microns) in continual mode and focusing optics. The distance between source substrate and target (i.e. glass, silicon or alumina sensor substrates) was varied between 1-100 micrometers. Deposition process was held in an inert gas (Argon, Nitrogen) at atmospheric pressure. Morphology and microstructure were studied by optical, electron microscopy and AFM. Chemical composition of deposited structures was studied by FTIR and compared with that of source substances. It was proved that chemical structure of all chosen substances is not affected by this deposition technique. The best lateral resolution of prepared structures was obtained for source layer thickness of 100-150 nm. Employing our technique we are able to achieve precise and reproducible laser transfer of organic semiconductors to the target sensor substrate with lateral structural resolution of 14 microns.

We can make an assumption that our technique could be used also for other organic semiconductors used in gas sensors which can be deposited by organic molecular evaporation.

TF-ThP32 Low Temperature Growth of VO_2 Films on Flexible Plastic Substrates using TiO2 Buffer Layer, ***DaeHo Jung***, *H.S. So, J.S. Ahn, S.B. Hwang, H. Lee*, Kyung Hee University, Republic of Korea

Vanadium dioxide (VO_2) with high transmittance of visible-ultra violet radiation but the complete blockage of infrared solar radiation can be used for `solar control` windows. A thermochromic smart window is designed such that the VO_2 films regulate solar infrared radiation. Polyimide has thermal stability, good film-forming ability, low dielectric constant, high chemical resistance, low coefficient of thermal expansion and high mechanical strength. Due to these reasons polyimides are largely used as matrix for various purposes and the advantages of polyimide (PI) have been utilized as flexible substrate. VO_2 thin films with ~50 nm in thickness were grown on TiO_2-buffered PI films using RF magnetron sputtering deposition using a VO_2 target. The sputtering pressure was set at 6 mTorr with 10 sccm flow of Ar gas. VO_2 thin films on TiO_2-buffered PI films were grown at 175°C. Since the PI substrates (75 mm-thick) can keep physical properties only up to 260 °C, low temperature growth of VO_2 films ($\leq$ 260˚C) is necessary, After sputtering deposition, all samples were annealed with 1 sccm of O_2 flow for 1hr. The structural and morphological properties of all VO_2 films were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. However, no peak for the monoclinic of phase of VO_2 appeared in Raman spectrum of growth of VO_2/TiO_2/PI at under 200ºC. It was difficult to observe XRD diffraction peaks of VO_2 because VO_2 thin films did not crystallize under 200ºC. The chemical compositions of VO_2 were probed by x-ray photoelectron spectroscopy. The measurement of depth-dependent O/V ratio also showed that the stoichiometry was independent of depth for VO_2 films.We measured the hysteresis curve of sheet resistance as a function of temperature. We measured the reflectivities of VO2 films below and above the metal-insulator transition temperature. The ratio of switching resistivity was 10^{-2}. VO2 films grown on plastic films can be applicable as flexible thermochromic films for energy-saving windows.

Reference:

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TF-ThP33 Single Junction GaAs Thin Film Solar Cells on Flexible Metal Tapes for Low Cost Photovoltaics, ***Devendra Khatiwada***, *P. Dutta, M. Rathi, S. Sun, Y. Yao, Y. Gao, Y. Li, S. Pouladi, J.-H. Ryou, V. Selvamanickam*, University of Houston

There is great interest in thin film solar cells for manufacturing cost-effective photovoltaics due to their advantages of light weight, versatile application, mechanical flexibility and scalable length. Thin film solar cells made of III-V semiconductor materials that have a high absorption coefficient over a wide range of the solar spectrum are strong candidates but have been largely unexplored so far. GaAs has high mobility, high band gap and high absorption coefficient and AlGaAs can be lattice matched with GaAs to form a heterojunction structure. While the highest efficiencies have been reported in III-V solar cells based on GaAs and Ge wafers, their application has been very limited due to high cost of these wafers.

Herein, we have developed high quality epitaxial semiconductor thin films on low-cost flexible metal tapes to overcome the wafer cost as well as benefit from the lower manufacturing cost of roll-to-roll processing. In our process, single-crystalline-like germanium films are grown on the flexible metal tape over which epitaxial (Al)GaAs semiconductor thin films are grown by metal organic chemical vapor deposition (MOCVD). The grown device architecture is further processed for contact deposition via photolithography.

The fabricated thin film III-V solar cells exhibit photon conversion efficiency of 7% with open circuit voltage (V_{OC}) of 565mV, short circuit current density (J_{SC}) of 17.9 mA/cm^2 and fill factor (FF) of 67% under A.M 1.5 (1 sun). Conversion efficiencies up to 11% have also been demonstrated with the thin film III-V solar cells. Further improvement in device efficiency is being pursued with new device architectures and optimization of the growth and fabrication processes.

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TF-ThP34 Optical and Microstructural Characterization of Epitaxial VO_2 on TiO_2 (001) and Niobium Doped TiO_2, ***Jason Creeden***, *I. Novikova, R.A. Lukaszew*, The College of William and Mary

The goal of this project is to optimize the efficiency of the optically induced insulator to metal transition (IMT) in the near-UV and UV regions, following the recent demonstration that VO_2 prepared on niobium doped TiO_2 (TiO_2:Nb) substrates can push the photoconductive response, ordinarily strong in the infrared, into the visible spectrum. Therefore, this project focused on the tailoring of the optical and microstructural parameters pertaining to the IMT in VO_2 thin films. This was done by controlling the microstructure of the films via deposition parameters and substrate doping and thus optimizing the VO_2 growth process for TiO_2 and TiO_2:Nb substrates. In doing so, we strained the monoclinic structure seen in the insulating phase toward the tetragonal structure seen in the metallic phase post-transition. The film composition was characterized via X-ray diffraction (XRD) and changes to the VO_2 optical transmissions, during the thermally induced IMT, were recorded using both a HeNe laser (1520 nm) and a 405 nm diode laser. With the HeNe laser, we could see strained bulk-like transitions of VO_2 occurring for samples grown on TiO_2 and small transitions for the samples grown TiO_2:Nb. The samples grown on TiO_2:Nb structurally exhibit a .25° shift in the XRD peak location in comparison to the un-doped samples. With the 405 nm laser, the samples grown on TiO_2:Nb exhibit sharp transitions that are comparatively large to those of the slight transitions seen in samples grown on TiO_2. Suggesting that the doping enhances the near-UV optical response of the film.

TF-ThP35 Characterizing the Field of Atomic Layer Deposition: Authors, Topics, and Collaborations, ***Elsa Alvaro***, Northwestern University, *A. Yanguas-Gil*, Argonne National Laboratory

Atomic layer deposition (ALD) has become one of the key techniques in thin film growth with applications in areas such as microelectronics, advanced sensors, energy storage, and more. Using a combination of bibliometric, social network, and text analysis, we describe the evolution of ALD as a field over time. In particular, we have examined the evolution in terms of publications, as well as changes in authors, journals, and collaborators.

The study of the collaboration network of ALD scientists over time shows how the ALD research community, originally consisting of small isolated clusters, becomes both larger and more interconnected. The formation of a single large connected component in the collaboration network coincides in time with the first AVS-sponsored symposium on the subject. As of 2015, the largest connected component spans 90% of the authors. In addition, the evolution of network centrality measures such as degree and betweenness centrality and author productivity allow us to identify the central figures in ALD according to each metric and their evolution over time, including the appearance of new "stars" in the last decade. Finally, we carried out a study of the title words of the papers in our dataset. Through the evolution of the technical terms in the titles we can map the evolution of the field. The results are consistent with a shift in focus on research topics towards energy applications and nanotechnology, and an increase in interdisciplinarity that correlates well with the evolution of the main scientific journals that publish ALD research.

TF-ThP37 Nano-laminates Encapsulation Films Fabricated via Spatially Separated Atomic Layer Deposition for High Stable Flexible OLED Electronics, *Y. Li*, ***Yuanyuan Liu***, *K. Cao*, Huazhong University of Science and Technology, China, *H. Hsu, J. Huang*, Wuhan China Star Optoelectronics Technology Co., Ltd (CSOT), China, *R. Chen*, Huazhong University of Science and Technology, PR China

The expansion demand for wearable and flexible electronics based on organic light emitting diode (OLED) displays have attracted great attention. Flexible OLED displays, however, widely utilize materials that are sensitive to oxygen and water which causes performance degradation or failure during usage. It is imperative to develop reliable and efficient thin film encapsulation methods to improve the stability and meet the requirements of miniaturization, flexibility and low cost. Atomic layer deposition (ALD) technique enables thin film fabrication with high quality, good uniformity and atomic level controllability in film thickness. It is quite promising as a practical method for future flexible electronics encapsulation.

This work focuses on the design and fabrication of encapsulation films for high stable flexible OLED electronics via spatially separated atomic layer deposition (S-ALD). S-ALD is proposed to separate different precursors' zones with inert gas in space ensure continuous deposition process. By optimizing the design of precursor injectors' structure and movement of sample stage, the uniformity and growth rate of deposited films are enhanced significantly. The oxides nano-laminates are fabricated with S-ALD method. The stacked sequence (ABAB, AABB) and thickness for every sub-layer are precisely controlled with ALD cycles. Recent research show that the water vapor transmission rate (WVTR) has been enhanced with nano-laminates compared with single layers with the same thickness. The WVTR is also influenced with the nano-laminates' structures as stacked sequence. Moreover, the organic sub-layers are introduced to form organic-inorganic multi-barriers to protect OLED devices. The composite encapsulate layers demonstrate both good bending mechanical properties as well as enhanced devices' stability towards hydrothermal aging.

TF-ThP38 Conductive Collagen: A Novel Material for Green, Transient Implantable Electronics, ***ArghyaKamal Bishal***, *C. Sukotjo, C.G. Takoudis*, University of Illinois at Chicago

In modern biomaterial based electronics, the choice of green and transient material is becoming attractive.[1, 2] This kind of materials require to have unique properties like biodegradability, bioresorbability, biocompatibility and environmentally safe.[1, 2, 3] The advantages behind using these materials are: low cost, energy efficient production due to their natural origin, no long term adverse effects, no need of retrieval as they can resorb and above all they can minimize hazardous waste for our environment.[2]

Collagen is an important biomaterial which is used in several biomedical applications. It has a triple helix structure made of polypeptide chains.[3, 4] Glycine, proline are the most abundant amino acids found in its structure. Collagen is a flexible biomaterial which is also biodegradable/bioresorbable[5], biocompatible[5] and piezoelectric[3] hence might be an ideal choice for this kind application in implantable electronics.

In this work, we present electrical properties of collagen membrane functionalized with a thin film deposited using Atomic Layer Deposition (ALD). For this study, a commercially available bioresorbable collagen membrane was used as ALD substrate. As a preliminary pilot study, thin film of titanium dioxide (TiO_2) was deposited on collagen membrane in a custom-made ALD reactor and different film thickness was achieved by varying the number of ALD cycles. The deposition was performed at room temperature using Tetrakis(dimethylamido)titanium (TDMAT) and ozone as metal precursor and oxidizer, respectively.[6] Electrical properties of the samples were measured using a 2-probe system. Preliminary results showed that the ALD coated collagen samples were more conductive compared to non-coated control and this conductivity increased with increase in number of ALD cycles.

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TF-ThP39 Alkali Halide Assisted Atomic Layer Etching of Metal Oxides, *J. Hennessy*, ***April Jewell***, *S. Nikzad*, Jet Propulsion Laboratory

The authors previously reported on the development and application of an atomic layer etching (ALE) procedure based on alternating exposures of trimethylaluminum (TMA) and anhydrous hydrogen fluoride (HF) implemented to controllably etch aluminum oxide. We have shown that conditioning the chamber with a thin film of lithium fluoride (LiF) enhances the ALE process, resulting in higher etch rates and better uniformity. We have hypothesized that the LiF participates in an intermediate reaction that promotes the loss of fluorine surface species and results in conformal layer-by-layer etching of aluminum oxide films. Etch properties were explored over a temperature range of 225–300 °C with the Al_2O_3 etch rate increasing from 0.8 to 1.2 Å per ALE cycle at a fixed HF exposure of 60 ms per cycle. We have since extended this work to include a variety of substrates (metal oxides) and etch enhancers (alkali halides). Preliminary results suggest that the TMA/HF chemistry is effective at etching hafnium oxide. Additionally, other alkali halide materials (e.g. KBr) behave as oxide etch enhancers, in some cases resulting in even higher etch rates than what was previously achieved with LiF.

TF-ThP40 Tribocorrosion Behavior of Ti-6Al-4V Alloy Coated with TaN/Ta Layers in Two Simulated Body Fluids, ***Jessica Estefania González Sevilla***, *M. Flores, R. Rosas, E. García*, Universidad de Guadalajara, Mexico

Ti-6Al-4V alloy is one of the most used materials in biomechanical industry due to the high corrosion resistance as well as its elastic modulus relatively close to that of bone tissue. This material also has excellent biocompatibility and its surface can be treated to promote osseointegration with the host tissue. However, suffer from a low wear resistance in dry and wet conditions. This work focuses on the synthesis of Tantalum Nitride and tantalum layers by magnetron sputtering on substrates of Ti-6Al-4V alloy. TaN and Ta coatings are biocompatible materials, both are chemically stable and TaN has high nanohardness, these properties make the coating of TaN/Ta resistant to the simultaneous attack of corrosion and wear. The structure and composition of coatings were studied by XRD and EDS techniques respectively. Raman spectroscopy and Scanning Electron Microscopy were used to analyze the wear track of the alloy and coated samples. The tribocorrosion tests were made in two different simulated body fluids. One made of deionized water plus salts with the same ions concentration than in human blood and other of Fetal Bovine Serum (FBS) and a compensatory ion solution to reach the ions concentration at blood. The load applied was between 0.5 and 2 N using a ball of Al2O3. Were measured the open circuit potential, friction coefficient and total lost material. The results showed a reduction of the wear, as a consequence of the TaN/Ta coating. The incorporation of proteins by means of FBS in the corrosive medium reduces the friction coefficient.

TF-ThP41 The Leakage Current Reduction in Atomic Layer Deposition Of Al_2o_3-Inserted $Srtio_3$ Films for Metal-Insulator-Metal Capacitors, ***Sang Hyeon Kim***, Seoul National University, Republic of Korea, *C.H. An*, Seoul National University, Korea, Republic of Korea, *D.S. Kwon, C.S. Hwang*, Seoul National University, Republic of Korea

The characteristics of atomic layer deposition (ALD) of Al_2O_3-inserted $SrTiO_3$ (STO) dielectric thin films were investigated in metal-insulator-metal capacitors for dynamic random access memory. STO thin films exhibit much higher dielectric constant compared with currently used ZrO_2-based films, but the leakage current density is generally higher due to their low band-gap energy. To decrease the leakage current density, ALD-Al_2O_3 cycles were included in the STO ALD at different positions of the stack. 1 to 5 cycles of Al_2O_3 were inserted in the top, bottom, or middle of the STO film. As a result, the leakage current of the STO thin film with a thickness of 8nm decreased from 10^{-6} A/cm^2 to 10^{-8} A/cm^2 at 0.8V. This improved the minimum attainable equivalent oxide thickness (EOT) of the (top) RuO_2/STO/Ru (bottom) capacitor from 1.0nm to 0.68nm, with an acceptable leakage current density (~8 X 10^{-8}A/cm^2). The degree of leakage current decrease was dependent on the locations of Al_2O_3 insertion into the STO thin film during the ALD. The leakage current reduction was more effective when Al_2O_3 was deposited at the top portion of the STO film than when it was deposited at the bottom portion. Only one cycle of Al_2O_3 at the bottom location significantly decreased the crystallinity of the STO layer grown on top, and thus, the higher post-annealing temperature was required to achieve high crystalline quality, which simultaneously increased the leakage by possibly involving nano- and micro-cracks. The Al_2O_3 at the top location did not induce such adverse effect while leakage current suppression effect was achieved.

2D Materials Focus Topic
Room: 15 - Session 2D+MI+NS+SS+TF-FrM

Nanostructures including Heterostructures and Patterning of 2D Materials
Moderators: Huamin Li, University of Buffalo, SUNY, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

8:20am **2D+MI+NS+SS+TF-FrM1 Electro-optics with 2D Semiconductors and Heterostructures**, ***Goki Eda***, National University of Singapore, Singapore **INVITED**

Despite being only a few atoms thick, two-dimensional (2D) semiconductors such as monolayer MoS_2 and phosphorene exhibit distinctly strong light-matter interaction compared to their bulk counterparts. Excitons and their complexes with giant oscillator strength play a fundamental role in mediating the strong coupling between light and a 2D semiconductor. These excitons are stable at room temperature and make 2D semiconductors attractive for a number of photonic devices including ultra-fast photo-detectors, optical modulators, on-chip photonic circuits, flexible photovoltaic devices, chiral light emitters, single photon sources, and ultra-low threshold lasers[1]. In order for these devices to be integrated for photonic devices, practical schemes for electrical generation, manipulation, and detection of excitons need to be developed. We create artificial quantum wells based on van der Waal heterostructures and investigate the dynamics of 2D excitons under various conditions to achieve the desired photonic functionalities. In this talk, I will start by discussing our findings on the ultrafast dipole-dipole energy transfer processes involving 2D excitons. I will show that exciton-exciton energy transfer in hetero-bilayers is among the fastest measured in nanomaterials[2]. Peculiar optical effects arising from strong exciton-plasmon coupling in 2D semiconductors hybridized with metal nanoparticles will also be discussed[3]. Finally, our recent efforts in realizing electro-optical (electroluminescence, electro-absorption, and Pockels effect) devices will be discussed. I will share our views on the potential advantages of 2D semiconductors over other materials and discuss our outlook for further studies.

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2. D. Kozawa *et al.* "Efficient interlayer energy transfer via 2D dipole coupling in $MoSe_2/WS_2$ heterostructures" Nano Lett. 16, 4087 (2016).
3. W. Zhao *et. al.* “Exciton-plasmon coupling and electromagnetically induced transparency in monolayer semiconductors hybridized with Ag nanoparticles” *Adv. Mater.* 28, 2709 (2016).

9:00am **2D+MI+NS+SS+TF-FrM3 Understanding Variations in Circularly Polarized Photoluminescence in Monolayer Transition Metal Dichalcogenides**, ***Kathleen McCreary***, *M. Currie, A.T. Hanbicki, B.T. Jonker*, Naval Research Laboratory

The unique electronic band structure in monolayer transition metal dichalcogenides (TMDs) provides the ability to selectively populate a desired conduction band valley by exciting with circularly polarized light. The subsequent valley population can be interrogated by measuring helicity-resolved photoluminescence (PL). A high degree of circular polarization has been theoretically predicted for resonant excitation of TMDs, yet rarely observed experimentally. In fact, a wide range of values for the degree of circularly polarized emission (P_{circ}), has been reported for monolayer TMDs, although the reasons for the disparity are unclear. Here we investigate the room-temperature P_{circ} in several TMD monolayers synthesized via chemical vapor deposition. The samples include as-grown WS_2, as-grown WSe_2, and WS_2 monolayers that have been transferred to a fresh substrate. In each system, a wide range of P_{circ} and PL intensity values are observed. There is a pronounced inverse correlation between P_{circ} and PL intensity: samples that demonstrate weak PL emission and short exciton relaxation time exhibit a high degree of valley polarization. We attribute these effects to sample-dependent variations in the exciton radiative and non-radiative lifetime components. The short exciton lifetime results in a higher measured polarization by limiting opportunity for depolarizing scattering events. These findings clarify the disparities among previously reported values and suggest a means to engineer valley polarization via controlled introduction of defects and non-radiative recombination sites.

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

9:20am **2D+MI+NS+SS+TF-FrM4 Multi-Junction Lateral 2D Heterostructures of Transition Metal Dichalcogenides**, ***Prasana Sahoo***, University of South Florida, *S. Memaran*, Florida State University, *Y. Xin*, National High Magnetic Field Laboratory, *L. Balicas*, Florida State University, *H.R. Gutierrez*, University of South Florida

Here we demonstrate the successful synthesis of lateral in-plane multi-junction heterostructures based on transition metal dichalcogenides (TMD) 2D monolayers. The heterostructures were synthesized using a modified chemical vapor deposition approach. By only controlling the carrier gas composition, it is possible to selectively growth only one TMD at the time. This introduces an unprecedented flexibility in the CVD process and allows a good control of the lateral size of each TMD segment. Heterostructures only containing MoS_2-WS_2 or $MoSe_2$-WSe_2 multiple segments, were fabricated. We also demonstrate the synthesis of heterostructures based on homogeneous TMD ternary alloys (MoS_xSe_y-WS_xSe_y). Introducing ternary alloys in heterostructures opens the horizon of possible chemical combinations and applications of 2D optoelectronic devices. The band gap modulation as well as spatial chemical distribution were studied by Raman and photoluminescence mapping. The crystalline quality of the heterostructures were characterized within an aberration-corrected scanning transmission electron microscope. Basic devices were also fabricated to study the transport properties across the junctions. Depending of the growing conditions, diffuse and/or sharp seamless interfaces with high-crystalline quality can be produced.

9:40am **2D+MI+NS+SS+TF-FrM5 Novel Electronic, Optoelectronic, and Topological Properties of 2D Materials and Their Heterostructures**, ***Xiaofeng Qian***, Texas A&M University **INVITED**

Low-dimensional materials exhibits dramatically distinct properties compared to their 3D bulk counterpart. 2D materials is such a fascinating platform with many exotic physical properties and unprecedented opportunities. In this talk, I will highlight some examples of interesting 2D materials and their heterostructures, including 2D multiferroics, 2D topological insulators and topological crystalline insulators, 2D nanostructured exciton funnels. First, I will present our discovery of 2D multiferroics in semiconducting Group IV monochalcogenide monolayers with giant spontaneous in-plane ferroelectric polarization and ferroelastic lattice strain that are strongly coupled. The multiferroicity and hence anisotropic 2D excitonic responses as well as low domain wall energy and migration barrier suggest their great potentials for tunable multiferroic functional devices such as 2D ferroelectric and ferroelastic memory, 2D ferroelastoelectric nonvolatile photonic memory, and 2D ferroelectric excitonic photovoltaics. In the second example, I will highlight our discovery on 2D topological insulators in binary and ternary transition metal dichalcogenides, and topological crystalline insulators in monolayer IV–VI semiconductors. We found electric field, elastic strain, and van der Waals stacking are able to induce topological phase transition (TPT), among which the electric-field induced TPT can be utilized for realizing topological field effect transistor distinctly different from conventional MOSFET. In the third example, I will discuss how macroscopic responses of materials can be tuned and configured by nanostructuring such as inhomogeneous strain engineering and van der Waals Moire patterning. Both nanostructures can modify local atomistic configurations and generate spatially varying electronic structures, thereby introducing novel excitonic photon funneling effect. The latter could be exploited for developing more efficient photovoltaics and light-emitting diodes. Finally, I will highlight relevant experimental progresses as well as some critical challenges and opportunities in 2D materials and their nanostructures.

10:20am **2D+MI+NS+SS+TF-FrM7 Imaging Nanoscale Heterogeneity at the Two-dimensional Semiconductor-Metal Heterointerface by Correlated Scanning Probe Microscopy**, ***Deep Jariwala****, California Institute of Technology, *A. Krayev, E. Robinson*, AIST-NT Inc., *M.C. Sherrott*, California Institute of Technology, *M. Terrones*, Pennsylvania State University, *H.A. Atwater*, California Institute of Technology

Transition metal dichalcogenides (TMDCs) of molybdenum and tungsten have recently attracted significant attention due to their band gaps in visible part of the spectrum for optoelectronic device applications. The ability to isolate these materials down to a monolayer with direct band-gap make TMDCs very attractive alternatives to graphene.

*** NSTD Postdoc Finalist**

While a lot of investigation has been devoted to understanding of crystalline and electronic quality of TMDCs in devices, little is known about the spatial distribution of electronic quality and interfaces with metals. Conventional Raman spectroscopy and confocal Raman microscopy have proved to be useful tools in this regard. However, the spatial resolution of these techniques is diffraction limited to a few hundred nanometers only. Tip enhanced Raman scattering (TERS) provides spatial resolution down to few nanometers, along with increased sensitivity due to dramatic enhancement of the Raman signal by the plasmonic tip and is therefore a suitable technique to probe nanoscale heterogeneity in TMDC samples.

Here, we report observation of nanoscale heterogeneity in exfoliated WSe_2 flakes on plasmonic Au and Ag substrates using a combination of spatial mapping with TERS, contact potential difference, topography and conductance measurements. In TERS mapping of exfoliated WSe_2 flakes, we observe the presence of domains with enhanced or depreciated Raman signal compared to adjacent material. We also observe that WSe_2 demonstrates a resonant Raman response with 638nm excitation, the TERS spectra of these domains feature a single peak at around 250 cm^{-1}, typical for non-resonant conditions. Distribution of these domains correlates extremely well with surface potential map, non-resonant areas being negatively charged compared to adjacent areas of WSe_2 that demonstrate a resonant Raman response.

We further correlate the TERS maps with concurrently recorded photocurrent maps, where we observe that domains showing both resonant and non-resonant Raman response, generated significant photocurrent, but of opposite polarities. Based on this observation, we conclude that in exfoliated layers of WSe_2, there exist nanoscale semiconducting domains with opposite doping types when in contact with the underlying metal. This hitherto unobserved heterogeneity is therefore critical to understanding of the metal-two dimensional (2D) semiconductor contact and important for optoelectronic device design and performance. The results presented here show that cross-correlation of TERS with local conductivity, surface potential and photocurrent is a vital characterization technique for nanoscale in-homogenities in 2D semiconductors and devices.

10:40am **2D+MI+NS+SS+TF-FrM8 Two-dimensional Circuitry Achieved by Defect Engineering of Transition Metal Dichalcogenides**, ***Michael G. Stanford****, *P.R. Pudasaini, A.N. Hoffman, P.D. Rack*, The University of Tennessee Knoxville

Two-dimensional materials, such as transition metal dichalcogenides (TMDs), have demonstrated promising semiconducting properties. The electrical and optical properties of TMDs can be fined tuned by altering material thickness as well as chemical composition. Properties can also be tuned by defect engineering. In this work, a focused He^+ beam as well as a remote plasma source were utilized to introduce defects into TMDs such as WSe_2 and WS_2 with fine control. Scanning transmission electron microscopy reveals that defects introduced into the TMDs range from chalcogen vacancies (0D defects) to 1D defects and extended defect networks. Tailoring defect concentration enables tunability of the electronic properties with insulating, semiconducting, and metallic behavior each obtainable. By tuning electronic properties, we demonstrate direct-write logic gates such as resistor loaded inverters with a voltage gain of greater than 5. We also demonstrate the fabrication of edge-contacted field effect transistors by defect engineering homojunctions between metallic and semiconducting WSe_2 with on/off ratios greater than 10^6. Defect engineering of TMDs enables the direct-write of complex devices into single flakes toward the goal of atomically thin circuitry.

11:00am **2D+MI+NS+SS+TF-FrM9 Scanning Tunneling Microscopy and Spectroscopy Studies of Atomically Precise Graphene Nanoribbons on Semiconducting Surfaces**, ***Ximeng Liu***, *A. Radocea, T. Sun*, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, *M. Pour*, Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, *N. Aluru*, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, *A. Sinitskii*, Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, *J.W. Lyding*, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign

Graphene nanoribbons (GNRs) with atomically smooth edges, controllable geometry and therefore tunable electronic band gaps have ignited enormous interest due to their high potential for future electronic devices. Among different techniques for GNR characterization, scanning tunneling microscopy and spectroscopy (STM/STS) provide both topographic details and local electronic structure with atomic resolution. Large-scale production of two different kinds of chevron-type GNRs (the double-wide (w) GNRs and the extended chevron (e) GNRs) was realized by a solution synthesis method [1]. Dry contact transfer technique [2] was implemented for depositing the solution-synthesized GNRs onto clean InAs (110) and hydrogen-passivated Si(100) semiconducting surfaces under ultrahigh vacuum conditions. For both GNRs, their structures were confirmed by high resolution STM imaging. The band gap of the eGNRs was determined to be 2.6eV via STS. For the wGNRs, detailed analysis and mapping of the electronic density of states both spatially and energetically was carried out with STS and current imaging tunneling spectroscopy. We found that the electron orbital shapes at the GNR edges are different from those at the centers, in agreement with computational simulations. The measured band gap of the wGNRs was only 2eV, which may result in a great improvement in conductivity. In addition, these GNRs are found to be transparent to the substrate when scanned at a small tip-sample separation, indicating a strong interaction when GNRs are pushed towards the substrate.

References:

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11:20am **2D+MI+NS+SS+TF-FrM10 Perfectly Perforated Monolayer WSe_2**, ***Kirby Smithe***, *C. Bailey*, Stanford University, *A. Krayev*, AIST-NT Inc., *E. Pop*, Stanford University

One of many prospective applications of 2D transition metal dichalcogenides (TMDs) is catalytic splitting of water for hydrogen generation. Strain in TMD layers, chalcogen atom vacancies, and increased length of the edges of TMD flakes all play an important role in increased catalytic activity, with the latter being the most effective way for improving performance. One possible way to achieve increased ratios of edge length to surface area is to use small flakes, preferably a few hundred nm across. Unfortunately, such small flakes are difficult to manipulate, and the structure of such flakes should also differ from the perfect structure of the inner areas of larger flakes[1]. Here we report that WSe_2 monolayers, grown by chemical vapor deposition (CVD) on Si/SiO_2 and transferred from the original substrate by means of dissolving the sacrificial SiO_2 layer, contain a significant concentration of perfect triangular holes. The result is confirmed by correlating the data of topography, the surface potential, friction and tip enhanced Raman spectroscopy (TERS) characterization of transferred flakes. The ratio of edge length to surface area in such perforated flakes could be up to 3 to 4 times higher compared to homogenous continuous flakes. These perforated flakes can be transferred to any surface, including corrugated ones, which should inevitably cause some strain that is also beneficial for hydrogen catalytic activity. The perfect triangular shape of the holes suggests high quality of the atomic structure of the hole edges, which also implies that the perforated flakes can be used as templates for growth of distributed in-plane heterostructures of different TMDs.

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Plasma Science and Technology Division
Room: 23 - Session PS+NS+SS+TF-FrM

Atomic Layer Etching II
Moderator: Edward Barnat, Sandia National Laboratories

8:20am **PS+NS+SS+TF-FrM1 Quasi-Atomic Layer Etching of Silicon Nitride with Independent Control of Directionality and Selectivity**, ***Sonam Sherpa***, *P.L.G. Ventzek, A. Ranjan*, Tokyo Electron Limited

Atomic layer etching (ALE) has emerged as a viable approach to address the challenges associated with continuous or quasi-continuous plasma processes. To this end, we previously reported the quasi-atomic layer etching of silicon nitride via sequential exposure to hydrogen and fluorinated plasma. The underlying premise was the surface modification via implantation of hydrogen ions into silicon nitride resulting in an anisotropic etch.

In this talk, we will demonstrate that similar enhancement in reactivity of silicon nitride can also be attained via diffusion of hydrogen atoms into silicon nitride with the resultant etch being isotropic. These results confirm the realization of self-limiting etch of silicon nitride with tunable directionality. This tuning capability is critical for sub-7nm technology node.

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* **National Student Award Finalist**

Illustrations of anisotropic (spacer RIE for self-aligned multiple patterning) and isotropic (spacer RIE for nanowire FET) etch by using this process will also be discussed. Selectivity to oxide is > 100 and damage to underlying silicon can be minimized by optimizing the flux of atomic fluorine during the exposure to fluorinated plasma. Thus, hydrogen plasma controls the directionality while fluorinated plasma step determines the selectivity to oxide and underlying silicon.

8:40am **PS+NS+SS+TF-FrM2 WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Etching Mechanisms**, ***Nicholas Johnson***, *S.M. George*, University of Colorado at Boulder

Atomic layer etching (ALE) of metals is important for the controlled removal of many valuable semiconductor materials such as conductors (e.g. W, Cu), metal gates (e.g. Ta, Ti) and metals in magnetic multilayers (e.g. Co, Fe). However, few reports exist for metal ALE using either plasma or thermal processes. Conventional thermal ALE that has defined recent work on metal oxide [1] and metal nitride [2] materials does not work for metals. New reaction pathways are required to etch metals. This study targets W ALE and examines both WO_3 ALE and W ALE as W oxidation to WO_3 is needed to define self-limiting reactions for W ALE.

WO_3 ALE was demonstrated using an AB exposure sequence with boron trichloride (BCl_3) and hydrogen fluoride (HF). BCl_3 and HF etch WO_3 by a "conversion-fluorination" mechanism. The BCl_3 converts the WO_3 surface to a B_2O_3 layer while forming volatile WO_xCl_y. HF then spontaneously etches the B_2O_3 layer producing volatile BF_3 and H_2O products. WO_3 films were formed by oxidizing W ALD films with an oxygen plasma at 280ºC. *In situ* spectroscopic ellipsometry (SE) studies determined that the BCl_3 and HF reactions were self-limiting versus exposure. WO_3 ALE etch rates increased with temperature from 0.55 Å/cycle at 128°C to 4.19 Å/cycle at 207°C. W served as an etch stop because BCl_3 and HF could not etch the underlying W film.

W ALE was performed using a three-step "oxidation-conversion-fluorination" mechanism. This is an ABC exposure sequence that where the W surface is first oxidized to a WO_3 layer and then the WO_3 layer is etched with BCl_3 and HF. SE could simultaneously monitor the W and WO_3 thicknesses and conversion of W to WO_3. Oxidation of the W surface was performed using O_3. SE measurements showed that the W film thickness decreased linearly with number of ABC reaction cycles. W ALE was shown to be self-limiting with respect to each part of the ABC process. The etch rates for W ALE were 2.4 Å/cycle at 207°C. An oxide thickness of ~20Å remained during W ALE, but could be removed with BCl_3/HF without affecting the W layer.

[1] Younghee Lee, et al., "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994-3003 (2016).

[2] Nicholas R. Johnson, et al., "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", *J. Vac. Sci. Technol. A* **34**, 050603 (2016).

9:00am **PS+NS+SS+TF-FrM3 Solving the Grand Challenges of Plasma Etch with Concurrent Engineering**, ***Mingmei Wang***, TEL Technology Center, America, LLC, *P.L.G. Ventzek*, *A. Ranjan*, Tokyo Electron Limited **INVITED**

A consequence of multiple patterning approaches enabling Moore's Law scaling to continue through 10nm to 7nm and beyond is that plasma dry etch process faces unprecedented challenges. "Scaling" of plasma etch to seemingly impossible capabilities is the key to meeting Moore's Law scaling. For example, etch process must achieve extremely high (almost infinite) selectivity in applications where self aligned patterning schemes are involved. Etch process is also required to achieve less than half nanometer (atomic scale) CD variations across 300mm wafers including the important "extreme edge" area as small as 2mm exclusion. These are but two examples of etch grand challenges. While the process requirements push the hardware design to the limits, understanding of process mechanisms becomes the most critical bottleneck to explore process regimes that are able to satisfy the most challenging patterning requirements. In fact, without process understanding at the atomic scale, it is difficult to imagine a means to innovate hardware designs.

In this talk, we will discuss concurrent engineering approaches including both modeling and experiment to understand and develop etching processes that meet grand challenge requirements. The core of the approach is an integrated chamber scale HPEM (Hybrid Plasma Equipment Model)-feature scale MCFPM (Monte Carlo Feature Profile Model) model [1]. The concurrent engineering approach comprises stages of development and prediction capability tests using both blanket wafer and patterned stack data and finally process parameter optimization. By using this approach, we are able to provide insights on how to resolve grand challenges in plasma etch with a minimum of engineering resources. The presentation will survey both experimental and computational results representing a few case studies in SAC quasi-ALE [2], Si ALE, organic etch CD uniformity, and LER/LWR improvement in EUV resist patterned sample etch. Furthermore, insights into the relationship between chamber function and critical surface interactions will be discussed.

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

[2] M.Wang, P. Ventzek, A. Ranjan, J. Vac. Sci. Technol. A 35, 2017.

9:40am **PS+NS+SS+TF-FrM5 Effect of Non-Uniform Polymer Deposition on the Atomic Layer Etching of 3D Features in SiO_2**, ***Chad Huard***, University of Michigan, *Y. Zhang*, *S. Sriraman*, *A. Paterson*, Lam Research Corporation, *M.J. Kushner*, University of Michigan

Atomic layer etching (ALE) typically separates the etch process into (at least**)** two self-limited steps, repeated cyclically – a passivation and an etch step. To obtain all of the benefits of ALE, each of the steps should be fully self-limited, and produce no continuous etching during either step. Only by the synergy between the two steps being repeated cyclically is atomic etching achieved. ALE etching mechanisms have been demonstrated for several materials (e.g., Si, Ge) that do not involve thick passivation layers. ALE-like etching has also been demonstrated for SiO_2 and Si_3N_4, however with the etching mechanisms for these materials relying on the non-self-limited deposition of a polymer layer, it is more difficult to obtain the full benefits of ALE in these systems.

To investigate the benefits and limitations of using an ALE-like pulsing scheme for etching SiO_2, a representation of the through-polymer etching mechanism of SiO_2 in $Ar/C_4F_8/O_2$ plasmas was developed and implemented into the 3-dimensional Monte Carlo Feature Profile Model (MCFPM). The model includes diffusion of radical atomic species (F and O) through the polymer capping layer and ion-energy activated reactions at the SiO_2/polymer interface stimulated by ions implanting through the polymer capping layer. These processes allow for the simulation of SiO_2 (and Si) etching through a finite thickness of polymer. The model reproduces systematic trends for selectivity and etch rates as a function of polymer thickness observed for continuous etching.

Results from the model suggest that the non-self-limited nature of the polymer deposition step can limit the benefits of applying ALE techniques to SiO_2, particularly in 3D features. The balance of polymer deposition by radical CF_x species and erosion by F radicals is subject to neutral transport issues and so are more sensitive to geometry and aspect ratio than for fully self-limited passivation, as occurs in ALE of Si using, for example, Cl_2 containing gases. The reactive sticking coefficients of CF_x radicals on the polymer surface depends, in part, on ion generated dangling bonds which can result in a non-uniform polymer thickness in 3D features. The etch depth per cycle (EPC) was found to depend on polymer thickness, introducing non-uniformity and aspect ratio dependent etch rates in 3D features during ALE. Methods for mitigating the dependence of EPC on polymer thickness using carefully controlled ion energies and the introduction of O_2 will be discussed.

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

10:00am **PS+NS+SS+TF-FrM6 Etching with Low Te Plasmas**, ***Scott Walton***, *D.R. Boris*, *S.C. Hernández*, Naval Research Laboratory, *S.G. Rosenberg*, ASEE Postdoctoral Fellow, NRL, *H. Miyazoe*, *A.V. Jagtiani*, *S.U. Engelmann*, *E.A. Joseph*, IBM T.J. Watson Research Center

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. The appropriate threshold and process windows are certainly material specific but it is reasonable to assume many applications require low energy ions. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{11} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. The flux at the surface will thus be characterized by a comparatively large amount of ions whose energies are < 5 eV, a value commensurate with the bond strength of most materials. Ion energies can be raised with substrate biasing, which makes these sources well-suited to meet the needs of energy requirements for precise, selective etching. In this work, we discuss SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds. We pay particular attention to the etch rates, selectivity (vs. carbon films, Si and SiO_2), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. These results are compared with plasma diagnostics to gain a better understanding of the process requirements and windows for threshold etching of SiN. This work is partially supported by the Naval Research Laboratory base program.

10:20am **PS+NS+SS+TF-FrM7 Thermal Atomic Layer Etching of Titanium Nitride Using Sequential, Self-Limiting Oxidation and Fluorination Reactions**, ***Younghee Lee***, *S.M. George*, University of Colorado at Boulder

Titanium nitride (TiN) is an important conducting material as a copper diffusion barrier and a gate electrode in semiconductor devices. Previous thermal atomic layer etching (ALE) studies have shown that TiN was not etched using fluorination and ligand-exchange reactions [1]. These results suggest that the ligand-exchange reactions do not produce stable and volatile reaction products.

In this work, a new etching mechanism based on sequential, self-limiting oxidation and fluorination reactions was developed for thermal TiN ALE. The oxidation reactant was either O_3 or H_2O_2. The fluorination reactant was hydrogen fluoride (HF) derived from HF-pyridine. In the proposed reaction mechanism, the O_3 reaction oxidizes the surface of the TiN substrate to a TiO_2 layer and produces gaseous products such as NO. HF exposure to the TiO_2 layer then yields TiF_4 and H_2O as volatile reaction products. The overall reaction can be written as: $TiN + 3O_3 + 4HF \rightarrow TiF_4 + 3O_2 + NO + 2H_2O$.

Quartz crystal microbalance experiments showed that HF can spontaneously etch TiO_2 films. Spectroscopic ellipsometry and x-ray reflectivity analysis showed that TiN films were etched linearly versus the number of ALE cycles using O_3 and HF as the reactants. The etch rate for TiN ALE was determined at temperatures from 150 to 350°C. The etch rates increased with temperature from 0.06 Å/cycle at 150°C to 0.20 Å/cycle at 250°C and stayed nearly constant for temperatures $\geq$250°C

The thermal ALE of many other metal nitrides should be possible using this new etching mechanism based on oxidation and fluorination reactions. This thermal ALE mechanism should also be applicable to metal carbides, metal sulfides, metal selenides, and elemental metals that have volatile metal fluorides.

[1] Y. Lee, C. Huffman and S.M. George, “Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions”, *Chem. Mater.* **28**, 7657 (2016).

10:40am **PS+NS+SS+TF-FrM8 Atomistic Simulations of H_2 Plasma Modification of SiN Thin-Films for Advanced Etch Processes**, ***Vahagn Martirosyan***, *E. Despiau-Pujo, O. Joubert*, LTM, Univ. Grenoble Alpes, CEA-LETI, France

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous wave (CW) plasma processes are not able to selectively etch ultra-thin films without damaging the active layers of advanced nanoelectronic devices. In particular, silicon nitride or low-k spacers etching must be performed with nanoscale-precision without creating defects to the underlayer substrate, to preserve device performances and be compatible with epitaxial steps. To solve this problem, one possible alternative is to use a recently developed etch technology, which consists of two steps [1]. In the first step, the material to be etched is exposed to a hydrogen (H2) or helium (He) ICP or CCP plasma; in the second step, the modified material is chemically etched by wet cleaning or exposure to gaseous reactants only.

Due to the complexity of plasma-material interactions, the successful development of such a new etch approach requires a more detailed understanding of the fundamental mechanisms involved in the process. Therefore, we develop Molecular Dynamics (MD) simulations to study the Si-N-He and Si-N-H systems and provide an overview of the reaction processes at the atomic scale. The objective is to understand the role of ion energy in the self-limited ion implantation, and to determine the relationship between the flux/energy of plasma species bombarding the surface and its chemical/structural modifications.

In this work, we investigate the interaction between hydrogen plasma species (Hx+ ions and H radicals) and silicon nitride via MD simulations. We first study the impact of ion energy (5-100eV), ion dose and ion type on a SiN substrate only exposed to ion bombardment. Then, the influence of a mixed exposure to both Hx+ ions and atomic H is investigated to observe how the hydrogen plasma composition will affect the SiN substrate modification. For pure ion bombardment conditions, simulations show an initial Hx+ ion implantation followed by the formation of a stable modified layer at steady state. Few or no SiN etching is observed for ion energies >25eV, which shows that hydrogen ions only induce a volume transformation and can modify the SiN substrate on a precise depth without etching it. By contrast, simulations of mixed ion/radical bombardment show that a high concentration of atomic hydrogen can crucially change the evolution of the substrate, since H radicals are able to slowly etch SiN along with the modification caused by Hx+ ions. Mechanisms of aforementioned phenomena, as well as comparison with experiments, will be discussed during the presentation.

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

11:00am **PS+NS+SS+TF-FrM9 Defectless Nanostructure Patterning of Germanium Using Neutral Beam Etching for Ge FinFET Devices**, ***Shuichi Noda***, Tohoku University, Japan, *W. Mizubayashi, K. Endo*, AIST, Japan, *S. Samukawa*, Tohoku Univeversity, AIST, Japan

Germanium FinFET has been becoming a promising candidates for highly scaled CMOS FETs due to large carrier mobility. However, etching mechanisms of Ge and optimization of etching method have not investigated deeply. We have already succeeded to apply a neutral beam etching (NBE) method to Si FinFET fabrication processes and shown excellent device performances owing to low-damage properties of NBE [1]. Since Ge is much more unstable material to apply to FET devices than Si, there must be much more advantages to use NBE method.

The NBE system consists of an inductive coupled plasma (ICP) source and a carbon aperture plate (neutralization plate) on which enormous number of high aspect ratio aperture holes are opened. Positive and negative chlorine ions generated in a pulse time modulated ICP are accelerated toward the aperture plate and effectively converted to the neutral beam by applying rf field on the aperture plate. Etching substrates beneath the aperture plate are etched mainly by directional chlorine neutral beams without any risky matters such as charged particles (electrons and ions) and irradiation of vacuum ultra-violet (VUV) light. We consider that the VUV irradiation has notable effect on the etching characteristics and defect generation that influences device performances.

We compared etching characteristics of Ge between the NBE and a plasma etching using the same ICP source. It was found that the Ge etching rate of NBE was about one order of magnitude smaller than that of the plasma etching. We consider that such a large differences is caused by surface defects induced by the VUV irradiation. Under the VUV irradiation, surface defects, that is high density dangling bonds of Ge, are created and the defect sites react with chlorine radicals actively and the chlorinated layer are etched off by the ion bombardment in the case of the plasma etching. On the other side, the Ge surface exposed to the neutral beam seems to be chlorinated more slowly and probably the chlorinated layer is much thinner than the plasma-like conditions. And the etching reaction occurs by the chlorine neutral atom beam bombardment. This smaller etch rate around 20 nm/min seems a little bit inefficient however it can be said this small etch rate is much more useful characteristics for the nanometer scale low damage etching processes. AFM observation showed that the etched surfaces by NBE were much smoother than that by the plasma etching. Etched side wall (to be Ge channel surface) by NBE were also very smooth and vertical. High magnification TEM images showed substantially atomic revel smooth side wall.

[1] K. Endo *et al.*, IEDM Tech. Dig. (2005) pp. 840-843.

11:20am **PS+NS+SS+TF-FrM10 Thermally-Driven Atomic Layer Etching of Metallic Tungsten Films Using O_2 and WF_6**, ***Wenyi Xie***, *P.C. Lemaire, G.N. Parsons*, North Carolina State University

The semiconductor industry is facing the challenge of manufacturing transistor devices with sub-10 nm high aspect ratio features. Understanding and developing self-limiting etching processes that allow precise control over the thickness of materials removed is essential for enabling the manufacturing complex transistor structures. In this work, we investigated chemical vapor etching of tungsten films using oxygen (O_2) as the oxidant source and tungsten hexafluoride (WF_6) as the etchant.

We propose that etching of tungsten proceeds in two steps: 1) oxidation of the tungsten film to form WO_x surface species and 2) formation and removal of volatile metal fluoride species upon reaction with WF_6. Using quartz crystal microbalance (QCM), we found that the oxidation step with O_2 is required for etching to occur during WF_6 exposure. In addition, etching of O_2 treated tungsten films showed saturation towards WF_6 exposure. This indicates that etching of tungsten using oxygen and WF_6 is a self-limiting process, making it promising as an atomic layer etching process. QCM results also showed that the rate of etching depends on the temperature. Minimal amount of etching was measured at temperatures less than 275 °C. Ex-situ characterization techniques were applied to analyze the etching of tungsten films deposited on SiO_2 substrates. Scanning electron microscopy (SEM) results revealed the change in morphology of tungsten films after different number of O_2-WF_6 ALE cycles. The tungsten film on SiO_2 started out as a coalesced film, which transformed into disjointed nuclei, and the nuclei appeared completely removed as the number ALE cycle increased. Lastly, X-ray photoelectron spectroscopy (XPS) analyses further confirmed etching of tungsten film and showed a minimal amount of fluorine remained on the surface after the O_2-WF_6 ALE process.

Thin Films Division
Room: 20 - Session TF-FrM

Self-assembled Monolayers and Organic/Inorganic Interface Engineering
Moderator: Adrienne Stiff-Roberts, Duke University

8:20am **TF-FrM1 Kinetics of Swelling and Deswelling in Thermoresponsive Polymers Deposited by Initiated Chemical Vapor Deposition**, *P. Salzmann*, Graz University of Technology, *A. Perrotta*, Eindhoven University of Technology, Netherlands, ***AnnaMaria Coclite***, Graz University of Technology, Austria

Thermo-responsive polymers, like the Poly-(N Isopropylacrylamide) p(NIPAAm), change their properties (e.g. thickness and wettability) upon small changes in the environment temperature. This makes them suitable for interesting applications as smart sensors, artificial muscles or drug delivery systems. The change in the film properties arises from a coil to globule transition from a swollen hydrophilic state at temperatures below the lower critical solution temperature (LCST) to a shrunken hydrophobic state when the material is heated to temperatures higher than the LCST.

Cross-linked thin polymer films of NIPAAm were synthesized by initiated chemical vapor deposition (iCVD) and their thermoresponse was studied in-situ in water and in humidity by ellipsometry.

The film thicknesses were up to three times higher at temperatures below the LCST than at higher temperatures. Temperature cycles and different heating ramps revealed different mechanism of swelling and deswelling. The response during the cooling (i.e. during the swelling) was characterized by an LCST of 23°C. During the heating process (i.e. deswelling) the LCST was as high as 36°C. Similar discrepancies were also observed with another thermoresponsive polymer (N,N-Diethylacrylamide) deposited by iCVD. The reason was ascribed to different diffusion kinetics of water in the polymer meshes, and different arrangements of the polymer chains at the interface with water, depending on the rate of increase or decrease in temperature. A detailed investigation of these processes will be shown due to its importance for sensing applications.

9:40am **TF-FrM5 the Curious Wetting Behavior of ALD Grown Al_2O_3 Thin Film Surfaces**, ***Yi Li***, *B.D. Piercy, M.D. Losego*, Georgia Institute of Technology

The curious wetting behavior of ALD grown Al_2O_3 thin film surfaces

Yi Li, Brandon D. Piercy, Mark D. Losego

Conventional wisdom suggests that Al_2O_3 surfaces should be hydrophilic. Recently, it was demonstrated by the Parsons lab at NC State that under certain conditions a few cycles of trimethylaluminum-water atomic layer deposition (ALD) transforms cotton fiber surfaces from hydrophilic to hydrophobic. These researchers suggest that adventitious carbon from ambient atmosphere is the source of this hydrophobicity, but they make no note of the universality of this phenomenon. In our effort to better understand this phenomenon, we discovered that ALD grown Al_2O_3 thin films of "any" thickness (1 nm to >50 nm) on "any" substrate (including silicon) can be transformed into a relatively hydrophobic surface state (water contact angles > 80°) when heat treated under appropriate conditions. After heat treatment, ellipsometry detects several angstroms increase in thickness and XPS suggests this layer is some form of hydrocarbon. In this talk, we will discuss our evaluation of three hypotheses for the source of this hydrocarbon layer: (1) contamination from the heating environment (e.g., oven), (2) carbon contamination from the ALD deposition process (i.e., unpyrolized ligands), and (3) adventitious carbon from the atmosphere. To address hypotheses (1) and (3), Al_2O_3 thin films grown by ALD to 10 nm thickness on silicon are found to become hydrophobic if we remove them from the ALD reactor and then re-anneal them in either a "dirty" ambient air oven or the "clean" ALD reactor under low-pressure and ultra-pure flowing nitrogen conditions. To further verify the purity of the ALD reactor, we have done this annealing step without breaking vacuum in the ALD reactor, leading to the Al_2O_3 surface remaining hydrophilic. Films annealed to 700 °C for 4 hours to fully pyrolyzed any remaining organics (still hydrophilic) and then re-heated to 150 °C for 30 min are also found to turn hydrophobic, suggesting that residual carbon within the film is also not the source. Thus, we believe that the Al_2O_3 surface is attracting adventitious carbon from ambient atmosphere and then reacting with the surface to form a hydrophobic layer. This reaction, which is thermally accelerated, appears to be key to the transition. We will report on how both temperature and time affect this surface reaction and our best understanding of the surface chemistry based on various surface spectroscopy techniques.

10:00am **TF-FrM6 Controlled Thicknesses of Vapor Deposited Silane Films**, ***Brian Johnson***, *A. Diwan, M.R. Linford*, Brigham Young University

Solution-based silane deposition is well known and has been widely studied. Increasingly, however, people are recognizing the importance of vapor phase deposition of these important reagents. Indeed, these gas phase depositions can be highly reproducible, they involve no solvent, and they can be integrated into production processes. Some of their disadvantages are the cost of the vacuum equipment/ovens needed, and the limitations inherent to the vapor phase, e.g., one cannot allow a polymerization of a silane to take place before the reagent/polymer is deposited on a surface as one can in a solution phase deposition. In this presentation we describe processes for controlling and increasing thicknesses of silane films on silicon surfaces. Variables studied in this work include process temperature, pressure, and reagent concentration. Silane films have been characterized by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), spectroscopic ellipsometry (SE), and wetting. The depositions described in this work were performed in a commercial chemical vapor deposition (CVD) oven (the 1224P by Yield Engineering Systems). Special emphasis in these studies was placed on minimizing carryover between runs.

10:20am **TF-FrM7 Supramolecular Heterostructures formed by Sequential Epitaxial Deposition of Two-Dimensional Hydrogen-Bonded Arrays**, *V.V. Korolkov, M. Baldoni*, The University of Nottingham, UK, *K. Watanabe, T. Taniguchi*, National Institute for Materials Science, Japan, *E. Besley*, ***Peter Beton***, The University of Nottingham, UK

The formation of two-dimensional supramolecular arrays provides a highly flexible route to the control of the spatial organization, down to the molecular scale, of the chemical functionality of a surface. These molecular networks, which can be formed through self-assembly processes on a variety of different substrates including semiconductors, metals, insulators[0] and layered materials, are, in almost all cases, limited to monolayer thickness. Progress towards the growth of higher layers has so far been much more limited, with demonstrations of bilayer growth and site-specific molecular adsorption. Specifically, the additional functional control, which may be achieved through the formation of heterostructures realized by placing one supramolecular layer on another and resulting in growth into the third dimension perpendicular to the substrate, has not been widely explored for these materials. Such additional control of material properties is well established for semiconductors, both organic and inorganic, and, more recently, layered materials, providing a strong motivation to explore analogue materials derived from stacked supramolecular networks. Here we describe the successful formation of heterostructures formed by the sequential growth of distinct one- and two-dimensional arrays. It is possible, using high resolution atomic force microscopy (AFM) to determine an epitaxial alignment between successive layers. Furthermore, we demonstrate using classical molecular dynamics (MD) simulations that the placement and dimensions of the layers may be robustly predicted using well established force-fields.

Supramolecular heterostructures[1] are formed by growing sequential layers of bi- and mono-component two-dimensional molecular arrays stabilized by hydrogen bonding. The heterostructures are formed on hexagonal boron nitride by depositing cyanuric acid/melamine (CA.M) followed by terephthalic acid (TPA) or trimesic acid (TMA) and imaged using atomic force microscopy under ambient conditions with resolution approaching 0.1 nm. A clear epitaxial arrangement is observed between these layers having intrinsically distinct symmetries and lattice constants, which for TMA/CA.M corresponds to a ($\sqrt{3}$ x $\sqrt{3}$)R30° phase, while TPA forms rows with a molecular separation that matches the CA.M period. Structures calculated using classical molecular dynamics are in excellent agreement with the orientation, registry and dimensions of the epitaxial layers. Calculations confirm that van der Waals interactions provide the dominant contribution to the adsorption energy and registry of the layers.

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

10:40am **TF-FrM8 Functionalization and Stabilization of Ultrathin Alumina Films with Rhenium Photosensitizers**, ***Wolf-Dietrich Zabka***, *D. Leuenberger*, Department of Physics, University of Zürich, Switzerland, *G. Mette*, University of Zürich, Switzerland, *C. Monney*, University of Zürich, Switzerland, *M. Mosberger*, University of Zürich, Switzerland, *B. Probst-Rüd*, University of Zürich, Switzerland, *R. Alberto, J. Osterwalder*, University of Zürich, Switzerland

Ultrathin (ut) oxide films with a thickness of few atomic layers are often used as model systems for oxide surfaces and their interaction with adatoms, particles and molecules. In particular, epitaxial ut-alumina films grown on NiAl alloys have been used to study a wide range of phenomena under UHV-conditions [1,2]. However, their instability under ambient conditions limits the possibilities for application [3,4].

We developed a new wet chemistry setup directly attached to an existing ultra-high vacuum system that enables us to deposit self-assembled monolayers (SAM) from highly purified solvents onto substrates prepared under UHV conditions without exposure to air. The setup, the procedure for SAM-deposition and the characterization of residual contamination detected with X-ray photoelectron spectroscopy (XPS) will be described. Rhenium photosensitizers functionalized with carboxyl groups (Re$(CO)_3$(NCS)bipycarb) are attached onto ut-alumina films. XPS measurements indicate that the resulting structure is stable in air. First results from time-resolved photoemission spectroscopy suggest that by altering the oxide thickness, a variation of the lifetime of excited electrons can be achieved. Both, the substrate stabilization and the control of hot electron lifetimes offer new prospects for the application of such ultrathin oxide films involving charge transfer and related mechanisms.

[1] N. Nilius, Surf. Sci. Rep. 64, 595 (2009).

[2] U. Diebold, S. C. Li, and M. Schmid, Annu. Rev. Phys. Chem. 61, 129 (2010).

[3] A. Shavorskiy, K. Müller, J. T. Newberg, D. E. Starr, and H. Bluhm, J. Phys. Chem. C 118, 29340 (2014).

[4] J. Evertsson, F. Bertram, F. Zhang, L. Rullik, L. R. Merte, M. Shipilin, M. Soldemo, S. Ahmadie, N. Vinogradov, F. Carlà, J. Weissenrieder, M. Göthelid, J. Pan, A. Mikkelsen, J.-O. Nilsson, and E. Lundgren, Appl. Surf. Sci. 349, 826 (2015).

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