Nanomanufacturing Science and Technology Focus Topic
Room: 207 - Session NM+MS+NS+TF-MoM

ALD for Nanomanufacturing
Moderator: B. Lu, AIXTRON Inc.

9:00am **NM+MS+NS+TF-MoM3 Industrialization of Atomic Layer Deposition: From Design to Deposition**, ***J.S. Becker***, *A. Bertuch, R. Bhatia, L. Lecordier, G. Liu, M. Sershen, M. Sowa, R. Coutu, G.M. Sundaram*, Cambridge NanoTech, Inc. **INVITED**

The demonstrated benefits provided by Atomic Layer Deposition (ALD) in producing films of exceptional uniformity, and conformality, has set the stage for its use in large area, batch processing, and Roll-to-Roll applications. In this work we discuss the use of Computational Fluid Dynamics (CFD) as a means of gaining insight into the system performance of such industrial instruments, but also as a technique for refining system design. Additionally we describe the basic underpinnings of design for ALD systems operated under atmospheric conditions, (for Roll-to-Roll use), along with the design factors which must be considered for zone separated ALD methods. Finally we will present film results taken from a zone-separated ALD system, and discuss the salient aspects of the deposition process.

9:40am **NM+MS+NS+TF-MoM5 Improved MOS Characteristics of CeO_2/La_2O_3 and MgO/La_2O_3 Gate Stacks Prepared by ALD**, ***T. Suzuki***, *M. Kouda,* Tokyo Institute of Technology and AIST, Japan, *K. Kakushima, P. Ahmet, H. Iwai,* Tokyo Institute of Technology, Japan, *T. Yasuda*, AIST, Japan

La_2O_3 is one of the candidate materials for the next-generation high-k gate stacks because it can achieve sub-1 nm EOT by forming direct-contact La silicate with Si. There have been many ALD studies for La_2O_3, however, the performance of the MOSFETs incorporating ALD-La_2O_3 needs much improvement. Our previous studies using EB evaporation showed that capping the La_2O_3 dielectrics with an ultrathin layer of CeO_2 or metallic Mg (~1 nm) effectively improved the channel mobility [1,2]. In this paper, we report fabrication of CeO_2/La_2O_3 and MgO/La_2O_3 gate stacks by ALD/CVD for the first time, and demonstrate that these stacks show improved electrical properties (k value, channel mobility, etc.) as compared to single-layer ALD-La_2O_3.

The experiments were carried out using a multi-chamber ALD/CVD system which was capable of in-situ metallization and RTA. The CeO_2/La_2O_3 and MgO/La_2O_3 gate stacks were formed on H-terminated Si(100) using $Ce[OCEt_2Me]_4$, $La(^iPrCp)_3$, and $Mg(EtCp)_2$ metal sources. La_2O_3 and MgO films were formed by ALD using H_2O as an oxidant. The ALD temperature was set at a relatively low temperature of 175°C in order to ensure the self-limiting growth [3]. CeO_2 films were formed in the CVD mode via thermal decomposition of $Ce[OCEt_2Me]_4$ at 350ºC. The gate electrodes were formed by sputtering of W. MOSFETs were fabricated by the gate-last process.

The effective k values for the CeO_2(1nm)/La_2O_3(3nm) and MgO(0.8nm)/La_2O_3(4nm) stack capacitors were approximately 16, which was significantly larger than those for La silicate without any capping layer (k=10~12). The k-value improvement by the CeO_2 capping is presumably due to the higher k value of CeO_2 (~23), whereas the improvement by the MgO capping is ascribed to suppression of excessive La-silicate formation.

We have also found that the CeO_2/La_2O_3 gate stack leads to excellent mobility characteristics. The mobility for the MOSFET with 1.43 nm EOT was 214 cm^2/Vs at an effective field of 1.0 MV/cm, which was 85% of the Si universal mobility. The mobility improvement by the CeO_2 capping is attributed to the reduced fixed-charge density, since V_{th} approached to the ideal values by the CeO_2 capping. On the other hand, the MgO capping induced a negative shift in V_{th} and consistently degraded the mobility. These effects of ALD-MgO capping are qualitatively different from those observed for EB-evaporated Mg [2]. The mechanisms causing such a difference between EB evaporation and ALD are now under investigation.

This work was carried out in Leading Research Project for Development of Innovative Energy Conservation Technologies supported by NEDO.

References: [1] T. Koyanagi, et al., JJAP, **48**, 05DC02 (2009); [2] M. Kouda, et al., 2009 VLSI Symp., p. 200; [3] K. Ozawa, et al.,2010 ICSICT, p. 932.

10:00am **NM+MS+NS+TF-MoM6 Highly Uniform and Conformal Thin Film Metallization with Thermal and Plasma-Enhanced Atomic Layer Deposition**, *M. Toivola, J. Kostamo, T. Malinen, T. Pilvi, T. Lehto,* ***C. Dezelah***, Picosun Oy, Finland

Ultra-thin, nanometer-scale metal or metallic films are a crucial component in e.g. several applications of modern MEMS/NEMS (Micro/NanoElectroMechanical Systems) and other advanced IC technologies, sensors, optical devices and catalyst manufacturing. When the component sizes keep diminishing and at the same time, the level of system integration increasing (for example the so-called “System-in-a-Package” multifunctional chip devices), it creates a drive from “conventional” 2D device architecture to 3D component integration. Through Silicon Vias (TSV) are a central structure in these 3D-stacked devices and there’s often a need to produce highly uniform and conformal thin films of metals or otherwise conducting materials on the insides of the vias. Due to the often very high aspect ratio (AR) of the TSV structures, Atomic Layer Deposition (ALD) is one of the only methods with which reliably uniform and conformal material layers can be deposited on the via walls.

Industrially upscalable ALD processes were developed for several metals and metallic compounds, i.e. Pt, Ir, Ru, Cu, Ag, Au, TiN and TiAlCN. Deposition of metals can be done with thermal ALD and plasma-enhanced (PEALD). The main benefits of the PEALD technique are the possibility to use reductive processes instead of oxygen, lower deposition temperatures which decreases the thermal stress on the substrates, and a wider variety of precursor chemicals.

Inductively coupled remote plasma source system was further developed to reduce any possibility of plasma damage, which can often happen in the more conventionally designed, direct plasma devices. Instead of direct ion bombardment, our plasma system utilizes highly reactive radicals. Protective flows and separating metal precursor inlets shield the plasma source from getting short-circuited by films from precursor back-diffusion. E.g. N_2/ H_2, H_2/Ar, O_2 and mixed gas plasmas can be generated with the system.

Structural design solutions were optimized for ALD reactors. Top flow delivery of the precursor gases ensures even distribution of reactive molecules inside the reactor vessel. This is beneficial especially in the case of non-optimal processes with precursor decomposition or etching or poisoning of reactive sites by reaction by-products. Less impurity and thickness gradient scan be achieved with the top flow, compared to the side-flow (cross-flow) design since all the area reacts at the same time leaving less reactive sites left for reaction with the by-products. Therefore, it is possible to get more challenging reaction chemistries working with the top-flow design, and also a forced flow for through-porous samples is possible. With modified stopped flow design, extended reaction time inside the chamber can be reached while still keeping the protective flows from the inlets on to prevent any back-diffusion of precursor and subsequent particle formation in the inlet lines.

Upscalable structure was specifically designed to bridge the gap between R&D and production. Smaller ALD tools can be used for process and chemical precursor development at for universities and research labs, whereas the larger, ALD tools can be fully automatized, upscaled and clustered into full scale high volume throughput industrial production unit capable of coating even several thousands of wafers per hour.

10:40am **NM+MS+NS+TF-MoM8 Atomic Layer Deposition for Continuous Roll-to-Roll Processing**, ***S.M. George***, *P.R. P. Ryan Fitzpatrick*, University of Colorado at Boulder **INVITED**

Atomic layer deposition (ALD) is currently being developed for continuous roll-to-roll processing. This development is significant because roll-to-roll processing would allow ALD to address many applications in a cost effective manner. This talk overviews the approaches and progress to date. The original idea of ALD with moving substrates and constant precursor flows was presented in a patent by Suntola and Antson in 1977. This scheme involved rotating the substrate between alternating precursor sources and vacuum pumping regions. One current approach under development is based on moving the substrate close to a gas source head. The ALD precursors continuously flow through slits in the gas source head that are separated and isolated by inert gas purging. A second version of this design involves using a gas bearing to set the gap spacing between the gas source head and substrate. Another ongoing approach is based on moving the substrate through separate regions of precursor pressure and inert gas purging. Limited conductance between the regions prevents the gas phase reaction of the ALD precursors. The talk examines the issues and prospects for achieving ALD for continuous roll-to-roll processing. Additional details

are presented for the dependence of precursor isolation on reactor parameters for a substrate under a model gas source head.

11:20am **NM+MS+NS+TF-MoM10 High Rate Continuous Roll-to-Roll Atomic Layer Deposition**, ***E. Dickey***, Lotus Applied Technology **INVITED**

Atomic Layer Deposition (ALD) is a unique thin film deposition process, capable of producing coatings with unmatched quality and performance. Its unique attributes include high conformality and outstanding thickness precision, enabling the deposition of dense, continuous pinhole-free films, even when extremely thin, and even on highly imperfect substrate surfaces. These qualities have made the process attractive for applications on flexible substrates, including dielectrics and semiconductors for flexible electronics devices, and high performance gas diffusion barriers to encapsulate and protect environmentally sensitive devices such as OLED displays and lighting, and CIGS photovoltaic modules.

Until recently, ALD films have generally been deposited using conventional static processing, in which the individual precursors are sequentially introduced into and purged from a common volume containing the stationary substrate. This sequence, commonly called an ALD cycle, typically requires at least several seconds and results in the growth of approximately 0.1nm thickness. As a result, the time required to deposit films of reasonable thickness can be quite long. Furthermore, the static nature of the process makes roll-to-roll processing impractical. In this presentation, we discuss the development of a new ALD process based on substrate translation, with the ALD cycle elements enabled by transport of the flexible substrate back and forth between the precursor zones. Because no time is required for introducing, saturating, and removing precursors for each cycle, the deposition speed is dramatically increased. In addition, this configuration naturally provides the unique feature of film deposition only on the substrate itself, as it is the only surface which is exposed to both precursors. In turn, this allows the use of steady-state plasma as the oxygen source, enabling a new technique of precursor isolation; "precursor separation by radical deactivation", in which the oxygen gas precursor actually mixes with the metal precursor, but is only reactive in the region of the plasma source. Together, this technology set has allowed the deposition of high quality ALD films on polymer substrates, including ultra-barrier films, at substrate speeds in excess of one meter per second.

Thin Film Division
Room: 107 - Session TF-MoM

Thin Films: Growth and Characterization I
Moderator: J.M. Fitz-Gerald, University of Virginia

8:20am **TF-MoM1 Heavy Ion Irradiation Effects on Ti/Al Multilayer Thin Films**, ***R.S. Vemuri***, The University of Texas at El Paso, *T. Varga, S.V. Shutthanadan, S.V.N.T. Kuchibhatla, M.H. Engelhard, P. Nachimuthu, C.H. Henager, C.M. Wang, S. Thevuthasan,* Pacific Northwest National Laboratory, *C.V. Ramana*, The University of Texas at El Paso

There has been growing interest in thin bi-metallic multilayer films for the usage under extreme radiation conditions because of their radiation healing properties. Recent discovery and research indicate that materials can be hardened against radiation damage by building nanolayered structures with an optimized layer thickness to increase point defect recombination relative to a non-layered structure and that can self-heal. In this study, we investigate whether the internal interfaces can be manipulated at the nanoscale to enhance dynamic recombination of radiation-produced defects, or self-healing, so as to dramatically reduce radiation damage without compromising other properties using Ti/Al multilayer films.

Ti/Al multilayer films were fabricated on Si (100) and epi polished MgO (100) substrates using DC magnetron sputtering and Molecular beam epitaxy (MBE) The growth parameters for each method, for sputtering – pressure, power and substrate temperature deposition rate; and for MBE-deposition rate and substrate temperature were optimized to achieve high-quality thin films. The films were characterized using x-ray diffraction (XRD), x-ray reflectivity (XRR), Rutherford backscattering spectrometry (RBS), and x-ray photoelectron spectroscopy (XPS) measurements. The films show mostly polycrystalline structure with no elemental interdiffusion at the interfaces. Detailed structural and compositional analysis was also performed using high resolution TEM/STEM and atom probe tomography (APT). The films were irradiated using 1-8 MeV Au ions to understand the radiation effects. The damage peak, stopping range and ion distribution were simulated using binary collision approximation based Monte Carlo method (SRIM software program). Au ion energies, estimated from the simulation, were used to position the damage peak at the interested interfaces and away from the interfaces to obtain the complete picture at the interfaces and in the bulk of the films. The interface and crystal lattice damage, amorphization, and defect density were studied by RBS, HAADF-STEM and APT, and compared with those results from the pristine samples. The relationships between film properties and radiation healing characteristics will be presented and discussed.

8:40am **TF-MoM2 Flux and Surfactant-Assisted Physical Vapor Deposition: New Approaches for Improving Complex Oxide Thin Film Growth**, ***J.-P. Maria***, *E.A. Paisley, B.E. Gaddy,* North Carolina State University, *M.D. Biegalski,* Oak Ridge National Laboratory, *D.L. Irving, A.R. Rice, R. Collazo, Z. Sitar*, North Carolina State University **INVITED**

Epitaxial integration of complex oxides with wide band gap polar semiconductors such as GaN (0002) presents the possibility for high-power, high-frequency, and high temperature GaN electronics by virtue of 2-D charge carriers at polar interfaces and possible access to non-linear dielectric properties. This work describes synthesis and characterization of such thin film heterostructures by MBE, with specific attention given to controlling film growth. Our previous work has shown growth of high-quality MgO (111) and CaO (111) films on GaN with measured valence band offsets > than 1 eV and conduction band offsets ~ 3.2 eV (MgO) and ~2.5 eV (CaO). However, the terminal 3D rocksalt growth surface is determined by the tendency for the high-energy (111) polar orientation to form (100)-oriented low-energy facets, and the interfacial symmetry between cubic MgO and hexagonal GaN. Therefore, realizing smooth oxide films on GaN requires the ability to overcome the rocksalt (001) faceting tendency through a surfactant growth method. In this presentation we will discuss a newly-developed surfactant approach to MBE growth of rocksalt oxides utilizing water vapor to hydroxylate CaO and MgO (111) surfaces *in situ*, which changes the equilibrium habit from cubic to octahedral, eliminating the (100) faceting tendency. RHEED oscillations and AFM images of these films show 2D growth, suggesting that altering the surface chemistry during growth plays a critical role in determining the surface orientation. We demonstrate through electrical property measurements the impact of smooth (111) rocksalt surfaces as leakage current densities for thin CaO films are reduced by two orders of magnitude when films of equivalent thickness are grown using a 2-D vs. a 3-D mode. Finally, we will present a set of temperature *ab-initio* thermodynamic calculations of CaO surface energies with and without H-containing terminations that validate the surface-chemical mechanism of facet stabilization.

9:20am **TF-MoM4 Initiated – Chemical Vapor Deposition of Organosilicones: from Growth Mechanism to Multilayer Moisture Diffusion Barriers**, ***G. Aresta***, *J. Palmans, M.C.M. van de Sanden, M. Creatore*, Eindhoven University of Technology, Netherlands

The state-of-the art approach in the encapsulation of high-end devices such as flexible (polymer) solar cells and organic light emitting diodes against water vapour permeation is an organic/inorganic multi-layer system. Although this approach allows increasing the lifetime of the encapsulated device, the optimization of a multi-layer is rather empirical as the mechanisms behind the improvement of the barrier performance are not yet unraveled. In particular, the role of the organic interlayer is rather controversial since effectively it does not act as a moisture vapor barrier, yet its application appears to be fundamental in the multi-layer solution. In this contribution, the role of the organic interlayer is investigated by selecting a system in which the barrier layer, a 100 nm-thick SiO_2 film, is plasma-deposited while the organic interlayer, a 200 nm- thick organosilicon film, is synthesized by means of initiated- chemical vapor deposition, i.e. via thermal decomposition of an initiator molecule promoting the polymerization of 1,3,5-trimethyl-1,3,5-trivinyl-cyclotrisiloxane (V_3D_3) at the substrate.

The implementation of *in situ* (real time) spectroscopic ellipsometry allows following the different growth stages in the V_3D_3 polymerization process. In particular, when applied to the polymer bulk growth, the determination of the growth rate allows monitoring the transition from a kinetic-limited (with activation energy of 65 ± 4 kJ/mol) to a mass transfer-limited regime. Furthermore, the deposition process is found to be monomer adsorption-limited with an activation energy of -39 ± 4 kJ/mol. When spectroscopic ellipsometry is applied to the initial monomer adsorption steps, isothermal adsorption/desorption studies provide insight into the microstructure of the underlaying SiO_2 barrier layer, characterized by a residual open porosity in the micro/meso transition region (pore radius ≤ 2nm). The microstructure characterization by means of the above-mentioned studies implicitly points out the role of the i-CVD organic interlayer in multi-layer barrier structures, i.e. the filling of the open micro-meso porosity of the inorganic barrier layer, therefore, improving the intrinsic barrier quality of the underlaying SiO_2 film. This outcome nicely correlates with the superior water vapor barrier performances (a barrier improvement factor of 2400 is reported with respect to the pristine polymer) of multi-layers based on the application of i-CVD organic interlayers with respect to fully-PECVD developed multi-layers.

9:40am **TF-MoM5 Processing and Characterization of Iron and Fluorine Co-Doped $Ba_{0.6}Sr_{0.4}TiO_3$ Thin Films**, ***F. Stemme***, *H. Gesswein, C. Azucena,* Karlsruhe Institute of Technology (KIT), Germany, *M. Sazegar,* Darmstadt University of Technology, Germany, *J.R. Binder, M. Bruns*, Karlsruhe Institute of Technology (KIT), Germany

Barium strontium titanate (BST) is a very promising material for tunable microwave applications like phase-shifters and tuneable filters. Due to this the influence of e.g. annealing conditions and processes on thin film properties and their dielectric performance were largely investigated. But very few researchers have tried to change the sputtered BST thin film properties by using different dopants at the same time. Such iron and fluorine co-doped thin films can be achieved by RF magnetron sputtering, with a co-sputter target and a two step annealing process after deposition. The first annealing process provides the crystallinity of the films. In the second annealing process the fluorine co-dopant is introduced into the BST thin films by a diffusion controlled process.

The present contribution focuses on the processing and characterization of the iron doped BST thin films with various amounts of fluorine co-dopant. The characterization of the thin films by X-ray photoelectron spectroscopy (XPS) provides chemical binding states and film composition. XPS and time of flight secondary ion mass spectrometry (ToF SIMS) sputter depth profiles prove the chemical homogeneity and the film thickness. Grazing incident X-ray diffraction (XRD) and Raman spectroscopy validate the crystallinity and the identification of chemical phases. Furthermore film morphology is determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Dielectric measurements, to investigate the influence of the donor and acceptor co-doping on the dielectric performance, were carried out in metal insulator metal (MIM) structures with ground signal ground probes.

10:00am **TF-MoM6 Advances in the Growth of Epitaxial Oxides for Neuromorphic Computing Applications**, ***J.D. Greenlee***, *W.L. Calley, W.A. Doolittle*, Georgia Institute of Technology

Present-day computing devices are approaching performance limits due to excess heat and parasitic capacitance degrading performance. One proposed solution, termed "neuromorphic computing", is to perform computations similarly to the brain.

A key enabling device for neuromorphic computing is the lithium niobite (LiNbO2) memristor[1]. Like synapses in the brain, LiNbO2 memristors can exhibit excitatory or inhibitory behavior. This is due to the ability to produce both n and p-type LiNbO2 memristors, a unique property for an oxide. As shown in Figure 1, when a voltage is applied across an n-type memristor (left), resistance increases over time, whereas a p-type memristor exhibits decreasing resistance (right). N-type memristors are grown with excess oxygen vacancies while p-type memristors are grown with excess lithium vacancies. N- and p- type films are very conductive, exhibiting resistances of 4.3x10-4 Ω-cm(p-type) and 3.9x10-4 Ω-cm(n-type) with carrier concentrations higher than 1021 cm-3 and Hall mobilities greater than 8 cm2/V·s.

The epitaxial growth of LiNbO2 is the enabling technology for the memristors described above. Growths are conducted using an oxy-chloride MBE system in which metal-halide sources interact with lithium and oxygen [2]. Lithium acts as a getterer for the chlorine from the metal-halide, and the resulting LiCl is desorbed from the heated growth surface. The bare metal then oxidizes under the application of a oxygen plasma and combines with lithium. This growth chemistry has been used to produce dielectric/ferroelectric lithium niobate (LiNbO3), semiconducting lithium niobite (LiNbO2), and lithium cobalt oxide (LiCoO2).

Insulating LiNbO3 (Figure 2) and semiconducting LiNbO2 (Figure 3) are grown using NbCl5, and the phase of the material is controlled by the niobium to oxygen ratio delivered to the growth surface. Both single crystal LiNbO3 and LiNbO2 have been epitaxially grown on Al2O3 and SiC. LiNbO3 is a promising lattice matched, ferroelectric transistor gate high-k oxide for its semiconducting sub-oxide, LiNbO2. LiNbO2 has a layered, lithium-intercalated structure [3] (Figure 4). When lithium is removed, holes are introduced which increases the conductivity of p-type material and decreases the conductivity of n-type material, thus producing the memristance effect described herein.

LiCoO2 is grown on Al2O3 using CoCl2 as the precursor (Figure 5). Like LiNbO2, LiCoO2 has a layered structure that facilitates lithium movement. The lattice spacing of LiCoO2 is closely matched to LiNbO2 (2.81 Å and 2.91 Å respectively), thus making it an attractive material for heterostructures of lithium-bearing semiconductor materials.

10:40am **TF-MoM8 New Method to Produce High-Quality Epitaxial Ge on Si Using SiO_2-Lined Etch Pits and Epitaxial Lateral Overgrowth for III-V Multijunction Solar Cells**, ***D. Leonhardt***, *S.M. Han*, University of New Mexico

Integrating a high-quality layer of epitaxial Ge on Si has been a longstanding engineering challenge, despite its technological importance. The applications of Ge-on-Si include 'virtual substrates' for III-V multijunction solar cells, high-mobility field-effect transistors, and optical interconnects monolithically integrated with Si-based circuitry. The primary difficulties in achieving Ge films of sufficient quality stem from the lattice mismatch that leads to a large density (> 10^9 cm^{-2}) of threading dislocations (TDs) and the thermal expansion coefficient mismatch between Ge and Si that leads to microcracks or delamination of Ge film upon cooling from growth to room temperature. Herein, we present a new method to reduce the TD density, using a minimal number of standard microfabrication steps. The method begins with growing a 500-nm-thick epitaxial Ge layer on Si. A post-growth anneal step leads to a TD density of approximately $5x10^7$ cm^{-2}, as revealed by plan-view transmission electron microscopy (TEM) and etch pit density (EPD) measurements. The close agreement between EPD measurements and TEM shows that the EPD measurements reliably decorate all TDs. Etch pits are created around the dislocation cores in the Ge film. A 15-nm-thick layer of SiO_2 is subsequently deposited on the etch-pit-decorated Ge film. A thin layer of polymethyl methacrylate is then spin-coated onto the sample, which fills the etch pits and planarizes the Ge surface. Next, a reactive ion etching step is used to remove the polymer and SiO_2 from the planar regions of the sample surface surrounding the etch pits. An O_2 plasma is then used to selectively remove the remaining polymer, so that SiO_2 remains only within the etch pits. Lastly, a second layer of Ge is selectively grown on the exposed Ge surface and laterally over the SiO_2-lined etch pits until a fully coalesced Ge film is created. A final polishing step produces an atomically flat continuous Ge film. Ensuing EPD measurements reveal that the density of twin defects and TDs in the upper Ge layer is approximately $1.7x10^6$ cm^{-2}, such that the overall defect density is reduced by a factor greater than 30 compared to that in the initial Ge layer. Both theoretical and experimental evidence suggest that the defect density in GaAs films on Ge/Si must be less than $2x10^6$ cm^{-2} to have a minority carrier lifetime comparable to GaAs films grown on Ge and GaAs substrates. Therefore, our new method of using SiO_2-lined etch pits to block the propagation of TDs in Ge may finally lead to device quality III-V materials integrated on Si substrates.

11:00am **TF-MoM9 Three Dimensional Reciprocal Space Measurements by X-ray Diffraction using Linear and Area Detectors: Application to Texture and Defect Determination in Oriented Thin Films and Nanoprecipitates**, ***S. Gaudet***, *S. Lambert-Milot, P. Desjardins,* École Polytechnique de Montréal, Canada, *K. Dekeyser, C. Detavernier,* Ghent University, Belgium, *J.L. Jordan-Sweet, C. Lavoie*, IBM T.J. Watson Research Center

Very thin films grown or deposited on oriented substrates are often composed of highly oriented phases. Traditional x-ray diffraction approaches, scanning only limited portions of the reciprocal space, can fail to characterize some phenomenon occurring in those thin films. We developed an approach for the fast and efficient measurement of complete volumes of the reciprocal space by x-ray diffraction using linear and area detectors. In this presentation, we show how it allowed a detailed understanding of the solid-state thin film reaction to form contacts on transistors and of the growth of magnetic nanoprecipitates by metalorganic vapor-phase epitaxy. We first explain the procedures and scan strategies required for transforming raw scattering data into three-dimensional maps of the reciprocal space, and we present a complete open source software package for advanced data processing, analysis, and visualization. Case studies, chosen to highlight the overall capabilities of the technique, are then introduced. First, thermal diffuse scattering from a monocrystalline Si substrate is characterized. The presence of lines linking diffraction peaks in reciprocal space reflects the interaction of the x-ray beam with the phonon spectrum of the monocrystal. Second, a detailed investigation of texture in multiphase thin layers permits to reveal the unambiguous presence of fiber, axiotaxial, and epitaxial components in extremely oriented films. The visualization of the entire reciprocal space allowed us to identify unexpected metastable phases that could not be deduced or observed from measurements carried out in the Bragg-Brentano geometry. Finally, we present an investigation of defects in two thin film systems: planar defects in nickel silicide layers formed by solid-state reactions and microtwins in a GaP matrix containing coherent MnP precipitates. In summary, the systematic acquisition of significant volumes of the reciprocal space allows for the observation of behaviors that could otherwise remain undetected when restricting the analysis to typical measurement scans.

11:20am **TF-MoM10 Surface Characterization of Zr/Ti/Nb Tri-layered Films Deposited by Magnetron Sputtering on Si(111) and Stainless Steel Substrates***, D.A. Tallarico,* Federal University of Sao Carlos, Brazil*, A.L. Gobbi,* Brazilian Synchrotron Light Laboratory, Brazil*, P.I. Paulin-Filho,* Federal University of Sao Carlos, Brazil*, A. Galtayries,* Ecole Nationale Superieure de Chimie de Paris, France*, **P.A.P. Nascente***, Federal University of Sao Carlos, Brazil

Titanium is a metal commonly used in medical implants, due to its interesting properties, such as high mechanical strength, good corrosion resistance in extreme conditions, and excellent thermal stability. Ti-6Al-4V is one of the main biomaterial alloys employed as implants, but the release of Al and V ions is associated to health problems and adverse tissue reactions. A new class of Ti alloys employs Zr for solid-solution hardening and Nb as β phase stabilizer. Metals such as Ti, Nb, and Zr, known as valve metals, usually have their surfaces covered by a thin oxide film spontaneously formed in air. This oxide film constitutes a barrier between the metal and the medium. The Ti-Nb-Zr alloys have mechanical and corrosion resistance characteristics which make them suitable for use as implants. Tri-layered films of Ti-Nb-Zr were deposited on both Si(111) and stainless steel substrates using a DC magnetron sputtering equipment, under an argon atmosphere. The films were deposited in the following manner: a 100 nm thick layer of Nb was deposited on a Si(111) substrate, then a 200 nm layer of Ti was deposited on top of Nb/Si, and lastly a 50 nm layer of Zr was deposited on top of Ti/Nb/Si. A similar Zr/Ti/Nb film was also grown on stainless steel substrate. The structure, morphology, and chemical composition of the films were analyzed by means of X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The XPS results for the Zr/Ti/Nb layers deposited on Si(111) presented a predominance of ZrO_2 on the surface, and Nb_2O_5 and a small quantity of TiO_2. For the layers deposited on stainless steel, only ZrO_2 and a small amount of niobium oxide were detected. The ToF-SIMS results indicated the formation a three-layered film on Si(111), with each metal in a distinct layer and a well-defined interface between the layers, while the deposition on the stainless steel substrate caused slight intermixing at the Nb/Ti and Ti/Zr interfaces. AFM images showed that the Zr/Ti/Nb tri-layer films presented nanostructured grains and low roughness, with the film deposited on stainless steel having the roughest surface.

11:40am **TF-MoM11 PECVD Synthesis of Hybrid Organic-Inorganic Nanolaminates***, **R. Patel**, C.A. Wolden*, Colorado School of Mines

Hybrid organic-inorganic nanolaminates combine the functionality of an inorganic material with the flexibility and mechanical integrity provided by the organic polymer layer. They are integral components in various applications serving as advanced dielectrics, flexible barrier coatings, and as optical components. This work focuses on the low temperature synthesis of alumina/silicone nanolaminates by plasma-enhanced chemical vapor deposition (PECVD) in a single chamber for dielectric applications.

Self-limiting synthesis of alumina was accomplished via pulsed PECVD at the synthesis temperature of ~ 100 °C using trimethyl aluminum (TMA) and oxygen as precursors. The deposition kinetics and film quality were evaluated as a function of precursor exposure, plasma power, substrate temperature, and pulse parameters. Film composition was assessed by using spectroscopic ellipsometry and Fourier transform infrared spectroscopy (FTIR). The deposition rate per pulse scaled with the degree of precursor exposure during the plasma off step. Through appropriate control of the TMA concentration and pulse duration, the depositing rate could be adjusted over a narrow range (1.6 – 2.8 Å/pulse). Alumina films deposited at 105 °C contained a very small concentration of hydroxyl impurities. Polymeric silicone-like coatings were deposited using hexamethyldisiloxane (HMDSO) and oxygen as precursors. A wide range of coatings, from inorganic SiO_2-like films to flexible polymeric films could be deposited by appropriate control of parameters including the rf power, substrate temperature and working pressure. Growth rates as high as 100 nm/min were obtained for polymeric silicone films.

Alumina/silicone nanolaminates were constructed as a function of nanolaminate composition and dyad thickness. Precise control of nanolaminate construction was confirmed through field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The dielectric performance of these structures was examined by using capacitance-voltage and current-voltage measurements. The effective dielectric constant could be controlled by changing the alumina content of the nanolaminates, and modeling these structures as capacitors in series accurately described the observed variations in κ.

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+TF+ET-MoA

Graphene: Electronic Properties and Charge Transport
Moderator: L. Colombo, Texas Instruments Incorporated

2:00pm **GR+TF+ET-MoA1 Electronic and Magnetic Properties of a Graphene Line Defect**, ***D. Gunlycke***, Naval Research Laboratory **INVITED**

Although graphene exhibits excellent electron and thermal transport properties, it does not have an intrinsic band gap, required to use graphene as a replacement material for silicon and other semiconductors in conventional electronics. The band structure of graphene, however, offers opportunities to develop non-traditional applications. One such avenue is to exploit the valley degeneracy in graphene. In this presentation, I will present a two-dimensional valley filter based on scattering of electrons and holes off a recently observed extended line defect. The transmission probability depends strongly on the valley and the angle of incidence of the incident quasiparticles. Quasiparticles arriving at the line defect at a high angle of incidence lead to a valley polarization of the transmitted beam that is near 100%.

I will also discuss results showing that the extended line defect gives rise to ferromagnetically coupled local moments. This ferromagnetism can be understood from a symmetry analysis of the boundary-localized eigenstates. The symmetry requires that the principal moments couple ferromagentically both along and across the line defect, leading to approximately 2/3 more spin-up electrons and than spin-down electrons per repeat unit along the line defect.

This work was supported by the Office of Naval Research, directly and through the Naval Research Laboratory.

2:40pm **GR+TF+ET-MoA3 Hydrogenation Induced Graphene-Metal Contact - Observation of States at Fermi Level**, ***S. Rajasekaran***, Stanford University, *S. Kaya, T. Anniyev,* Stanford Synchrotron Light Source, *F. Yang, D. Stacchiola,* Brookhaven National Laboratory, *H. Ogasawara, A. Nilsson*, Stanford Synchrotron Light Source

Graphene has received tremendous interest due to its unique electronic structure. Manipulating its electronic structure has received considerable interest. Hydrogenating graphene to open a band gap has been proposed and certain groups have demonstrated hydrogenation induced band opening for graphene on metal substrates.

We employed carbon specific soft x-ray spectroscopy (X-ray photoelectron (XPS), X-ray absorption (XAS) and X-ray emission spectroscopy (XES)) and scanning tunneling microscopy (STM) to investigate how hydrogenation changes the geometric and electronic structure of graphene on Pt(111). Graphene growth on Pt(111) is accompanied with Moiré structure due to periodic rippling in the graphene overlayer due to lattice mismatch and weak interaction between graphene and Pt. Hydrogenation leads to complete disappearance of long range order, although STM indicates that ripple periodicity survives even after hydrogenation. We show that hydrogenation of the unit cell of Moiré nano-patterns is accompanied by pinning of the graphene layer to underneath metal substrate. Structural changes involved in the process of hydrogenation induce covalent graphene-metal interaction. Angle resolved XES and XAS make it possible to probe symmetry resolved states in σ and π bond geometry. XES-XAS indicates that the density of states (DOS) of graphene is very similar to that of graphite. Hydrogenation induces significant changes in the electronic DOS, most of which reflect the formation of C-H σ bonds. For disordered hydrogenated graphene, contrary to band opening, we observe states at the Fermi level after hydrogenation which we reason to arise due to graphene metal interaction and localized C-H bonds. This effect is proposed to be a way to tailor its electronic properties as a possible method to form better graphene-metal contact.

3:00pm **GR+TF+ET-MoA4 First-Principles Studies of Atomic and Electronic Structure of Graphene on Sn/Ni(111) Surface Alloy**, ***L. Adamska***, *R.Q. Addou, A. Dahal, M. Batzill, I.I. Oleynik*, University of South Florida

Graphene-substrate interactions can be exploited to modify the electronic structure of free-standing graphene. Although most of the efforts were directed towards investigation of graphene on pure metallic substrates, less is known about properties of graphene grown on surface alloys. Sn/Ni(111) surface alloy is of particular interest because this structure has the surface lattice constant of Ni(111), i.e. almost a perfect match with graphene's lattice constant, and its surface is highly corrugated due to the substantially large atomic radius of Sn compared to Ni. Here we present results of first-priniciples density functional theory investigations of structural and electronic properties of graphene on sqrt(3)xsqrt(3)R(30) Sn/Ni alloy substrate. It was found that the presence of Sn atoms (1/3 monolayer) results in substantial weakening of graphene-substrate interactions, as is evidenced by large graphene-substrate separation. Nevertheless, the electronic structure of graphene is substantially affected by the underlying substrate as is as seen on simulated STM images. The theoretical predictions for the atomic and electronic structures of graphene on Sn/Ni(111) substrate are compared with experimental results.

3:40pm **GR+TF+ET-MoA6 Charge Transport through Graphene: the Role of Metal Contacts**, *M.Y. Chou, M.E. Kindermann,* ***S. Barraza-Lopez***, Georgia Institute of Technology

Graphene is a flat form of carbon only one-atom tick. Formed by two interweaving triangular sublattices, it has two atoms on its unit cell. Under normal conditions the charge carriers in graphene can be described with an effective single-particle picture. They display an isotropic and linear (i.e., conical) electronic dispersion around the charge neutrality level. This dispersion is described by a Dirac-like equation with a pseudo-spin (related to the sublattice degree of freedom) instead of the standard electron spin. The pseudo-spin is responsible in great part for the strongly suppressed back-scattering in graphene that results in coherent quantum charge transport on lengths up to the micrometer scale, making graphene a relevant material for electronic applications. Yet for applications and for electrical measurements metal contacts are patterned onto graphene. Then the two following questions naturally arise: (i) How graphene interacts with these metal contacts? (ii) How this interaction affects the conductance of a metal/graphene/metal junction in comparison with the hypothetical conductance of pristine (and contactless, infinite) graphene?

In this talk I will discuss quantitatively –within a single-particle description– the quantum transport of charges through graphene, with a focus on the signatures that metal/graphene interfaces imprint on the conductance features. The metals considered are normal (i.e., not superconducting), and spin unpolarized. A crucial observation is that not all metal form covalent bonds to graphene. The conductance is obtained as a function of the separation between contacts, the width of the junctions, as well as the thickness of the metal layers when necessary. From these calculations we are able to extract the basic physics involved in transport for all normal metals [1]. Our studies aim towards a comprehensive modeling of graphene devices at the quantitative level.

[1] S. Barraza-Lopez, M. Vanevic, M. Kindermann, and M.-Y. Chou. "Effects of metallic contacts on electron transport through graphene." *Phys. Rev. Lett.* **104**, 076807 (2010); S. Barraza-Lopez, M. Kindermann and M.-Y. Chou. "Charge transmission through short two-terminal graphene junctions with normal bonding metal contacts." (In preparation.)

4:00pm **GR+TF+ET-MoA7 Layer Number Determination and Thickness-dependent Properties of Graphene Grown on SiC**, ***W. Zhu***, *C. Dimitrakopoulos, M. Freitag, Ph. Avouris*, IBM T.J. Watson Research Center

The electronic properties of few-layer graphene grown on the carbon-face of silicon carbide (SiC) are found to be strongly dependent on the number of layers. The carrier mobility is larger in thicker graphene because substrate-related scattering is reduced in the higher layers. The carrier density dependence of the mobility is qualitatively different in thin and thick graphene, with the transition occurring at about 2 layers. The mobility increases with carrier density in thick graphene, similar to multi-layer graphene exfoliated from natural graphite, suggesting that the individual layers are still electrically coupled. The Hall coefficient peak value is reduced in thick graphene due to the increased density of states. A reliable and rapid characterization tool for the layer number is therefore highly desirable. To date, AFM height determination and Raman scattering are typically used since the optical contrast of graphene on SiC is weak. However, both methods suffer from low throughput. We show that the scanning electron microscopy (SEM) contrast can give similar results with much higher throughput.

4:20pm **GR+TF+ET-MoA8 Graphene: Scratching the Surface**, ***M. Fuhrer***, University of Maryland at College Park **INVITED**

Graphene is of interest for its unique electronic structure: electrons in graphene obey the Dirac equation for massless particles, complete with a two-component spinor degree of freedom that mimics the spin of a relativistic particle. But graphene is also composed entirely of surface atoms, making the techniques of surface science useful in studying its

properties. I will discuss experiments which combine ultra-high vacuum (UHV) surface science with electronic transport measurements to understand graphene and the adsorbed species on its surface. Surface science techniques can be used to controllably modify graphene's properties: potassium atoms can be deposited to form charged impurity scatterers; ice can be deposited to modify the dielectric environment of graphene and tune the electron-electron interaction strength; and ion irradiation can be used to create atomic vacancies which act as Kondo impurities. Graphene's transport properties are extraordinarily sensitive to surface adsorbates, and can be used to detect e.g. correlations in the positions of potassium atoms at concentrations below 1/1000th of a monolayer, and phase transitions in few-monolayer water.

5:00pm **GR+TF+ET-MoA10 Metallic and Insulating Adsorbates on Graphene**, ***K.M. McCreary***, *R.K. Kawakami*, University of California, Riverside

While several experiments have separately investigated the doping of graphene by metallic and insulating adsorbates, the

transition from metallic to insulating behavior of the adsorbates has not yet been explored. We directly compare the effect of metallic titanium (Ti) and insulating titanium dioxide (TiO_2) on the transport properties of single layer graphene. The deposition of Ti results in substantial *n*- type doping and a reduction of graphene mobility by charged impurity scattering. Subsequent exposure to oxygen largely reduces the doping and scattering by converting Ti into TiO_2. In addition, we observe evidence for short-range scattering by TiO_2 impurities.

5:20pm **GR+TF+ET-MoA11 Electron Transport in Carbon Nanotube - Graphene Contacts**, *B. Cook, W. French,* ***K. Varga***, Vanderbilt University

Graphene and carbon nanotubes are two of the most promising materials for future applications due to their unique properties. Devices combining the two materials are expected to be particularly advantageous. The interface of carbon nanotubes and various metal electrodes has been previously studied, both experimentally (Chen et al. Nano Lett. 2005, Zhang et al. Nano Lett. 2007) and theoretically (Shan et al. PRB 2004, Zhu et al. APL 2006, He et al. APL 2009). These studies focus on the search for materials with a low p-type Schottky barrier. Hybrid graphene-carbon nanotube structures have been previously demonstrated (Tung et al. Nano Lett. 2009). We propose the use of graphene as a electrode material for carbon nanotube based FET devices. To this end the carbon nanotube - graphene contact is investigated with first-principles calculations within density functional theory of the Schottky barrier height (SBH) and transport properties. Total energy and electronic structure calculations are carried out with a plane-wave basis set and the transport characteristics are calculated with a localized atomic orbitals basis within the non-equilibrium Green's function framework. We consider only the side-contact geometry, nanotubes laying atop graphene. The SBH for (5,0), (8,0) and (10,0) nanotubes on graphene is calculated. The transport characteristics of a combined graphene - nanotube device are considered. In the case of small diameter nanotubes (~0.6nm) a SBH of ~0.09 eV is found when graphene contacts are used, much lower than the typical reported values (0.3 eV and higher).

Thin Film Division
Room: 107 - Session TF-MoA

Emerging ALD Applications
Moderator: G. Scarel, James Madison University

2:00pm **TF-MoA1 Atmospheric ALD of Al_2O_3 for a High Throughput c-Si Solar Cell Passivation**, ***V.I. Kuznetsov***, *P. Vermont, E.H.A. Granneman*, Levitech BV, Netherlands **INVITED**

Surface passivation of advanced solar cells becomes more important with decreasing silicon wafer thickness (increased surface to bulk ratio). The International Technology Roadmap for Photovoltaics predicts that the thickness of wafers processed in mass production will be 100 µm by 2020. By 2012 new processes with lower Cost of Ownership (CoO) and better passivation properties will be needed [1].

It is widely accepted that Al_2O_3 layer has excellent surface passivation capabilities [2]. Solar cells with Al_2O_3 layers < 10 nm demonstrate the best results: higher efficiency and more stable structures when annealed at high temperatures [3,4]. ALD is an ideal technique for the deposition of thin layers. However, conventional ALD equipment can not be used in the PV industry because of the low throughput and associated high CoO. A suitable way to reduce the tool cost per cell is to increase the throughput of the system. The ITRPV requires a minimum throughput of production tools from 3600 wph in 2012 to 7200 wph in 2020.

We developed an ALD tool which meets these throughput requirements and is capable to process at a cost of 3-4 cent per wafer. In this tool we implemented a new approach: atmospheric, spatial ALD. Silicon wafers are transported in a linear track passing areas with TMA and H_2O precursor gas curtains. N_2 purges in between these curtains separate the different precursors thereby avoiding deposition on the track walls. The wafers are transported on a gas bearing (levitate) inside a narrow track. The Levitrack system operates in-line and has a length of ~10 m for the deposition of 10 nm of Al_2O_3. At the conference Levitrack tool details and process results will be presented. Some items are:

· Passivation quality: effective lifetime of 6.1 ms in mono-silicon 10 Ω cm at injection level of 3E15 cm^{-3}.

· Layer characteristics: 1σ uniformity <3% on 156x156 mm wafers, intrinsic layer charge of -4E12 cm^{-2}

· Tool options: deposition on both or one side of the wafer (N_2 flow protects the back side of the wafer against Al_2O_3 deposition)

· Tool automation (automated wafer loading/unloading, 100 wafer cassettes and use inline, control of process, safety, and other parameters)

· Tool reliability (reliable performance at marathon runs with throughput of ~4000 wph)

· Current solar cell results (efficiency obtained for p-type crystalline silicon cell is 16.6% and for n-type is 18.3%. Improvement of 1-2% is expected to be achieved by optimizing local BSF below metal contacts and contact/shunt resistances)

1. ITRPV.net, 2nd edition, 2011

2. S.Chunduri, Photon Int., p.146, 2011

3. P.Brand, 37th IEEE PV Conference, Seattle, 2011

4. I.G.Romijn, 25th. EU PVSEC, 2010

2:40pm **TF-MoA3 Atomic Layer Deposition of Al_2O_3 for Quantum Computing**, ***A.C. Kozen***, *M. Khalil, B. Sarabi, K.D. Osborn,* University of Maryland, College Park*, C. Musgrave,* University of Colorado, Boulder*, C. Lobb, G.W. Rubloff*, University of Maryland, College Park

Josephson junctions (JJ) are a primary building block of superconducting quantum computers. The JJ structure is a superconductor-dielectric-superconductor stack, with the conventional dielectric layer fabricated by thermal oxidation of an aluminum metal electrode. The coherence time of these qubits is limited by high loss tangents in the dielectric layer thought to be due to defect-related quantum two level systems (TLS) inherent in the Al_2O_3. We have identified the –OH rotor TLS associated with hydroxyl species in the Al_2O_3 as a prime defect candidate based on TLS energetics. Simulations indicate that replacement of the –OH defect with the –OD defect will reduce the dielectric loss in these systems. We demonstrate the fabrication of Al_2O_3 dielectric thin films using atomic layer deposition (ALD) from trimethylaluminum and both H_2O and D_2O precursors as a function of substrate temperature and precursor dose. ALD enables precise control of film growth at the atomic scale, while comparison of H_2O vs. D_2O as the oxidation precursor enables isotopic defect loading in the Al_2O_3 and replacement of the –OH defect with the –OD defect. We have developed the D_2O based ALD process, and characterized both D_2O and H_2O based ALD Al_2O_3 thin films by SIMS, XPS and spectroscopic ellipsometry. Our resulting Al_2O_3 films are physically identical with the exception of –OH and –OD defects, making this system an ideal platform for the study of TLS defect related dielectric loss in JJ qubits. To this end we have fabricated MIM capacitor test structures and superconducting resonators using Re and Al electrodes and performed electrical measurements. Correlation between these data and low temperature superconducting microwave resonator performance will be discussed.

3:00pm **TF-MoA4 Supported Core-Shell Pt-Pd Nanoparticles Synthesized by Atomic Layer Deposition**, ***M.J. Weber***, *A.J.M. Mackus,* Eindhoven University of Technology, Netherlands*, M.A. Verheijen, C. van der Marel,* Philips Innovation Services, Netherlands*, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, atomic layer deposition (ALD) has become the subject of great interest as a new way to synthesize supported metallic nanocatalysts (1, 2). In comparison to their single-metal counterparts, bimetallic nanoparticles (NPs) can present a higher selectivity and an enhanced catalytic activity. In this contribution, we present an innovative ALD process enabling the synthesis of supported bimetallic core-shell NPs. Although ALD was primarily developed to deposit conformal thin films, metals have the tendency to form nanoclusters on the substrate during the initial cycles of the process. In this work, Platinum-Palladium core-shell NPs were successfully deposited on Al_2O_3 using ALD of Pt and Pd. The selective growth property of noble metal ALD (3) has been exploited to cover Pt

nanoclusters with a Pd shell. An ALD process using $MeCpPtMe_3$ and O_2 has been used to deposit Pt nanoclusters, and ALD with $Pd(hfac)_2$ and H_2 enabled to selectively cover them with a Pd shell. High Angle Annular Dark Field (HAADF) TEM images confirm the fact that bimetallic core-shell NPs of 3-4 nm were synthesized (on Al_2O_3 covered TEM windows). Information on the chemical state of the Pd and Pt was obtained from XPS analysis. Average values of the Pd shell thickness as obtained by a model analysis of the XPS data were found to be in agreement with the TEM data. This new process is expected to be also applicable to other Platinum group metals. The tailoring of such NPs by changing the ALD process parameters in order to obtain different particles sizes and compositions is also addressed. It is expected that the fuel cells industry, but also advanced sensors technologies, can benefit considerably from an enhancement of catalytic activity and selectivity of nanocatalysts prepared by ALD.

1: Stair, *J. Chem. Phys.* **2008**, 128, 182507

2: Christensen et al., *Small* **2009**, 5, No. 6, 750-757

3: Mackus et al., *J. Appl. Phys.* **2010**, *107* (11), 116102-1/3

3:40pm **TF-MoA6 Photoluminescence Characteristics of TiO_2 Film Deposited on Vertically Oriented Si Nanowire by Remote Plasma Atomic Layer Deposition**, ***J.S. Lee**, T.Y. Park, Y.B. Ko, H.Y. Jeon, J.G. Park, J.H. Ryu, H.T. Jeon*, Hanyang University, Republic of Korea

Titanium dioxide (TiO_2) has been regarded as one of the most promising photocatalysts for environmental protection because of its high photocatalytic activity, high chemical stability, low toxicity, and low cost. Anatase and rutile structures of TiO_2 are two main phases with band gap energies of 3.3 and 3.1 eV, respectively. The structures of both anatase and rutile consist of chains of TiO_6 octahedra. However, two crystal structures are obviously different. It is well-known that the difference in crystal structures causes different mass density (3.894 g/cm^3 for anatase and 4.250 g/cm^3 for rutile) and electronic band gap. The anatase phase has a more negative conduction band edge than that of the rutile phase. It results in superior photocatalytic activity of anatase phase than that of the rutile phase. Therefore, the structure of TiO_2 films and high surface area are heavily important factors in photocatalytic efficiency.

In this study, TiO_2 film was deposited by remote plasma atomic layer deposition(RPALD) and its phase formation temperature, impurity concentration, and chemical states of the were characterized by various analyses such as Auger electron spectroscopy (AES), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The TiO_2 film was deposited on the flat Si substrate and vertically oriented Si nanowire by using remote plasma atomic layer deposition (RPALD) method. RPALD method has advantage to deposit thin film with uniform thickness on the 3-dimensional structure like vertically oriented Si nanowire. In addition, the RPALD method is possible to reduce damage by high energetic ion and to enhance the chemical reactivity between metal-organic precursor and reactant gas for deposition of high quality film. The vertically oriented Si nanowire was fabricated by Ar-annealing of Si substrate with Au nanocrystal at 1000 °C. And we have compared the photoluminescence (PL) features of these TiO_2 films with these two different specific surface areas. We have found that TiO_2 film deposited vertically aligned Si nanowire has higher PL intensity than that of TiO_2 deposited flat Si substrate due to large area density of vertically oriented Si nanowire.

4:00pm **TF-MoA7 Fast Atomic Layer Deposition for High Throughput and Low Temperature Applications**, ***P. Poodt**, A. Illiberi, M. Smets, R. Knaapen,* TNO, Netherlands*, F. Roozeboom,* TNO & Eindhoven University of Technology, Netherlands*, A. van Asten*, TNO, Netherlands

Atomic Layer Deposition is a deposition technique capable of producing ultrathin conformal films with control of the thickness and composition of the films at the atomic level. The major drawback of ALD is its low deposition rate (~ 1 nm/min). Recently, fast ALD concepts were developed based on the *spatial* separation of the half-reactions, instead of temporal, combined with gas-bearing technology[1]. With this technique, deposition rates for Al_2O_3 of more than 1 nm/s have been reported[2]. This has led to the development of the high-throughput, industrial scale ALD tools for surface passivation of crystalline silicon solar cells[2, 3].

A new field of applications for fast ALD are flexible electronics[4], including system-in-foil, flexible displays, OLEDs and solar cells. Flexible electronics are slowly but surely evolving from lab-scale to industrial production. This opens up new possibilities for fast ALD as high-throughput production tool for functional layers such as transparent oxide (semi)conductors (e.g. ZnO) and moisture barriers (e.g. Al_2O_3). One important prerequisite is that these applications require low temperature processes (below 100°C), as they are often temperature sensitive. We present two approaches for low temperature Fast ALD; low temperature *thermal* fast ALD and atmospheric plasma enhanced fast ALD.

A *low temperature thermal fast ALD* process for alumina from tri-methyl aluminum and water has been developed. It was observed that the kinetics of the water half-reaction is significantly different than at high temperatures (>200°C). Multilayer adsorption of water molecules at low temperatures seems to hinder the self-limiting nature of the ALD process at temperatures below 75°C. Nevertheless, if very low temperatures are not required, low temperature thermal fast ALD is a very suitable technique. Potentially lower deposition temperatures could be achieved by *atmospheric plasma enhanced fast ALD*. We have integrated an atmospheric plasma source in our reactor in which an He/O_2 plasma is created to act as the oxidant half reaction. However, the chemistry of atmospheric plasmas is different than that of conventionally used low pressure plasmas and has a lower reactivity that can limit the throughput.

Another important aspect of fast ALD for flexible electronics is the processing of flexible substrates, either sheet-to-sheet or roll-to-roll. Approaches for roll-to-roll fast ALD, their challenges and possible solutions will be briefly discussed.

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

[2] www.solaytec.com .

[3] I. Cesar, *et al*, , *Proc. 35th IEEE PVSC*, Honolulu, Hawaii (2010), in press

[4] J. van den Brand *et al*., *Microelect. Rel.* 48 (2008) 1123

4:20pm **TF-MoA8 Industrial ALD Equipment for PV and OLED Applications**, ***M. Putkonen***, Beneq Oy, Finland

Atomic Layer Deposition (ALD) has been successfully applied to antireflection, buffer and passivation layers for PV as well as moisture barriers for OLED packaging. In these applications ALD offers superior performance compared to the corresponding layers deposited with other methods. Outside IC manufacturing ALD has largely been confined to laboratories so far due to non-availability of larger scale, high throughput ALD systems. For example, ALD is widely seen as the desired manufacturing technology for producing high quality functional layers into solar cells: e.g. buffer layers into CIGS and surface passivation into both p-type and n-type c-Si solar cells, but ALD commonly considered too slow for high throughput manufacturing.

In this presentation we introduce commercial high capacity ALD tools for PV and OLED diffusion barrier applications as well as discuss more about the requirements for high throughput industrial ALD tools. Conventional ALD deposition parameters and characteristics, such as stability of precursor temperatures even with extremely high precursor doses and optimising the flow path are needed before strict coating requirements can be fulfilled.

The TFS 1200 deposition system is designed to improve efficiency of $CuInGaSe_2$ (CIGS) type thin film PV cells using Zn(O,S)) buffer layer. It has throughput in inline and off-line configurations of 12 and 24 modules/hour, respectively. (substrate size 120 x 120 cm^2, 20 nm Zn(O,S)) We have obtained thin film thickness uniformity of ± 3 % with the cycle time of 2.0 s. With 60 x 120 cm^2 substrate size these numbers will be doubled to 24-48 modules/hour. These values fulfill the throughput requirements of CIGS production lines (20-60 modules/h). Even higher throughputs can be obtained using batch type tools for CIGS buffer layers.

TFS NX 300 is a fully automated cassette to cassette ALD manufacturing system for Al_2O_3 surface passivation. It consists of 4 processing tubes each with the capacity for a 500 wafer batch. For this application we have modified thermal ALD-process for Al_2O_3 which has a higher growth rate than the conventional thermal (TMA/H_2O) ALD process and the film quality is equal to plasma assisted ALD film quality giving throughput of >3000 wafers/h.

The Beneq TFS 600 is a vacuum-line integrated ALD system for OLED moisture barrier coating. Reaction chamber is designed for batch processing up to 35 substrates measuring 500 mm x 400 mm. For this application we have been developing low-cost multilayer barrier structure giving WVTR $<10^{-6}$ $g/m^2/d$.

4:40pm **TF-MoA9 Conductive Coatings on Nonwoven Fiber Mats by Atomic Layer Deposition**, ***W. Sweet**, J.S. Jur, G.N. Parsons*, North Carolina State University

Conductive fiber mats offer unique possibilities in the development of many sensing and protective electronic systems. In this work, atomic layer deposition (ALD) is applied to produce conformal coatings of conductive ZnO on complex fiber systems such as nonwoven polypropylene and nylon. The conductivity of these materials were evaluated using a modified 4-probe method specific for fabric structures and correlated with the overall mass gain of the fabric samples after ALD processing. This analysis provided a detailed evolution of the conductive films on the fabric mats. For example, nonwoven polypropylene coated with ZnO showed a significant initial mass increase, eventually becoming linear with increasing ALD

cycles. The corresponding conductivity of these films remained low (< 3 S cm^{-1}), even after 500 ALD ZnO cycles. Inserting a thin insulating ALD Al_2O_3 layer prior to the ZnO growth, linear ZnO mass gain was achieved after low ALD cycles. Transmission electron microscopy shows that the Al_2O_3 barrier reduces the penetration of the ZnO vapor phase reactants into the polypropylene. As a result, a higher effective conductivity (> 25 S cm^{-1}) was achieved after 200 ALD ZnO cycles that corresponded well with measurements from simultaneous ZnO growth on a planar silicon oxide surface. For comparison, ZnO deposition on nonwoven nylon-6 exhibits uniform growth without Al_2O_3 pretreatment and the conductivity again changes significantly with the Al_2O_3 pretreatment. Implications of the deposition temperature, film thickness, and the use of aluminum doping, on the chemical, mechanical, and electrical properties of ZnO films deposited on polypropylene and nylon nonwovens will be discussed.

5:00pm **TF-MoA10 ALD IrOx Thin Film to Improve Microelectrode Array Performance in Stem Cell Applications***, **T. Ryynänen***, *J. Lekkala,* Tampere University of Technology, Finland*, L. Ylä-Outinen, S. Narkilahti,* University of Tampere, Finland*, J. Hämäläinen, M. Leskelä*, University of Helsinki, Finland

We promote atomic layer deposition (ALD) and especially ALD deposited iridium oxide (IrOx) thin film [1] as a novel alternative to improve electrical characteristics of microelectrode arrays (MEAs) used in stem cell and other tissue engineering applications. The additional microelectrode coating on microelectrode base material is traditionally used to decrease impedance and noise levels, and to increase charge transfer capacity of microelectrodes in MEAs. However, most of the common microelectrode coatings suffer from certain drawbacks. For example 1) electrochemical activation used to decrease the impedance of sputtered IrOx by one decade is not applicable for long term cell measurements due to rather fast deactivation, 2) widely used electrodeposited platinum (Pt black) suffers often from poor adhesion on underlying microelectrode base material, and 3) lately actively studied carbon nanotube (CNT) coatings still have unsolved issues related to difficult fabrication processes and concerns about biocompatibility and long term adhesion. Thus there is obvious demand for another stable solution in addition to sputtered titanium nitride (TiN) thin film favored by one of the leading commercial MEA manufacturers.

In our initial studies the about 120 nm thick ALD IrOx layer decreased the impedance of 30 µm diameter titanium microelectrodes down to 450 kΩ at 1 kHz, which is several times less than without the coating and consistent with the impedance reported for unactivated sputtered IrOx coated microelectrodes [2]. Stem cell growth experiments performed with human embryonic stem cell derived neuronal cells (hESC-N) [3, 4] showed that in field potential measurements ALD IrOx thin film decreases the noise level significantly compared to non-coated microelectrodes. Also, no biocompatibility or adhesion problems were detected. Even if already as such the ALD IrOx thin film clearly improves the MEA performance, we expect that by optimizing the thin film thickness and ALD process parameters from the default 3000 cycles of $Ir(acac)_3$ and ozone, the impedance level of the ALD IrOx coated microelectrodes can be decreased even further. Thus impedance levels of 100 kΩ and below could be reached, which would make ALD IrOx thin film a strong competitor for the other commonly used microelectrode coatings. In addition to offering an economical, easily controllable, and highly reproducible fabrication process for a thin film improving the electrical characteristics of MEAs, ALD technology may in the future offer also other interesting coating solutions for cell culturing platforms, for example controlling cell growth via functionalized coatings.

[1] J. Hämäläinen *et al.*, Chem. Mater. 20 (2008) 2903.

[2] S. Gawad *et al.*, Front. Neuroeng. 2 (2009) 1.

[3] R. Lappalainen *et al.*, Regen. Med. 5 (2010) 749.

[4] T. Heikkilä *et al.*, Exp. Neurol. 218 (2009) 109.

Electronic Materials and Processing Division
Room: 210 - Session EM+TF-TuM

High-k Dielectrics for MOSFETs Part 1
Moderator: R.M. Wallace, University of Texas at Dallas

8:20am **EM+TF-TuM2 *In Situ* TMA Pre-Treatment Study of GaAs and $In_{0.53}Ga_{0.47}As$ Surfaces**, ***B. Brennan***, *D.M. Zhernokletov, H. Dong, R.V. Galatage, J. Kim, E.M. Vogel, R.M. Wallace*, University of Texas at Dallas

One of the major issues preventing the integration of high mobility III-V semiconductors into next generation CMOS devices is the formation of high levels of interfacial defects at the high-k/III-V interface. These can have the effect of pinning the Fermi level and preventing optimal operation of the devices. Engineering the interface between these materials therefore becomes of critical importance to try and reduce the defect density. Identification of the individual defects however is not a trivial matter with correlation between electrical data and physical measurement techniques rarely seen. This study aims to investigate the effect of *in-situ* chemical treatments prior to Al2O3 deposition on (NH4)2S treated GaAs and InGaAs surfaces, in terms of both physical characterization by X-ray photoelectron spectroscopy (XPS) and electrical measurements from MOS capacitors.

The reduction of interfacial oxides through a "clean up" effect by a ligand exchange mechanism with the tri-methyl aluminum (TMA) precursor for atomic layer deposition (ALD) of Al2O3 is well known, [1,2] however little work has been carried out to optimize this process and determine whether variations in the effect are seen as a result of changes in the number of TMA cycles or pulse time prior to oxide deposition. Variations in the presence of arsenic surface features, (i.e. As-As bonding or surface dimers) come under particular focus.The effect of post deposition annealing is also investigated specifically in terms of the potential role hydrogen could play in passivating defects at the interface. [3]

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8:40am **EM+TF-TuM3 Half-cycle Atomic Layer Deposition Studies of HfO_2 on the GaSb(001) Surface**, ***D.M. Zhernokletov***, *H. Dong, B. Brennan, J. Kim, R.M. Wallace*, University of Texas at Dallas

Since GaSb(001) is a candidate surface channel material for p-MOSFET and an interfacial passivation layer for buried channel quantum well and tunneling FETs (GaSb static dielectric constant of ~ 16), it is necessary to understand its interface with high-κ dielectric materials which would act as gate dielectrics in these devices[1]. An *in-situ* half-cycle atomic layer deposition/X-ray photoelectron spectroscopy (ALD/XPS) study is conducted in order to investigate the evolution of the HfO_2 dielectric interface with the GaSb(001) surface after sulfur passivation procedures and HCl etching designed to removed the native oxides. Monochromatic XPS is used to examine the surfaces following the various surface treatments and then without breaking vacuum, after each individual ALD pulse of tetrakis-dimethyl-amino-hafnium (TDMA-Hf) and deionized water (DIW) precursors (i.e. single TDMA-Hf pulse/XPS scan; single DIW/XPS scan; etc.) for two full cycles and finally after 1 nm of HfO_2 deposition to determine whether there is any "clean up" effect of the native oxides due to the ALD process. The various surface preparation techniques are compared to determine which is more effective at minimizing native oxides. The behavior of the sulfides and the effect of HCl surface cleaning procedure upon HfO_2 deposition are discussed as well as a comparison to previous results from half cycle Al_2O_3 deposition on GaSb [2]. This work is supported by the Semiconductor Research Corporation FCRP MSD Focus Center, the Nanoelectronics Research Initiative and the National Institute of Standards and Technology through the Midwest Institute for Nanoelectronics Discovery (MIND). and the NSF (ECCS-0925844).

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9:00am **EM+TF-TuM4 Remote Phonon and Surface Roughness Limited Universal Electron Mobility of $In_{0.53}Ga_{0.47}As$ Surface Channel MOSFETs**, ***E.M. Vogel***, *A.M. Sonnet, R.V. Galatage,* University of Texas at Dallas*, P.K. Hurley, E. Pelucchi, K. Thomas, A. Gocalinska,* Tyndall National Institute*, J. Huang, N. Goel, G. Bersuker,* SEMATECH*, W.P. Kirk, C.L. Hinkle*, University of Texas at Dallas **INVITED**

The inversion layer electron mobility in n-channel In0.53Ga0.47As MOSFET's with HfO2 gate dielectric with several substrate impurity concentrations (~1×1016 cm-3 to ~1×1018 cm-3) and various surface preparations (HF surface clean, (NH4)2S surface clean and PECVD a-Si interlayer with a HfO2 gate dielectric) have been studied. The peak electron mobility is observed to be strongly dependent on the surface preparation, but the high field mobility is observed to be almost independent of the surface preparation. A detailed analysis of the effective mobility as a function of electric field, substrate doping, and temperature was used to determine the various mobility components (surface roughness, phonon, and coulombic scattering limited mobility components). For the substrates with high doping concentration, the electron mobility at low vertical electric field is dominated by Coulomb scattering from the substrate dopants, whereas, for lower substrate doping the Coulombic scattering is dominated by the disorder induced gap states. Low temperature measurements were used to determine the surface roughness scattering and phonon components. The results show that room temperature mobility of In0.53Ga0.47As surface channel MOSFETs with HfO2 gate dielectric at high electric field is limited primarily by remote phonons whereas the Al2O3 gate dielectric is limited by surface roughness scattering.

9:40am **EM+TF-TuM6 Structural Characterization of Ultra-thin High-*k* Gate Oxide Films through a Multi-technique Approach**, ***E.J. Bersch***, *J.D. LaRose, I.B. Wells,* University at Albany*, S.P. Consiglio, R.D. Clark, K.N. Tapily, G.J. Leusink,* TEL Technology Center, America, LLC*, A.C. Diebold*, University at Albany

High-*k* HfO_2-based gate oxides have recently been put into production in CMOS-based integrated circuits, and their future use in this capacity depends on how well they can continue to be downscaled. To this end, efforts to increase the dielectric constant (*k*) of HfO_2-based gate oxides are ongoing. Recent work has shown that by tailoring annealing procedures, *k* values for HfO_2 films of greater than 30 have been obtained.[1] These higher *k* values for HfO_2 occur for the metastable tetragonal and cubic crystalline phases, while the thermodynamically preferred monoclinic phase has a lower *k* value (~20). To evaluate the crystalline structure of ultra-thin (< 100 Å) HfO_2 films which have undergone various annealing treatments, we used several techniques, including grazing incidence in-plnae X-ray diffraction (GIIXRD), X-ray and UV photoemission spectroscopy (XPS and UPS, respectively) and spectroscopic ellipsometry (SE). GIIXRD measurements showed that ~60 Å HfO_2 films grown with a sequence of depositions and anneals (so-called DADA process[2]) were monoclinic, while those which were post deposition annealed (PDA) were in a mixture of monoclinic and either tetragonal or orthorhombic phases. Pole figure measurements of these films showed that the DADA film had a monoclinic (-111) fiber texture, while the PDA film was randomly oriented. For HfO_2 films with thicknesses of ~25 Å, GIIXRD measurements showed that DADA films were tetragonal or orthorhombic, while PDA films were also tetragonal or orthorhombic, but also possibly with a monoclinic component. XPS and UPS measurements of the valence bands of HfO_2 films were found to be useful in distinguishing between crystalline and non-crystalline films, but were not useful in distinguishing between crystalline phases.[3] SE has been shown to be useful in indentifying crystallinity in HfO_2 through a feature that appears in the HfO_2 extinction coefficient curve at the absorption edge. We have observed this absorption edge feature for films that were crystalline and strongly monoclinic, but not for films that were only weakly crystalline or mostly non-monoclinic, in keeping with previous work.[4]

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10:40am **EM+TF-TuM9 Research Advances on III-V and Ge MOS/MOSFETs Beyond Si CMOS**, *T.D. Lin, M.L. Huang, Y.C. Chang, W.C. Lee,* National Tsing Hua University, Taiwan, Republic of China*, T.W. Pi,* National Synchrotron Radiation Research Center, Taiwan, Republic of China*, J. Kwo,* National Tsing Hua Univ. and National Taiwan Univ., Taiwan, Republic of China*, **M. Hong***, National Tsing Hua University, Taiwan, Republic of China **INVITED**

Metal-oxide-semiconductor (MOS) and MOS field-effect-transistors (MOSFETs) of high k dielectrics on high carrier mobility channels of InGaAs and Ge have been feverishly studied, as they are now strongly considered for technologies beyond Si complementary MOS (CMOS) integrated circuits (ICs). The post Si CMOS research is now facing unprecedented challenges in materials and physics, as key material/electrical/processing issues have to be met/solved in order to realize the new advanced devices; these include equivalent oxide thickness (EOT) < 1 nm, interfacial density of state (Dit) ≤ 1011 eV-1cm-2, high-temperature thermal stability for self-aligned process, low parasitic, and integration with Si. Using *in-situ* ultra high vacuum (UHV) and *in-situ/ex-situ* atomic layer deposited (ALD) high k's of Ga2O3(Gd2O3), Al2O3, and HfO2 on InGaAs and Ge, this research group has made advances in achieving an EOT of 0.5 nm, Dit of low 1011 eV-1cm-2(with a flat distribution versus energy within the semiconductor bandgap), and high-temperature stability of the MOS structures (rapid thermal annealing to 800-900°C and 500-600°C for the high k's/InGaAs and /Ge, respectively). Atomic manipulation to perfecting the high k's/InGaAs and /Ge interfaces is the key for the above achievements. Probing of the interfaces and gaining insightful understanding of the electronic properties was made possible using our uniquely designed experiments of *in-situ* synchrotron radiation photoemission. High-performance self-aligned inversion-channel high k's/InGaAs MOSFETs in achieving record-high drain currents and transconductances, and record-low sub-threshold swings, and high k's/Ge MOSFETs without employing interfacial passivation layers will also be discussed.

11:20am **EM+TF-TuM11 SiO_2 Interlayer Thickness Dependence of the Density and Polarity of Charges in $Si/SiO_2/Al_2O_3$ stacks**, ***N.M. Terlinden***, *G. Dingemans, M.M. Mandoc, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

In this contribution, we investigate the influence of the SiO_2 thickness on the *density* and *polarity* of built-in charges in SiO_2/Al_2O_3 stacks deposited on Si(100). Such charges lead to the development of a space-charge region (SCR) in the Si at the dielectric interface, having consequences such as flat band voltage shifts in MOS devices and electric-field induced passivation in optoelectronic devices like solar cells. We have employed the nonlinear optical technique of second-harmonic generation (SHG) to probe the Si(100) SCR electric field through the effect of electric-field-induced SHG (EFISH). Using this non-intrusive and contactless technique we found previously that the built-in charge density at the SiO_2/Al_2O_3 interface is independent of the Al_2O_3 thickness down to ~2 nm.[1] Here we report on the influence of the interfacial SiO_x layer, present between the Si(100) substrate and the atomic layer deposited (ALD) Al_2O_3 film, addressing the origin, density, and polarity of the charges. For this reason, we have synthesized SiO_2/Al_2O_3 stacks with intentionally grown SiO_2 interlayers having a thickness in the range ~1.4-150 nm using various deposition methods (e.g. thermal oxidation, PECVD, ALD). Spectroscopic SHG measurements were carried out with a femtosecond pulsed Ti:sapphire laser tunable in the 1.33-1.75 eV photon energy range. From the obtained spectra we found that the charge density is highly influenced when increasing the SiO_2 thickness, dropping from 10^{13} to 10^{11} cm^{-2}, with the polarity switching from negative to positive. These measurements were confirmed by *C-V* measurements and surface voltage measurements employing corona charging of the stacks. On the basis of the observations the mechanism and consequences of charge trapping in $Si/SiO_2/Al_2O_3$ stacks will be addressed.

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11:40am **EM+TF-TuM12 Study of the Interface Barrier of Atomic Layer Deposited (ALD) Al_2O_3 on GaN**, *M. Esposto, S. Krishnamoorthy, D.N. Nath, S. Bajaj, S. Rajan, **T.-H. Hung***, Ohio State University

We report on the deposition and energy band diagram analysis of high-quality low-leakage Al_2O_3/GaN using atomic layer deposition. As GaN-based transistors are scaled to achieve higher frequency operation, atomic layer deposition techniques offer a promising way to achieve low leakage while scaling gate-to-channel distance. In addition, applications of GaN in power switching systems require ultra-low leakage that can be achieved using metal-insulator-semiconductor (MISHEMT) structures. In this work, we have made quantitative estimates of conduction band offsets and interface charge density.

MIS structures with varying oxide thickness were fabricated on an n+/n-GaN sample grown by RF plasma MBE on low dislocation density Lumilog GaN templates. Three Al_2O_3 layers of nominal 6 nm, 12 nm, and 18 nm were deposited by atomic layer deposition at 300˚C, using trimethylaluminum (TMA) and H_2O as precursors. The pre-deposition treatment of the surface consisted in a 10:1 HF-dip for 15s. All three samples were then annealed at 600˚C in forming gas for 1min. A new ALD deposition procedure was also developed to achieve low leakage in these structures.

A quantitative analysis of the interface barrier of Ni/Al_2O_3/GaN capacitors was carried out to determine conduction band discontinuity, interface fixed charge and pinning effects. The I-V measurements show extremely low current density for thin dielectric films. A quantitative energy band diagram was estimated from capacitance voltage (C-V) measurements by extracting the apparent charge profiles of the MIS capacitors taking into account the spontaneous polarization in GaN and doping. The extracted flat-band voltages were -0.36 V, -1.55 V and -2.73 V for the 6 nm, 12 nm and 18 nm-thick oxide respectively. The hysteresis in the C-V profile for the 6nm-thick capacitor pointed out a D_{it} charge density of approximately $5x10^{11}$ cm^{-2} and higher for the thicker capacitors. This was because the deposition and post deposition annealing conditions were optimized for very thin oxide layers (~ 5-6 nm). A linear relationship between the flat-band voltage and the oxide thickness was experimentally observed, indicating absence of Fermi-level pinning at the Al_2O_3/GaN interface. The conduction band offset at the Al_2O_3/GaN interface was calculated to be 2.66 eV. In addition, we estimate that a non-zero field of approximately 2 MV/cm exists in the oxide under flat band conditions in the semiconductor. This non-zero field is attributed to a fixed charge density at the Al_2O_3/GaN interface of $2.79x10^{13}$ cm^{-2}.

Nanomanufacturing Science and Technology Focus Topic
Room: 207 - Session NM+MN+MS+TF-TuM

Lithography Strategies for Nanomanufacturing
Moderator: T.S. Mayer, Penn State University

8:00am **NM+MN+MS+TF-TuM1 A SANE Approach to Programmable Soft Lithography**, ***T.W. Odom***, Northwestern University **INVITED**

The prototyping of nanoscale features has rarely been separated from the scaling of them. In order to create arbitrary patterns, serial techniques such as e-beam lithography or focused ion beam milling must start from scratch every time; also, the patterns cannot be generated over large areas. In contrast, parallel fabrication methods such as molding, imprint lithography and soft lithography can scale patterns, but they are limited to transferring the same pattern on the mold. The development of new tools that can combine the strengths of serial approaches (prototyping patterns, high resolution) with those of parallel ones (high throughput, large patterned areas) is critical for next-generation applications based on nanostructures.

This talk will describe an all-moldable nanofabrication platform that can generate—from a single master—large-area nanoscale patterns with programmable densities, fill factors, and lattice symmetries. Solvent-assisted nanoscale embossing (SANE) can increase the spacing of patterns up to 100% as well as decrease them down to 50% in a single step by stretching or heating a thermoplastic substrate. In addition, SANE can reduce critical feature sizes as small as 45% compared to those on a master by controlled swelling of patterned molds with different solvents. SANE can also produce different and reconfigurable lattice symmetries, which enables new opportunities to manipulate the electronic, photonic, and magnetic properties of nanomaterials.

8:40am **NM+MN+MS+TF-TuM3 Micromolding Surface-Initiated Polymerization: A Versatile Route for Microscale Replication onto a Solid Support**, *C.A. Escobar, J.C. Tuberquia, N. Nizamidin, **G.K. Jennings***, Vanderbilt University

This presentation will introduce the use of confined surface-initiated ring-opening metathesis polymerization (SI-ROMP) of perfluoroalkyl or alkyl norbornene monomers from solid substrates to synthesize surface-bound polymer structures with tunable physical and chemical properties that accurately replicate those exhibited by Nature's engineered, microscopically rough, and highly functional surfaces. This approach not only allows mimicking of highly evolved and functional surface architectures but also provides versatility in that it introduces a wide variety of chemical compositions available in materials chemistry, including partially fluorinated polymers with ultralow critical surface tensions. Optical microscopy and scanning electron microscopy confirm growth of the polymer structures and the precise replication of the microscale and nanoscale features exhibited by the target natural surface with the added

freedom to expand beyond Nature's chemical building blocks. Contact angle measurements show that the surface architectures exhibit both hydrophobic and oleophobic behavior, and in some cases, superhydrophobic properties. This approach is not limited to natural surfaces and could be applied in a straightforward manner to a variety of synthetic surfaces that have microscale features.

9:00am **NM+MN+MS+TF-TuM4 Si Mold Etching with Hard Mask for Bit-Patterned Media**, ***M. Kurihara***, Hitachi, Ltd., Tokyo, *M. Satake, Y. Tsuchiya, T. Nishida,* Central Research Laboratory, Hitachi, Ltd., Japan, *Y. Tada, H. Yoshida,* Hitachi Research Laboratory, Hitachi, Ltd., Japan, *N. Negishi*, Central Research Laboratory, Hitachi, Ltd., Japan

Bit-patterned media (BPM) is one of the promising candidates for hard disk media with areal density greater than 1.0Tb/in^2. Nanoimprint lithography (NIL) for BPM has also been investigated as a patterning technique to reduce the production cost. One of the critical issues in NIL mold fabrication is the etching selectivity between silicon and the organic mask pattern due to the following two reasons. One is a significant decrease of pattern thickness to meet the photo-lithography requirements. This decrease remained when applying the self-assembly polymer process to fine patterning. The other is the micro-loading effect that causes the etching rate drop with pattern size shrinking.

In this work, we have developed a hard mask process to compensate for the low etching selectivity. First, the micro-loading effect in the $HBr/Cl_2/O_2$ gas chemistry was evaluated with a SiO_2 hard mask of 20-nm thickness. This SiO_2 hard mask was patterned from 30 to 50 nm by EB lithography and etched with CHF_3 gas chemistry. The coefficients of micro-loading in silicon etching were evaluated based on the relationship between hole depth and etching time with a hole diameter of 30, 40, and 50 nm respectively. With increase of the sidewall taper angle, the micro-loading effect could be improved by about 60%. We also confirmed that there was a hole with a depth of 87 nm with a diameter of 30 nm. Extrapolating this micro-loading effect, it is expected that a hole with a depth greater than 80 nm with a diameter of 10 nm will be achieved. This result will satisfy the pattern aspect ratio of 2, which is required in NIL. We will also demonstrate the Si mold etching with a hard mask by applying the self-assembly polymer in which the areal density is greater than 1.0Tb/in^2.

9:20am **NM+MN+MS+TF-TuM5 Directed Assembly of Block Copolymers to Advance the Performance of Conventional Lithography**, ***P.F. Nealey***, University of Wisconsin **INVITED**

Our research program aims to integrate self-assembling block copolymers into current manufacturing practice. The fundamental concepts of the approach are that 1) the most advanced production-oriented exposure tools (e.g. 193 nm, EUV, or electron beam lithography) and resist materials are used to create patterns of differing chemical functionality on the substrate, and 2) films of block copolymers can be directed to assemble in the presence of the chemical pattern into predictable and desirable morphologies, thereby augmenting and enhancing the lithographic process. In comparing the pattern in resist to the pattern of domains induced to assemble in the block copolymer film, directed assembly has been demonstrated to achieve high degrees of pattern perfection, placement of features at the precision of the lithographic tool used to make the chemical pattern, improved dimensional control of features, improved line edge and line width roughness, and resolution enhancement by factors of two to four. In addition, the approach has been demonstrated to robustly achieve non-regular device-oriented geometries used in the fabrication of integrated circuits also with resolution enhancement by multiplication of feature density by interpolation on low duty cycle chemical patterns. After describing current capabilities, remaining technological questions and pathways towards implementation in specific applications will be discussed.

10:40am **NM+MN+MS+TF-TuM9 Measured Backscattered Electron Profile for Optimized Proximity Effect Correction**, ***D.A. Czaplewski***, *L.E. Ocola*, Argonne National Laboratory

Electron beam (e-beam) lithography has been used to create nanoscale patterns in myriad of resists with features as small as single nanometers. When creating resist features on the single nanometer length scale, the process window to create the desire resist structure becomes increasingly small. Overdosing or under dosing of critical features causes changes in critical dimensions. In addition to the dose required for a single feature, the contribution of additional dose due to proximity of nearby features must be considered. To solve this problem, finite element analysis software packages are available for adjusting dose assignments for different features based on size, shape, and placement with respect to other features. The FEM software can only work as good as the input parameters. These parameters come from the backscattered electron profile. Here, we present the measured electron backscattered profile using a negative e-beam resist. In order to measure the backscattered profile, we use a pattern of intersecting lines surrounded by a large annulus. The lines are measured while the annulus provides a circularly symmetric backscattered electron dose. The lines and annuli are written with varying doses. By measuring the thickness of the resist, the contribution from both the lines and the annulus can be determined for different doses and different shapes by using the resist contrast curve. By using the contrast curve to assign doses to specific resist thicknesses, the specific resist and developer effects are removed from the data. The resultant backscattered electron profile can be used as input into the FEM model to create more accurate resist dose assignments for proximity effect corrected patterns for all resists.

11:00am **NM+MN+MS+TF-TuM10 CMOS Density Scaling in Non-Planar Multi-Gate Devices: A Patterning Perspective**, ***M.A. Guillorn***, *J. Chang, S. Bangsaruntip, C.-H. Lin, W.E. Haensch*, IBM T.J. Watson Research Center **INVITED**

The use of planar Si CMOS device technology may continue beyond the 22 nm node. However, the requirements for the gate dielectric and junction depth needed to maintain control of short channel effects might prove to be unobtainable in devices scaled to meet the integration density requirements of the 14 nm node and beyond. Consequently, an additional method for improving the electrostatics of the device is required. This realization has driven a steady increase in research on non-planar multi-gate CMOS devices over the past 5 years. Raising the Si channel out of the plane of the substrate creates the opportunity to form the gate electrode around multiple sides of the channel. This geometry results in a superior situation from an electrostatics standpoint compared to a planar device where the gate electrode is present only on the top surface of the channel.

In this talk, we will discuss the challenges of fabricating three non-planar multi-gate devices from Si on insulator (SOI) substrates: (1) the FinFET, where the gate controls two sides of a thin Si mesa or fin (2) the Trigate where the gate controls three sides of a Si fin and (3) a gate-all-around nanowire transistor where the gate electrode surrounds all sides of a suspended Si channel. We will present experimental results from advanced prototypes of these devices fabricated at dimensions and densities relevant to 14 and 10 nm node technology. An emphasis will be give to the unique role lithography and patterning play in determining the electrical behavior of these devices. These results offer insight into what may lie ahead for Si CMOS scaling and how it will impact the demands placed on patterning and metrology.

11:40am **NM+MN+MS+TF-TuM12 High Resolution Dry Development**, *D.L. Olynick,* ***D.G. De Oteyza****, P. Perera, P. Kulshreshtra, P. Ashby, M. Schmidt, S. Dhuey, B.D. Harteneck, R.M. Falch, A. Schwartzberg, P.J. Schuck, S. Cabrini*, Lawrence Berkeley National Laboratory

As features sizes continue to shrink, new approaches are required to overcome roadblocks toward high-resolution lithographic patterning. One significant roadblock towards miniaturization is pattern collapse due to capillary forces during drying.[1] We have invented a dry development method for creation of high resolution and high aspect ratio resist features. We use resists that undergo an optical absorption change after exposure to high-resolution radiation (here we use electron beam lithography). This optical change allows the material to be selectively laser ablated such that the resolution is defined by the high-resolution radiation and not limited by the laser spot size. Using methyl-acetoxy calix[6]arene, a CW 532 nm laser, and spot sizes ~300 nm, we have produced features down to 10 nm in a film 120 nm thick, with pitch resolution down to 30 nm(Fig. 1). Calixarene was introduced as a high resolution electron-beam resist [2] and has demonstrated 12.5 nm half-pitch in extreme ultra-violet lithography.[3] Typically, films are spun thin to prevent high-resolution pattern collapse in thicker films but using the dry development, the patterns are well defined even in the thick films. Note, the resist acts negative with solvent development, as the cross-linked material can not be removed, whereas it is positive under laser dry development at the same electron-beam dose conditions. This is in contrast to the thermal dry development process where calixarenes are developed in negative tone.[4] With thermal development, patterns were demonstrated at 25 nm half-pitch in a 25 nm film (1:1 aspect ratio.

We have systematically studied the optical absorption contrast behavior as a function of electron beam dose, laser wavelength, and laser dose. At 532 nm laser wavelength, we identified that the absorption is a two photon process and found one functional group which is responsible for the optical contrast. We will discuss the options for materials beyond calixarenes.

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Plasma Science and Technology Division
Room: 202 - Session PS+MN+TF-TuM

Plasma Processing for Disruptive Technologies
Moderator: M.C.M. van de Sanden, Eindhoven University of Technology

8:00am **PS+MN+TF-TuM1 Scallop Free TSV Etching Method for 3-D LSI Integration**, ***Y. Morikawa***, *T. Murayama, T. Sakuishi, S. Toyoda, K. Suu*, ULVAC, Inc., Japan **INVITED**

Thru silicon via (TSV) etch process for deep and high-aspect ratio structure has been studied thoroughly for applications such as MEMS and CMOS devices. Recently, TSV used in 3D-LSI devices for logic devices may be a few microns in diameter and about 50 um deep. On the other hand, TSVs used in stacking memory devices, the via diameter and depth would be several tens of microns. Therefore, development of TSV etching process is very important for realizing these applications. In this study, a large via size etching in a high-pressure process was focused by using very high frequency capacitive coupled plasma (VHF –CCP) with an ultra self-confined system. This plasma system is simple parallel plate CCP about 100Pa or more process. High-pressure process was carried out on the plasma confined, because mean free pass is very short. And, ion energy distribution (IED) is also controllable by high-presser process with VHF bias. The bimodal IED changes under high-pressure. The peak of high-energy side is reduced, and a charge exchange peak appears. It is considered that the charge exchange is important to anisotropic Si etching of large size TSV with VHF bias.

And next, the high-density and small size of TSV below 10um diameter is indispensable to the utilization and improvement in high performance of 3D-LSI. We have developed a new etching system for TSV application for small size and high aspect ratio via. This system is a planer type magnetic neutral loop discharge (NLD) plasma. For high rate silicon etching, it is very important to understand not only the high density of the ICP plasma generation but also the high density of fluorine atoms. In this study, a novel RF antenna ‘Multi Stacked rf Antenna’ has been developed for highly accurate and high rate etching process. This antenna consists of multistage spiral turn rf antennas to reduce self-inductance (L). The L of this antenna is below 1.0 uH and it is a lower than the standard spiral antenna. As a result of performing the electron density measurement of the planer NLD plasma using this MS antenna, it succeeded in the high-density plasma production of $1x10^{12}$ / cm^3 by the process pressure of 7 Pa. Next, the Si etching process development was performed using the advanced NLD etcher. As a result, the etching rate improved 4 times more compared to the standard cylindrical NLD plasma. Finally, the diameter of 2um was attained by the anisotropic etching of 5 um/min, and the aspect ratio is above 10 using the planer NLD etcher. VHF CCP and planer NLD etching processes are non-cycle etch methods, and these processes were demonstrated about smooth sidewall TSV formation.

8:40am **PS+MN+TF-TuM3 Deep Silicon Etching of 0.8 µm to Hundreds of Microns Wide Trenches with the STiGer Process**, ***T. Tillocher***, *W. Kafrouni*, GREMI, France, *J. Ladroue*, STMicroelectronics - GREMI, France, *P. Lefaucheux*, GREMI, France, *M. Boufnichel*, STMicroelectronics, France, *P. Ranson, R. Dussart*, GREMI, France

The STiGer process is designed to achieve high aspect ratio features in silicon. Like the Bosch process, passivation steps (SiF4/O2 plasmas) and etching steps are cycled to get vertical structures. The etching steps can be purely isotropic (SF6 plasmas) or anisotropic (SF6/O2 plasmas). It is required to cool the silicon substrate with liquid nitrogen to form a SiOxFy passivation layer. It desorbs and disappears when the substrate is heated back to room temperature. Thus, there is no need to clean neither the microstructures nor the chamber walls after each process run. Then, the robustness of the process is enhanced in comparison with standard cryoetching: the profiles are less sensitive to temperature or flow rate variations. But, like in Bosch etching, a scalloping is present on the sidewalls.

Submicron trenches having critical aperture of about 0.8 µm can be etched with high aspect ratios (> 40). In these cases, the average etch rate is around 1.8 µm/min. These features exhibit both undercut and a special defect, which is called “extended scalloping”. This defect is composed of anisotropic cavities developed on the feature sidewalls, just below the mask. It originates from ions scattered at the feature entrance that hit the top profile and remove locally the passivation layer. This defect is observed only for high aspect ratios (typically above 10). Thus, we will also investigate the role of trench critical dimension (from 0.8 µm to 100 µm). A mechanism explaining the formation of the extended scalloping will be proposed.

We have studied the influence of both the duty cycle (tetch/(tetch+tpassivation)) and the chamber pressure on the profiles and the extended scalloping. Basically, when the duty cycle increases, etching dominates passivation, which leads to higher defects. Pressure is a way to tune the slope of the sidewalls. Actually, decreasing the chamber pressure helps to shift from positively tapered features to more vertical profiles, and even negative slopes, hence with dovetailed shape.

This will be correlated with plasma analysis by means of mass spectrometry and optical emission spectroscopy. Actually, it is relevant to investigate how changes in the plasma chemistry can modify the trench profiles.

These trends have been used to optimize two methods that can help to reduce the extended scalloping. The first consists in adding a low oxygen flow in the etch cycle, favouring a low additional passivation. The second technique consists in gradually increasing the SF6 flow from a low value to the nominal value. Consequently, the process starts with a low etch rate and a more efficient passivation, which helps to limit the extended scalloping.

9:00am **PS+MN+TF-TuM4 Evaluation of Alternative Passivation Chemistries for TSV Applications**, *E.A. Joseph*, IBM T.J. Watson Research Center, *G. Matsuura*, ZEON Chemicals L.P., *S. Engelmann*, IBM T.J. Watson Research Center, *M. Nakamura*, ZEON Chemicals L.P., ***N.C.M. Fuller***, *E.M. Sikorski, M. Gordon, B.N. To*, IBM T.J. Watson Research Center, *H. Matsumoto, A. Itou*, Zeon Corporation

With the current advent of 3D integration for advanced interconnect and packaging applications, there has been a renewed focus on deep silicon etch technology to satisfy the need for Through Silicon Via (TSV) patterning. The most common etch method used to fabricate said devices is a time-muliplexed (BoschTM) process, based on years of maturity in the MEMS field.[i] However, issues such as scalloping, mask undercut and limited etch rates are becoming more pronounced as feature sizes scale to meet the ITRS roadmap requirements. This has prompted efforts to attempt to either develop a more conventional etch process[i][ii]or to modify the Bosch process to circumvent these issues.[iii][iv] [v] In this work, we explore a novel polymerizing feedgas chemistry for the deposition step of the Bosch process to improve mask undercut while simultaneously increasing TSV etch rate. Initial results indicate a 5x larger deposition rate as compared to C4F8 (under nominal conditions) and under optimized conditions, enables a 50% decrease in undercut along with 10% increase in TSV etch rate. Optical emission spectra also differ substantially between the two feed gases, indicating different dissociation pathways and radical densities. Further results and a detailed characterization of the deposition properties of the novel chemistry will also be discussed leading to a proposed mechanism for the profile improvements as compared to C4F8. [i] B. Wu, A. Kumar and S. Pamarthy, J. of Applied Physics 108, 051101 (2010) [ii] I. Sakai, N. Sakurai and T. Ohiwa, J. Vac. Sci. Technol. A 29(2), Mar/Apr 2011 [iii] N. Ranganathan et al, Proceedings of the Electronics Components and Technology Conference, 2005 [iv] H. Rhee et al, J. Vac. Sci. Technol. B 27(1), Jan/Feb 2009 [v] S.-B. Jo et al, J. Vac. Sci. Technol. A 23(4), Jul/Aug 2005

9:20am **PS+MN+TF-TuM5 Wafer Scale Hermetic Packaging of MEMS**, ***C.S. Gudeman***, IMT **INVITED**

The explosion of MEMS in automotive and cell phone markets has been enabled by low cost wafer level packaging (WLP) technology that provides a robust and hermetic enclosure for an otherwise delicate device. The more obvious advantage of WLP is greatly improved reliability, because the device is protected from organic and particulate contaminants while in the hands of the end user. A less obvious advantage is the protection provided by WLP during the manufacturing process, which often produces the highest levels of stress that a MEMS device experiences. These processes include wafer grinding, wafer dicing, and chip solder re-flow attachment to circuit boards and other chips. Firstly in this talk, wafer level packaging technologies will be outlined, focusing on the truly hermetic methods -- alloy, glass frit, Au-Au thermo-compression, anodic, and fusion bonding.

Secondly the integration of Through Silicon Vias (TSV) with WLP will be discussed. Finally the performance of these technologies will be compared from a manufacturing perspective, including yield and thermal budget.

10:40am **PS+MN+TF-TuM9 Challenges in Plasma Etch for NVM: Scaling and Materials**, ***M. Kiehlbauch***, Micron Technology, Inc. **INVITED**

With advances in non-volatile memory, the major challenge confronting plasma etch is the introduction of new materials while simultaneously shrinking critical dimensions. This talk will address key development aspects including profile control, feature level uniformity, and plasma microdamage. Plasma microdamage is not the traditional, charge/voltage/current based impact to, for example, gate oxides. Rather, it is the changes to the atomic scale morphology in the sidewall or landing film of a plasma etch process. This results in a disruption of local stoichiometry, film defects, and other issues that impact device performance. The etch process and hardware changes to address this will be presented.

11:40am **PS+MN+TF-TuM12 Mechanisms of Selective Etching for Magnetic Materials: Ni, Co and Ta Etching by Carbon Monoxide/Methyl Alcohol Based Plasmas**, ***K. Karahashi***, *T. Ito, S. Hamaguchi*, Osaka University, Japan

Dry etching of magnetic thin films is a crucial step in micro fabrication of magnetic random access memories (MARMs) and read/write heads for magnetic data storages. Argon (Ar) ion milling seems to be almost the only etching technique available in the current manufacturing processes. However Ar ion milling is incapable of achieving anisotropic and selective etching of magnetic films (Ni, Co etc.) over hardmasks (Ta etc.) and therefore highly selective reactive ion etching (RIE) of magnetic thin films is a highly sought-after technology. RIE processes based on CO/NH_3 or CH_3OH is a candidate for selective etching of magnetic thin films. In this study, we have examined etching processes of Ni, Co and Ta thin films by energetic CO^+, O^+ or OH^+ ions, which are considered to be major etchants of CO/NH_3 or CH_3OH plasmas. We have determined the etching yields and analyzed surface reactions, using a mass-selected ion beam system. The ion beam system is designed to inject mono-energetic single-species ions into a sample surface in ultra-high vacuum conditions. The reaction chamber, where the sample is placed, is equipped with an X-ray photoelectron spectroscopy (XPS) for in-situ chemical analyses of irradiated surfaces. The ion beam energy used in this study is in the range of 150-1000 eV. The etching yields are determined from measured depth profiles of irradiated surfaces and ion fluxes. The etching yields of Ni and Co by CO^+ ions are higher than that by O^+ ions but lower than the yields of possible physical sputtering, which are estimated from interpolation of sputtering yield data of inert atom ions (He^+, Ne^+, Ar^+, Kr^+ etc.). From XPS analysis for O^+ irradiated Ni and Co surfaces, oxidation is found to occur under O^+ irradiation, which suggests that the oxide layer hinders sputtering by ion bombardment. It is found that little oxidation occurs on Ni or Co surfaces under CO^+ ion irradiation and etching by CO^+ ion bombardments proceeds. On a Ta surface, on the other hand, in the both cases of O^+ and CO^+ irradiations, oxidation occurs and its etching yield is far smaller than the yield of its possible physical sputtering. Therefore we have found that high selectivity of Ni and Co etching against hard masks (Ta, TaN) arises from the prevention of sputtering by mask oxidation. Etching characteristics by OH^+ irradiation were also studied in a similar manner. This work was supported by the Semiconductor Technology Academic Research Center (STARC).

Thin Film Division
Room: 107 - Session TF+EN-TuM

ALD for Energy
Moderator: W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

8:20am **TF+EN-TuM2 Controlling the Dispersion and Size of Platinum Nanoparticles Using Pt Atomic Layer Deposition and Surface Treatments**, ***V.R. Anderson***, University of Colorado, Boulder, *N. Leick*, Eindhoven University of Technology, Netherlands, *K.E. Hurst*, National Renewable Energy Laboratory, *A.S. Cavanagh*, University of Colorado, Boulder, *S. Kocha, K. Jones, A.C. Dillon*, National Renewable Energy Laboratory, *S.M. George*, University of Colorado, Boulder

Platinum nanoparticles are used as the catalyst on the cathodes of proton exchange membrane (PEM) fuel cells. Controlling the dispersion and size of the Pt nanoparticles is important for efficient and cost-effective fuel cells. When Pt atomic layer deposition (ALD) is performed on oxide or carbon substrates, nucleation difficulties and the high surface energy of Pt lead to Pt nanoparticles rather than continuous films. This research explored strategies to control the dispersion and size of Pt nanoparticles using Pt ALD together with various surface treatments. Pt ALD was performed using Pt hexafluoroacetylacetonate $Pt(hfac)_2$ and formalin as the reactants. Titanium oxide (TiO_2) and tungsten oxide (WO_3) were explored as the substrates. We used *in situ* transmission Fourier transform infrared (FTIR) spectroscopy to monitor the surface species during Pt ALD. Surface poisoning by hfac species was observed during the nucleation of Pt ALD on TiO_2, in agreement with our previous studies of Pd ALD [1]. Trimethylaluminum (TMA) was able to remove the hfac species from TiO_2 and promote more facile nucleation of Pt ALD, also as expected by our earlier work on Pd ALD [2]. We then used hfacH adsoption prior to Pt ALD to block surface sites, delay Pt ALD nucleation and decrease Pt nanoparticle dispersion. In addition, we used TMA exposures after $Pt(hfac)_2$ exposures to facilitate Pt ALD nucleation and increase Pt nanoparticle dispersion. The Pt nanoparticles were detected by the rising absorbance baseline of the FTIR spectrum, and transmission electron microscopy images of Pt nanoparticles on TiO_2 and WO_3 particles. The size of the Pt nanoparticles was dependent on the number of ALD reaction cycles.

1. D.N. Goldstein & S.M. George, *Thin Solid Films* (In Press).

2. D.N. Goldstein & S.M. George, *Appl. Phys. Lett.* **95,** 143106 (2009).

8:40am **TF+EN-TuM3 Nucleation & Growth of Continuous and Ultrathin Pt ALD Films for Improved Oxygen Reduction Activity in Fuel Cells Using W ALD Adhesion Layers**, ***L. Baker***, *A.S. Cavanagh, S.M. George*, University of Colorado, Boulder, *A. Kongkanand, F.T. Wagner*, General Motors Research & Development

Transition metals, such as Pt, are important as catalysts in fuel cells. The cost of Pt requires that this metal be utilized as efficiently as possible. Previous studies have demonstrated that flat, continuous Pt surfaces have an activity for the fuel cell oxygen reduction reaction (ORR) per surface Pt atom that is 5-10 times *larger* than the activity of 3 nm Pt nanoparticles on carbon-supported electrocatalysts. Consequently, very thin continuous Pt layers are needed to achieve high activity per mass of Pt and favorable economics.

Pt has a high surface energy and does not readily wet low surface energy oxide and carbon material surfaces. Instead, Pt nanoclusters are formed during the nucleation of Pt ALD on these low surface energy supports. A continuous Pt film is possible only after the coalescence of the nanoclusters when the film thickness is >5 nm. One possible route to obtain a continuous and ultrathin Pt film is to deposit on an adhesion layer that has a *higher* surface energy than Pt. In this case, the Pt will wet the adhesion layer because the deposited Pt film will lower the surface energy. One material that has a higher surface energy than nearly all other metals, including Pt, is tungsten (W).

W ALD using WF6 and Si2H6 is known to nucleate and grow rapidly on Al2O3 ALD surfaces [1]. The surface chemistry of W ALD is able to form chemical bonds to the underlying Al2O3 substrate that overcome the surface energy differences. In this study, Pt ALD is performed using MeCpPtMe3 and H2 plasma on W ALD adhesion layers grown on Al2O3 ALD films. X-ray photoelectron (XPS) and x-ray reflectivity (XRR) studies have demonstrated that Pt ALD nucleates *nearly immediately* on the W ALD adhesion layers. The XPS and XRR data are consistent with a layer-by-layer growth model. Pt ALD films can be deposited that are 1 nm thick, conformal and continuous. Initial electrochemical measurements on these thin films have yielded a large proportion of the anticipated ORR activity benefit.

[1] R.A. Wind, F.H. Fabreguette, Z.A. Sechrist and S.M. George, "Nucleation Period, Surface Roughness and Oscillations in Mass Gain per Cycle during W Atomic Layer Deposition on Al2O3", *J. Appl. Phys.* 105, 074309 (2009).

9:00am **TF+EN-TuM4 Engineering $Li_xAl_ySi_zO$ Ion Conducting Thin Films by Atomic Layer Deposition for Lithium-ion Battery Applications**, *Y.-C. Perng*, ***J. Cho***, *D. Membreno, N. Cirigliano, B. Dunn, J.P. Chang*, University of California Los Angeles

Lithium (Li)-ion batteries have drawn much attention for their outstanding performance in portable electronics applications. However, formation of the solid electrolyte interphase (SEI) layer on the surface of electrodes during the charge-discharge cycling can reduce battery capacity and the long-term reliability of current battery technology. The use of solid electrolyte layers can effectively suppress formation of the SEI. Another application for thin solid electrolytes is in microbatteries, especially those based on the engineering of electrodes into 3D architectures involving high aspect ratio

pillars. To realize this potential, an ultra-thin and highly conformal electrolyte layer is needed to coat the 3D electrode array. The ionic conductor lithium aluminosilicate ($LiAlSiO_4$) synthesized by atomic layer deposition (ALD), is a promising candidate for these battery applications. The material exhibits high ionic conductivity along its c-axis because of channels formed by the alternating tetrahedra of aluminum-oxygen (Al-O) and silicon-oxygen (Si-O).

The self-limiting characteristic of ALD allows for precise control of thickness and composition of complex oxides and results in a highly conformal and pinhole-free coating suitable in 3D micro-battery applications or electrolyte surface coatings. The metal precursors used in this work are tetraethyl orthosilicate (TEOS), trimethylaluminum (TMA) and lithium t-butoxide (LTB). These precursors, along with water vapor as the oxidant, were used to deposit SiO_2, Al_2O_3 and Li_2O, with deposition rates in the range of 0.8~2Å/cycle, respectively. The deposition rate of stoichiometric $LiAlSiO_4$ was ~5Å/cycle at a temperature of 290°C. The concentration of each metal element in $Li_xAl_ySi_zO$ (LASO) thin films is found to correlate closely to ALD cycles and the associated incubation times. Complex impedance measurements show that the ionic conductivities of as-deposited LASO films are in the range of 10^{-7} to 10^{-8} S/cm and directly related to the lithium content in the film. The LASO ALD coating on 3D features, such as NWs and nanopaticles (NPs), were confirmed to be conformal and uniform by transmission electron microscopy (TEM) imaging. Further electrochemical tests to check pinhole-free coatings on 2D and 3D features were performed as well. The crystallinity of the films after post-deposition rapid thermal annealing (RTA) was a function of cation concentration. The epitaxial relation of LASO to silicon, a potential anode material, was found to be β-LiAlSiO4 (-1 2 -1 0) || Si (400) and β-LiAlSiO4 (1 0 -1 0) || Si (004).

9:20am **TF+EN-TuM5 ALD: Enabling Designer Nanostructures for Energy Applications*, G.W. Rubloff***, University of Maryland **INVITED**

Nanostructures will dominate next-generation energy technologies. Progress in nanofabrication increasingly allows design flexibility control of structural geometry and material combinations to achieve high performance multifunctional 3-D nanostructures for energy harvesting and storage. Such designs derive advantage from high surface areas, ultrathin films, structures with high aspect ratios, heterogeneous materials combinations, and control over 3-D profiles of material compositions and nanostructure shapes. Self-assembly, self-alignment, and self-limiting reactions enable both nanofabrication of desired energy nanostructures and their scaling to unprecedented levels of integration.

Atomic layer deposition (ALD) plays a pivotal role in this paradigm because of its intrinsic attributes: thickness control at the atomic scale; exceptional conformality to apply this control in the most demanding of nanogeometries; and a growing portfolio of ALD materials choices from new precursors and processes. As a result, ALD is becoming common, even pervasive, in nanostructure-based energy research, spanning applications from heterogeneous nanowires to passivating electrochemical layers and high-efficiency catalytic nanostructures.

Two primary challenges will determine whether ALD's potential is realized in next-generation energy technology.

First, integration of ALD with other processes into suitable process sequences determines how well nanostructure designs can be fabricated and tailored for the energy application. For example, in high aspect ratio trenches, pores, or aperiodic porous materials, ALD films can be highly conformal or tapered "top-down" to thinner layers deeper in the structure, while electrodeposited films can be grown "bottom-up" from a working electrode at the bottom, together offering more design flexibility in vertical profiles than does either process alone.

Second, scaleup of ALD equipment, processes, and control is required for cost-effective ALD manufacturing. Significant efforts are already underway to develop these technologies, notably including roll-to-roll and other high throughput approaches, as well as atmospheric pressure ALD to circumvent the cost and complexity of vacuum-based equipment.

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10:40am **TF+EN-TuM9 Functionalized Quartz Fibers by Atomic Layer Deposition for Dye-Sensitized Solar Cells*, D. Kim***, *H.J. Koo, M. Woodroof, J.S. Jur, B. Kalanyan, K. Lee, C.K. Devine, G.N. Parsons*, North Carolina State University

Dye-sensitized solar cells (DSCs) are a promising alternative to Si-based photovoltaic cells because of their high efficiency, low cost, and simple processing. To improve the efficiency, the light harvesting properties of the DSC photoanode structure should be improved.

This work shows the ability to improve DSCs efficiency by the incorporation of quartz fiber mats functionalized by ALD with a conformal nanoscale TiO_2 coating for the photoanode. The TiO_2 atomic layer deposition allows precise nanoscale thickness control throughout the quartz fiber mat. In addition, thermal stability of the quartz fiber also enables the annealing of TiO_2 films at high temperatures in order to obtain anatase crystallinity, which is the preferred TiO_2 phase in DSCs due to faster electron transfer kinetics. As a result, we obtained very stable anatase TiO_2 on quartz fibers by annealing at as high as 1050 °C. The micro-sized randomly oriented structure of coated quartz fibers caused high light scattering effect inside the photoanode, so that it increased the photon adsorption. At the same time, TiO_2-coated quartz fibers were successfully sensitized by more dye molecules compared to bare quartz fibers.

The use of the dye-sensitized quartz fiber mats in a DSC framework produces devices with overall efficiency exceeding 7% in our laboratory, compared to ~ 6% for similar devices without the coated fiber scattering layer. We will present X-ray diffraction, morphological changes, and optical properties of TiO_2-coated quartz fibers, as well as I-V and IPCE data for the DSCs. The effects of various integration schemes for introducing quartz fibers into the DSC photoanode will be discussed. Moreover, it is believed that the combination of quartz fiber and ALD is very attractive especially to energy research fields where they need finely tuned nanostructures to meet intricate requirements.

11:00am **TF+EN-TuM10 Angle Dependent Electromotive Force in an Al_2O_3/Al/Thermoelectric Power Generator System Interacting with Infrared Radiation**, *A.J. Vincent-Johnson, K.A. Vasquez,* James Madison University*, A.E. Masters,* Custom Thermoelectric, *X. Hu,* ***G. Scarel***, James Madison University

We present a fundamental study of the interaction between infrared radiation and an Al_2O_3 film on Al sheet placed on a thermoelectric power generator (system 1). We compare the results with those obtained for a system consisting in an Al sheet on a thermoelectric power generator (system 2). The Al_2O_3 film in system 1 is prepared using atomic layer deposition, which provides smooth and well defined air/film and film/substrate interfaces. Infrared spectra show that Al_2O_3 films on the aluminum foil absorb an increasing amount of infrared radiation at increasing angle of incidence. This behavior, known as the Berreman effect, is caused by the radiative surface polaritons excited close to the frequencies of longitudinal optical phonons by the infrared radiation at the interfaces of Al_2O_3/Al. Our work demonstrates that a similar trend occurs when infrared radiation is absorbed by system 1: as the infrared radiation starts illuminating system 1 in its initial condition, the electromotive force jumps up to a maximum (EMF_{max}) and then decays exponentially. The EMF_{max} value and its amplitude increase with the increasing incidence angle of the infrared radiation. Since system 2 exhibits only a weak dependence of the EMF_{max} value and amplitude on the incidence angle of the infrared radiation, we conclude that the behavior of the electromotive force during the transient in system 1 is caused by radiative surface polaritons in Al_2O_3/Al. This research is at a seminal stage and needs further understanding. However many routes can be investigated to enhance the efficiency of the electromotive force production. The results are relevant to energy generation from radiation, sensors, and electromagnetic wave detectors.

Thin Film Division
Room: 104 - Session TF+SE-TuM

Glancing Angle Deposition (GLAD) I
Moderator: T. Karabacak, University of Arkansas at Little Rock

8:20am **TF+SE-TuM2 Progress in Glancing Angle Deposition Technology for Practical Applications*, M. Suzuki***, Kyoto University, Japan **INVITED**

Recently, advanced top-down processes for the fabrication of nanostructures have been developed; however, these processes are long predated by the process of shadowing growth by glancing angle deposition

(GLAD), which affords the fabrication of the self-assembled nanostructures over a much larger area at significantly lower costs. In the past two decades, significant progress has been made in the development of 3D nanomorphologies well-controlled by the GLAD such as the zigzag and helix morphologies. Much effort has also been expended to gain a theoretical and numerical understanding of the growth mechanism of nanostructures in order to improve their morphology. Many researches are being carried out in academia to investigate the useful properties of nanocolumnar thin films, such as magnetic anisotropy, birefringence, dichroism, and optical activity *induced by nanoshapes*; high-performance catalysis and electrodes *using large surface area*; and various *size effects*. On the other hand, most companies seem hesitant to introduce the GLAD technique in the factory because of the prejudice that obliquely deposited thin films are not durable and reproducible. However, some products of obliquely deposited thin films are already being manufactured, although their production processes have not necessarily been disclosed. In this presentation, we discuss the previous products and investigations of GLAD thin films and demonstrate that this prejudice can be overcome. In addition, we introduce our recently commercialized products manufactured by GLAD, namely, surface enhanced Raman substrate[1] and low-reflectivity wire-grid polarizers[2]. Because GLAD films have the great potential of enabling humankind to overcome the energy and environmental problems it confronts, it is important to encourage the industry to adopt GLAD by removing the prejudice against GLAD films.

[1] M. Suzuki *et al.*, "Au Nanorod Arrays Tailored for Surface-Enhanced Raman Spectroscopy," Analytical Sciences **23**, 829 (2007).

[2] M. Suzuki *et al.*, "Low-Reflective Wire-Grid Polarizers with Absorptive Interference Overlayers," Nanotechnology **21**, 175604 (2010).

9:00am **TF+SE-TuM4 Engineering Columnar Nanostructures for Organic Photovoltaics**, ***R.T. Tucker***, Univ. of Alberta, Canada, *D.A. Rider,* NRC-Nat. Inst. for Nanotech., Canada, *J.G. Van Dijken, M. Thomas, B.J. Worfolk, A. Lalany, K.M. Krause,* Univ. of Alberta, Canada, *M.D. Fleischauer,* NRC-Nat. Inst. for Nanotech., Canada, *M.T. Taschuk,* Univ. of Alberta, Canada, *K.D. Harris,* NRC-Nat. Inst. for Nanotech., Canada, *J.M. Buriak, M.J. Brett*, Univ. of Alberta, Canada

Organic photovoltaics (OPVs) represent one possible route to widespread adoption of solar energy production [1]. The most promising OPV technology to date has been the bulk heterojunction, a photoactive mixture which bridges the gap between exciton diffusion lengths (~15 nm) and typical device length scales (~ 200 nm). However, bulk heterojunctions are typically disordered, which can limit charge extraction and thereby reduce OPV performance. The ideal OPV bulk heterojunction structure has been identified as ordered interpenetrating columnar electron donor and acceptor layers [2]. The interface morphology of such structures may be fabricated with glancing angle deposition (GLAD), a well-developed, robust nanostructuring technique that has been demonstrated for numerous materials at the length scales required for high quality OPV devices.

Here we present a summary of organic solar cell research utilizing GLAD at the University of Alberta. GLAD's flexibility lends itself to structuring both the transparent conductor layer as well as the donor and acceptor photoactive layers. We have demonstrated GLAD structuring of indium tin oxide (ITO), copper (II) phthalocyanine (CuPc), and fullerene (C60). ITO nanopillars fabricated by GLAD have been incorporated as three dimensional high surface area electrodes in organic photovoltaic devices [3]. The nanostructured electrodes demonstrated 30% improved performance compared to planar ITO anodes, due to increased optical absorption and high surface area. Typical OPV donor and acceptor materials, CuPc and C60, have also been successfully structured by the GLAD technique [4,5]. Advanced motion control algorithms, designed to form thinner columns, were used to optimize the material nanostructures and produce highly desirable ordered bulk heterojunctions when coupled with complementary polymers. In the case for GLAD C60 devices, the short-circuit current was double that of bulk heterojunction devices. The GLAD technique has proven to be an incredibly useful method for fabricating and tuning electrode and bulk heterojunction morphologies in OPVs.

[1] H. Spanggaard and F.C. Krebs, *Sol. Energy Mater. Sol. Cells* **83** 125-146 (2004)

[2] F. Yang and S.R. Forrest, *ACS Nano* **2** (5), 1022-1032 (2008)

[3] D.A. Rider et al., *Nanotechnology* **22** (8), 085706 (2011)

[4] J.G. Van Dijken et al., *J. Mater. Chem.* **21** (4), 1013-1019 (2011)

[5] M. Thomas et al., *ACS Appl. Mater. Interfaces* (in press, 2011)

9:20am **TF+SE-TuM5 Enhanced Photoconductivity Response of Glancing Angle Deposited Indium Sulfide Nanorod Arrays for Photodetector Device Applications**, ***H. Is***, *M.F. Cansizoglu, T. Karabacak*, University of Arkansas at Little Rock

Photoconductivity (PC) in semiconductors can be detected by measuring the change in electrical conductivity when the material is exposed to light. Photosensitive materials with high PC response can be useful especially for photodetector applications. Compared to conventional thin film geometry, semiconducting nanostructures can provide enhanced photoresponse due to their low dark conductivity and superior capability of absorbing light, which leads to an enhanced PC response even to the minimal changes in light intensity. Glancing angle deposition (GLAD) provides a unique capability of producing nanostructured arrays of various materials with controlled shapes, size, and separation. In this study, we fabricated semiconducting indium sulfide nanorod arrays by GLAD on ITO coated glass substrates in various lengths and capped them with a silver film as metal contact to form a proof-of-concept photodetector device. PC response of these devices was measured at different wavelengths with altered light intensities. We show that GLAD nanorods have a superior PC response than conventional thin film, which is believed to be mainly due to their enhanced light trapping and high optical absorption property.

10:40am **TF+SE-TuM9 Catalytic Nanomotor Control: Design Techniques Using Dynamic Shadowing Growth**, ***J.G. Gibbs***, *Y.P. Zhao*, University of Georgia

Catalytic nanomotors with nanometer-to-micrometer dimensions convert chemical energy into mechanical work via catalysis allowing for autonomous self-propulsion. They are an emerging nanotechnology field and promise important technological advances in drug delivery, transport, assembly, and other processes at the nano-scale. Catalytic nanomotors are inorganic analogues of cellular motor proteins that convert chemical energy into work through stored energy. One of the greatest challenges in this field is the manipulation and direct control of motion and swimming behaviors.

We focus upon the geometric design of catalytic nanomotors to modulate motion behaviors. To achieve this goal, a dynamic growth technique must be implemented. Most research uses template-directed electroplating (TDEP) allowing only simple geometries. We use dynamic shadowing growth (DSG) for fabrication which is a dynamic process allowing for construction of a much wider range of structures and shapes.

Depositing different materials and controlling the overlapping area is the first method of motion modulation used. To alter the swimming speed of a spherical nanomotor, Au is overlapped with the Pt-catalyst to varying degrees; the Au surface area A is changed systematically. The average moving speed u is found to follow the scaling relationship, , which agrees with the self-electrophoresis mechanism.

Swimming behaviors can also be altered by geometrical design, easily implemented by DSG making the technique useful to engineer different types of motion. Various swimming behaviors are exhibited by altering the geometry, and/or changing the location of the Pt catalyst accomplishable. Two very similar structures were fabricated and move based upon the location of the catalyst. Multi-component rotational nanomotors consisting of Pt coated TiO_2 nanoarms grown upon ~ 2.01 µm diameter silica microbeads are designed by dynamic shadowing growth. When exposed to hydrogen peroxide, H_2O_2, the structures rotate about an axis through the center of the microbead and perpendicular to the TiO_2 nanoarm at a rate of 0.15 Hz per % H_2O_2 concentration. The other nanomotors are tadpole-like structures that swim in large sweeping circular trajectories. The swimming trajectories are fine-tuned by altering the arm length and orientation exploiting geometry-dependent hydrodynamic interactions at low Reynolds number. The curvature, angular frequency, and radius of curvature of the trajectories change as a function of arm length. Simulations based on the method of regularized Stokeslets are also described and correctly capture the trends observed in the experiments.

11:00am **TF+SE-TuM10 Fabrication of Cr-doped TiO_2 Nanorod Arrays by Oblique Angle Co-Deposition and Their Photocatalytic Properties**, ***G.K. Larsen***, University of Georgia, *R. Fitzmorris, J.Z. Zhang,* University of California Santa Cruz, *Y.P. Zhao*, University of Georgia

In order to achieve efficient photocatalytic behavior in the visible light range, transition metal ions are often doped into TiO_2. Of these transition metal dopants, Cr appears superior in extending the photoresponse of TiO_2 into the visible range. However, different fabrication methods have produced mixed results regarding the effect of the Cr dopant on photocatalytic efficiency. In this study, a unique fabrication method, oblique angle co-deposition (OACD), is used to deposit a well-aligned array of Cr-doped TiO_2 nanorods that exhibit optical absorption in the visible region. These films are compared with TiO_2 nanorod arrays fabricated by oblique angle deposition (OAD). Due to the similarity of fabrication methods, the effect of the dopant on the structural, optical, and

photocatalytic properties of TiO_2 can be isolated. The Cr dopant alters the TiO_2 lattice structure, with an increase in the crystallization temperature of the anatase phase and a decrease in the rutile crystallization temperature. Additionally, Cr is found to segregate out of the TiO_2 matrix and migrate to grain boundaries and the surface of the nanorods. The photocatalytic efficiency and IPCE of the Cr:TiO_2 films is reduced when compared to intrinsic TiO_2 due to changes in the photocatalyst's surface and charge transport properties as a result of the formation of intergranular Cr(VI) oxide clusters. The presence and the effects of the Cr(VI) phase is the result of exceeding the solubility limits of Cr within the TiO_2 lattice.

11:20am **TF+SE-TuM11 Optimal Conditions for Visualization of Fingerprints with the Conformal-Evaporated-Film-By-Rotation Technique**,
***D.P. Pulsifer**, S.A. Muhlberger, R.J. Martín-Palma, R.C. Shaler, A. Lakhtakia*, Pennsylvania State University

The conformal-evaporated-film-by-rotation (CEFR) technique was investigated for use as a development technique to visualize sebaceous fingerprints of forensic importance. A variation on oblique angle deposition, the CEFR technique requires the substrate holder to rapidly rotate about a perpendicular axis. The combination of an obliquely directed, collimated vapor flux and rapid rotation of the substrate gives rise to a conformal coating on the residue left behind on a substrate by the friction ridges of the finger. The coating has a closely packed nanocolumnar morphology. We conducted a systematic study of various deposition parameters in order to identify those conditions which are optimal for the development of fingerprints with the CEFR technique. We varied: base pressure during deposition, vapor flux angle with respect to the substrate plane, substrate rotation rate, deposition rate, and final film thickness. By qualitatively comparing fingerprints before and after development for various values of each deposition parameter, we were able to identify optimal conditions for development. For all depositions chalcogenide glass of nominal composition $Ge_{28}Se_{60}Sb_{12}$ was used to coat sebaceous fingerprints placed on glass microscope slides. We found the optimal conditions to be: a vapor flux angle of 10 deg as measured from the substrate plane, a rotation rate of 3 rps, a deposition rate of 1 nm/s, a final film thickness of 500 nm, and a deposition pressure of 0.1 mTorr. These values are close to those reported previously for CEFR coating of fingerprints with the exception of the base pressure. An optimal base pressure of 0.1 mTorr significantly relaxes the vacuum requirements of an evaporation chamber to be used for this purpose, making the technique very accessible to forensic scientists and law enforcement agencies. This work was supported by Grant No. 2010-DN-BX-K232 from the U.S. Department of Justice.

Energy Frontiers Focus Topic
Room: 108 - Session EN+TF-TuA

Thin Films for Solar Cells
Moderator: C.A. Wolden, Colorado School of Mines

2:00pm **EN+TF-TuA1 Thin Film Silicon Approaches to Future Generations of PV Materials**, ***P.C. Taylor***, Colorado School of Mines **INVITED**

Silicon is a material of choice for photovoltaic (PV) applications for several reasons. First, there is perhaps more known about the properties and processing of Si than any other semiconductor due to its prominence in electronic devices. In addition, Si is a non-toxic, abundant element that is potentially inexpensive to produce in large quantities. The major problems with Si for use in future PV applications are the inefficient absorption of light due to its electronic band structure and a fundamental limit on the efficiency of any single junction bulk device due to transmission of photons below the optical band gap energy and loss of energy to heat for photons above the optical gap energy (so-called Shockly Queiser limit). Nanostructured films of Si have the potential to overcome these problems by decoupling the absorption length for photons from the collection length for carriers and by introducing additional optically excited carriers due to the quantum confinement in nanostructured films. The most promising possibilities for more efficiently exciting and collecting carriers include the production of more than one electron-hole pair per absorbed photon for photon energies greater than twice the optical gap energy, the absorption of photons of below gap energies by the introduction of an intermediate band of states within the optical energy gap due to the inclusion of quantum confined structures with the appropriate properties, and the collection of excited carriers before they lose their energy to phonons. Progress in utilizing these mechanisms for dramatically increasing the efficiencies of future PV devices based on Si will be discussed.

2:40pm **EN+TF-TuA3 On the Influence of the Amorphous Silicon Microstructure on the Crystallization Kinetics Towards Poly-Crystalline Silicon for Solar Cells**, ***M. Creatore***, *K. Sharma, M.C.M. van de Sanden*, Eindhoven University of Technology, the Netherlands

Polycrystalline silicon (poly-Si) is considered to be a promising candidate for thin film PV, coupling the high quality crystalline Si technology with large area and low- cost manufacturing. Our initial studies [1] on poly-Si layers have shown grains extending through the whole thickness (1 μm) upon solid phase crystallization (SPC) of high growth rate plasma deposited amorphous silicon (a-Si:H) films. Furthermore, larger grains are promoted by an increase in the a-Si:H microstructure parameter R* [2], which represents the order (low R*)/disorder (high R*) in the matrix according to the Si-H bond distribution in mono-/di-vacancies (–low stretching mode-LSM) and nano-sized voids (–high stretching mode-HSM), and it is quantified by the integrated IR absorption band ratio $I_{HSM}/(I_{LSM}+I_{HSM})$.

The SPC of a-Si:H follows the steps of incubation, nucleation and grain growth. With the purpose of providing insight on the crystallization process, this contribution addresses a detailed crystallization kinetic study of plasma deposited a-Si:H films by means of in-situ X-ray diffraction (XRD). a-Si:H films having R^* in the range of 0.05-0.6, with an hydrogen content of 5-14 at. %, were annealed at 600 ℃.

The medium range order (MRO) of the a-Si:H layers, quantified by the XRD line-width, and representing the most ordered regions in the matrix (up to 15-25 Å from the mono-vacancies), is found to affect the incubation time (t_o), in agreement with [3]: low R* and high MRO promote a faster nucleation (t_o in the range of 50-100 min), since the most ordered regions act as nucleation centers; as the structural disorder increases, the MRO decreases and the incubation step is delayed up to 450 min. However, for R*> 0.3 and an hydrogen content above 9%, the incubation time unexpectedly decreases. Therefore, the R* and the MRO evolutions during the annealing step are studied. High R* layers, characterized by hydrogen mainly bonded to nano-sized voids, are more prone to hydrogen out-diffusion upon annealing, as inferred by the quantitative decrease of the HSM mode with respect to the LSM mode. The hydrogen evolution is then followed by the rearrangement of the a-Si:H into more ordered regions, as witnessed by the increase of the MRO upon annealing, promoting a decrease in incubation time. In conclusion, next to the established role of the MRO , the nano-sized voids play also a role in the crystallization kinetics, as they affect the overall microstructure and medium range order upon annealing.

[1] Illiberi et al., *Material Letters* **2009**, *63*, 1817.

[2] Sharma et al., *Advanced Energy Materials* **2011**, DOI: 10.1002/aenm.201000074

[3] Mahan et al., *Adv. Funct. Mater.* 2009, *19*, 2338.

3:00pm **EN+TF-TuA4 Deposition of Microcrystalline Silicon Thin Films by Radio Frequency PECVD using Voltage Waveform Tailoring**, ***S. Pouliquen***, *P.-A. Delattre, E.V. Johnson, J.-P. Booth*, Ecole Polytechnique (Palaiseau), France

This paper shows the feasibility of depositing thin films of hydrogenated microcrystalline silicon (μc-Si:H) for photovoltaic applications by radiofrequency discharge using voltage waveform tailoring. Contrary to typically used sinusoidal waveforms, the films were deposited using asymmetric voltage waveforms, resembling "peaks" and "valleys", composed of a fundamental frequency of 15 MHz and three harmonics. Such waveforms lead to an electrical asymmetry effect in the plasma, and a different ion bombardment energy on each electrode. For these experiments, we used a gas mixture of silane diluted in hydrogen (from 1-4%), a total flow rate less than 100 sccm, and a range of pressure from 100 up to 1000 mTorr. We show that the chemical, optical and structural properties - as measured by FTIR, spectroscopic ellipsometry, Raman scattering and profilometry – are strongly determined by the shape of the voltage waveform, and therefore the ion bombardment energy. We observe this effect on the Si-Si bond configuration (microcrystalline vs amorphous peaks in Raman scattering between 480 and 520 cm^{-1}) as well as on the Si-H bond configuration (FTIR peaks at 2000-2100 cm^{-1}). We examine the strength of the effect for varying process parameters, including pressure, total gas flow, voltage amplitude, and SiH_4/H_2 dilution ratio. For the range of parameters used, a growth rate for highly microcrystalline silicon of up to 3 Å/s was achieved without exceeding a pressure of 100 mTorr.

4:00pm **EN+TF-TuA7 Amorphous and Nanocrystalline Silicon Thin Film Photovoltaic Technology on Flexible Substrates**, ***B. Yan***, *A. Banerjee, J. Yang, S. Guha*, United Solar Ovonic LLC **INVITED**

Because of the rapid increase of energy demand and growing concern of environmental impact, renewable energy from photovoltaic (PV) has gained a great deal of attention in the last decade. Various PV technologies have been developed. However, solar panels using conventional crystalline silicon have dominated the market. Thin film silicon is one of the so-called second generation PV technologies. Nowadays, majority of thin film silicon PV products are made with hydrogenated amorphous silicon (a-Si:H) and amorphous silicon germanium (a-SiGe:H) alloy. The advantages of a-Si:H based technology are low lost, capability of large scale manufacturing, abundance of raw materials, and no environmental concerns. One disadvantage of a-Si:H PV technology is its lower efficiency than solar panels made of crystal silicon and compound crystal thin film semiconductors. To resolve the low efficiency issue, significant effort has been made by the researchers. In order to use the solar spectrum effectively, multi-junction structures are normally used by incorporating a-SiGe:H in the bottom cell. In recent years, hydrogenated nano-crystalline silicon (nc-Si:H) has been used as a potential replacement of a-SiGe:H bottom cell in multi-junction structures. The pros of nc-Si:H are its stability under sun light, high photocurrent capability, and no Ge-containing gases required in the process; the cons are thick intrinsic layer that needs high rate deposition and technical challenges for large-area deposition. United Solar has been heavily involved in research and development of a-Si:H and nc-Si:H based PV technology. We have made significant progress in efficiency improvements of a-Si:H and nc-Si:H multi-junction solar cells and modules. We have achieved (i) a 15.4% initial active-area (~0.25 cm^2) solar cell efficiency, (ii) an NREL measured stable total area (~0.25cm^2) efficiency of 12.5%, and (iii) NREL measured initial and stable module (~400 cm^2) efficiencies of 12.0% and 11.4%, which all set new record efficiencies achieved by a-Si:H, a-SiGe:H, and nc-Si:H multi-junction cell structures. Based on these achievements, we have started working on the development of roll-to-roll manufacturing technology for a-Si:H and nc-Si:H multi-junction structures on flexible substrates. We expect to launch 12% stable aperture area a-Si:H and nc-Si:H product in 2012. In this presentation, we will review the progress made by the community and challenges a-Si:H and nc-Si:H PV technology face.

4:40pm **EN+TF-TuA9 High Efficiency, Large Area Silicon Thin Film Solar Modules**, ***L. Li***, *T. Guo, Y. Meng, Z. Xu, F. Dai, F. Zhang, W. Li, Z. Lei, C. Cai, H. Li, B. Tang, D. Zhou*, ENN Solar Energy Co. Ltd. **INVITED**

Hydrogenated amorphous and microcrystalline silicon based thin film solar cells have long shown great potential for various photovoltaic applications due to its better electricity generation under low light and high temperature, shorter energy payback time and greener manufacturing processes, as well as unique applications for BIPV. However, this technology hasn't fully

realized its market potential, as low module efficiencies at mass-production level being one of the major limiting factors. In this paper we report over 9% stabilized module efficiencies in volume production achieved on 5.7 m2 substrates from a-Si:H/uc-Si:H tandem junction solar modules, which reflects significant efficiency improvement by process tuning of silicon thin films, back contact, and device structure, etc.. Several application case studies are also reported which demonstrate excellent field performance of ENN silicon thin film solar modules.

5:20pm **EN+TF-TuA11 Metal-Modulated Epitaxy Growth of InGaN/GaN p-i-n Solar Cells***, **B. Gunning**, M.W. Moseley, J.E. Lowder, W.A. Doolittle,* Georgia Institute of Technology*, J. Wierer, S. Lee, D. Koleske, Q. Li*, Sandia National Laboratories

InGaN alloys have great potential in the field of photovoltaics due to their excellent light absorption and tunable bandgap (0.7-3.4eV) which spans the visible spectrum. However, the growth of this material remains a challenge due to thermal decomposition, indium surface segregation, and phase separation. To combat these issues, low substrate temperatures and high growth rates must be implemented in combination with in situ surface monitoring via RHEED. Metal modulated epitaxy (MME) has been shown to achieve single-phase InGaN alloys throughout the miscibility gap with sub-nm RMS roughness.

In this study, MME is applied to the growth of n-GaN/i-InGaN/p-GaN solar cells. Unintentionally doped InGaN layers 50/200nm thick with 16% In composition are grown on a 3μm n-type GaN template. The topmost layer consists of p-type GaN with varying hole concentrations. Transient RHEED signals are monitored closely during InGaN growth to prevent indium surface segregation and ensure a smooth film.

The absorption characteristics are determined as shown in Figure 1, and the material is characterized via AFM, XRD and PL prior to being fabricated into device structures. The InGaN layers are found to be approximately 80% strain relaxed as determined by XRD analysis of the (20-25) reflection (Figure 2). During device testing, the solar cells exhibit low turn-on voltages below the expected value, as well as low external quantum efficiency. These inconsistencies indicate carrier loss due to electrical shorts and defects. The scanning TEM images in Figure 3 show striations in the InGaN layer similar to those in a superlattice structure but with a period that does not correspond to the shutter cycles. Even though the x-ray diffraction indicates predominantly relaxed epitaxy, TEM images are unable to resolve individual threading dislocations. It is not clear at present if this is indicative of extremely large dislocation density or a new method of relaxation related to the above mentioned striations. Finally, post-growth annealing processes are explored as possible ways to improve device performance.

The work at Georgia Tech was supported by Air Force Office of Scientific Research, under a basic science grant managed by Kitt Reinhardt.

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Thin Film Division
Room: 107 - Session TF-TuA

ALD: Fundamental Reactions and Film Properties
Moderator: S.M. George, University of Colorado, Boulder

2:00pm **TF-TuA1 Indium Oxide Atomic Layer Deposition Facilitated by the Synergy between Oxygen and Water***, J.A. Libera, J.N. Hryn,* ***J.W. Elam***, Argonne National Laboratory

This study describes how In_2O_3 films can be prepared by ALD using alternating exposures to cyclopentadienyl indium (InCp) and *combinations* of H_2O and O_2, even though H_2O and O_2 are ineffective when used individually. Nanostructured photovoltaics would benefit enormously from the capability to deposit conformal indium-tin oxide (ITO) films inside of high aspect ratio structures. For instance, our previous In_2O_3 ALD method using InCp and O_3 enabled ITO growth inside of anodic alumina membranes producing higher photocurrents through radial charge collection in dye-sensitized solar cells. However, this process yielded poor thickness conformality due to the In_2O_3-catalyzed thermal decomposition of O_3, and this shortcoming motivated our search for an O_3–free process. We were surprised to discover that when H_2O and O_2 were used together, either as a simultaneous exposure (SE) or in the sequence H_2O-O_2 (WO) or O_2-H_2O (OW), very uniform, highly conducting In_2O_3 films were deposited at 1.0-1.6 Å/cycle over large areas (12"x18") at temperatures as low as 100°C. *In-situ* quartz crystal microbalance, mass spectrometry, and Fourier transform infrared measurements revealed that the H_2O and O_2 work synergistically to facilitate the In_2O_3 ALD. Each molecule performs a necessary but distinct role in the growth mechanism. Next, we conducted a thorough study of this process for all three growth modes (SE, WO, OW) over the temperature range 100-250°C using spectroscopic ellipsometry, ultraviolet-visible transmission, X-ray diffraction, scanning electron microscopy, and Hall probe measurements. These measurements identified a remarkable correlation between the film structure and electrical properties around an amorphous-to-crystalline phase transition near the deposition temperature of 140°C.

2:20pm **TF-TuA2 Engineering AlN Thin Films by Atomic Layer Deposition on Wide Bandgap Semiconductors as Gate Dielectric***, **Y.-C. Perng**, J.P. Chang*, University of California Los Angeles

Wide bandgap semiconductors, such as SiC and GaN, are known as base materials in electronic devices operating under high temperatures and high electric fields. Aluminum nitride (AlN) is a promising interfacial layer or dielectric material for SiC and GaN due to its material properties, such as wide bandgaps, similar atomic arrangement and small lattice mismatch (1.3% and 2.6%). Although various deposition methods, such as chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE), have been used, synthesizing high quality AlN thin films for those applications is still an issue, especially in the view of controllability in atomic scales. Atomic layer deposition (ALD) is used to synthesize AlN thin layer on SiC, GaN and Si to achieve atomic controllability and assess the possibility to extend this deposition method to nitride growth and how the substrate properties affect the interface quality and corresponding electrical properties of the synthesized film

The AlN thin films were synthesized at 400~600°C via a chamber with the base pressure as 10^{-7} torr, using trimethylaluminum (TMA) and blue grade ammonia (NH_3) as precursors. The surface structure during the deposition was monitored via *in-situ* RHEED and the growth rate was 0.5~2Å/cycle as a function of the deposition temperature. The surface composition, including the impurities, was found to be correlated to the deposition temperature, verified by *in-situ* x-ray photoelectron spectroscopy (XPS). The surface morphology of the films was studied by transmission electron microscopy (TEM) and atomic force microscope (AFM) and found to be conformal because the rms value was found to be less than 10Å on SiC, which is the same as that of the substrate surface roughness. The capacitance/conductance-voltage characteristics were measured to determine the dielectric constant of the ALD film and interpret the interface states density, which were 8 and on the order of 10^{12} $cm^{-2}eV^{-1}$, respectively, comparable to that reported for MBE synthesized AlN.

2:40pm **TF-TuA3 Paul Holloway Award Lecture - Gas-Surface Interactions during Atomic Layer Deposition***, **S. Agarwal****, Colorado School of Mines **INVITED**

Atomic layer deposition (ALD) is an ideal technique for depositing amorphous and polycrystalline films that require atomic layer control over the film thickness and chemical composition, and can provide conformal coverage with sharp interfaces on high-aspect-ratio nanostructures. ALD has been used to deposit oxide, nitride, elemental and compound semiconductors, and metal films for various applications. The primary challenges in ALD are control over the film's microstructure and residual impurities, which in turn affect their structural, electrical, and transport properties. To overcome these problems, an understanding of atomic-scale events that occur during growth is required. In this presentation, we will discuss the mechanisms of the surface reactions of radicals and molecular precursors supplied during growth using a suite of *in situ* diagnostic tools. We will specifically discuss the reaction mechanisms during plasma- and ozone-assisted ALD of TiO_2, Al_2O_3, and SiO_2, and how such reactions influence the film properties.

4:00pm **TF-TuA7 Mechanical Properties of ALD Thin Films***, **H. Baumgart***, Old Dominion University **INVITED**

Atomic Layer Deposition (ALD) is recognized as the preferred method to deposit technologically important thin films of novel high-k dielectric metal oxides or semiconducting metal oxides for CMOS and MEMS technology with Angstrom accuracy. Large bodies of extensive studies exist on the

* Paul Holloway Award Winner

electrical characterization of ALD films, however, there exists a lack of systematic studies regarding the mechanical properties of ALD grown thin films. Elevated temperatures cause phase changes in many ALD metal oxide films, which affect the mechanical properties and surface morphologies. Little is known about the impact of those phase changes on the nanomechanical properties of ALD HfO_2. Phase change of ALD HfO_2 impacts the mechanical and electrical properties of high-k dielectric gate insulators depending on whether a Gate First or Gate Last process integration has been adopted. Nanoindentation is the most appropriate testing mechanism that accurately investigates the mechanical properties of extremely thin film specimens such as microcrystalline ALD thin films. Nanoindentation testing was conducted to investigate the impact of the different phase changes of HfO_2 on the mechanical properties. We have deposited ALD HfO_2 at low temperature and measured the mechanical properties of the various phase changes of HfO_2 following various thermal annealing cycles. After crystallization by annealing in a rapid thermal annealing (RTA) chamber, the modulus was found to decrease from 370±20GPa to 240±20GPa as the HfO_2 films transition from amorphous to polycrystalline structure past the phase change transition temperature of 600°C. Similarly, the hardness measurements reveal a high value of 18±1GPa for amorphous HfO_2 films and a decrease to 15±1GPa following the transition temperature to polycrystalline HfO_2 films.

Piezoelectric films such as ALD ZnO are finding applications in microelectromechanical systems (MEMS), piezoelectric transducers and oscillators, micro-resonators, gyroscopes, and energy harvesters. Since piezoelectricity of ZnO involves internal generation of electrical charge resulting from an applied mechanical force deforming the static structure of the ZnO crystals, studying the mechanical properties of novel ALD thin films of ZnO is important for these technical applications. Obtaining a better understanding of the structural and mechanical properties of novel ALD ZnO films is essential to improve key performance parameters of MEMS micro-devices.

An overview of the measured mechanical properties of selected ALD thin films will be presented. The mechanical properties of ALD thin films differ significantly from published values of bulk material.

4:40pm **TF-TuA9 Effect of Atomic Layer Deposition on the Mechanical Properties of Synthetic Nonwoven and Electrospun Polymer Fibers**, ***C.K. Devine***, *C.J. Oldham, J.S. Jur, G.N. Parsons*, North Carolina State University

Nonwoven fiber mats and electrospun nanofiber films have been widely researched for their use in filtration, sensing, scaffolding for biological applications, and in many other areas. Nano- and microscale fibers can be functionalized using thin coatings deposited using ALD to impart mechanical strength, catalytic character, and increase conductivity while maintaining the fiber structure. We are interested in the mechanical properties of ALD coated micro and nano-sized fibers. Increasing the mechanical strength of these fibers allows for their use in more robust applications; however it is desirable for the fibers to maintain their flexibility. For this study, nylon nanofibers formed by electrospinning were coated with either TiO_2 or ZnO at temperatures between 60 and 75°C, and the mechanical tear resistance was characterized by optical microscopy under the application of lateral strain. For the TiO_2 coated samples, the tear resistance remained the same when coated with smaller cycle numbers. As the films become thicker the mechanical properties are more dependent on the character of the coating. Specifically, after oxide coating, the fibers show a more brittle response to bending, resulting in visible cracking under optical microscopy after bending by less than 5° for thicker coatings. Similar trends are observed when nylon nanofibers are coated with ZnO or Al_2O_3, however, using our technique, the measureable change in mechanical response was observed at lower cycle numbers for ZnO and even lower for Al_2O_3 , consistent with very different reactions between the nylon and the various ALD precursors. The difference in the tear resistance between these materials may be a result of the reactivity of the ALD precursors. Choosing a more robust and less brittle material to deposit on the fiber mats should improve their mechanical properties will maintaining the fiber structure and flexibility.

5:00pm **TF-TuA10 In Situ Studies of Oxide ALD for Crystalline Oxide Growth on Silicon**, ***B.G. Willis***, *H. Wang,* University of Connecticut, *C. Zhang,* Chinese Academy of Sciences, China, *X. Jiang*, University of Connecticut **INVITED**

Thin films of crystalline oxides integrated with silicon are of interest for novel electronic devices that utilize a rich variety of functional properties of oxide materials. These useful properties include piezoelectricity and ferroelectricity among others. Growth of crystalline oxides on silicon requires careful control of a nanometer thin transition region between the film and substrate to avoid deleterious side reactions such as oxidation of the substrate. Submonolayer surface reconstructions of alkaline earth metals such as Sr are critical for controlling the interface for successful growth. In this paper, we show how atomic layer deposition (ALD) can be used to precisely control the interface reactions for epitaxial growth. X-ray photoelectron spectroscopy and *in-situ* spectroscopic ellipsometry are used to monitor the growth and interface evolution of oxides deposited by ALD. Ellipsometry provides real time feedback on sequential adsorption cycles including precursor adsorption and oxidation. X-ray photoelectron spectroscopy provides detailed insight into the evolution of the interface structure during annealing and oxide desorption. Using this high degree of control enables the successful deposition of critical Sr/Si reconstructions for heteroepitaxy. The results show that ALD crystalline oxide heteroepitaxy is promising.

5:40pm **TF-TuA12 Nucleation and Interface Formation of Al_2O_3 on HF-treated InGaAs(100) by Atomic Layer Deposition**, *A.J. Muscat,* ***B. Granados****, F.L. Lie*, University of Arizona

III–V compound semiconductors are alternative channel materials for high-speed, low-power digital logic devices because their electron transport and breakdown properties are superior to that of Si. However, robust surface passivation processes and thermodynamically stable interfaces are barriers to its wider adoption. Additionally, the scaling down of integrated circuits has prompted the use of alternative high-*k* dielectric films to replace SiO2 as the gate in metal-oxide-semiconductor field effect transistors (MOSFETs). Recent work demonstrated oxide removal and passivation of III-V surfaces by depositing high-*k* dielectrics using atomic layer deposition (ALD).

In this study, the ALD of Al2O3 was investigated on liquid and vapor HF-etched In0.53Ga0.47As(100) samples. Both half and complete ALD cycles of trimethylaluminum (TMA) and H2O at 170°C were used to better understand nucleation and film growth. Aqueous HF etching was performed by a 49% HF dip 1 min and 15 s water rinse. *In situ* gas phase HF/H2O etching was run at 29°C and 100 Torr with an HF to water partial pressure ratio of 1.23.

The initial 8.0±1.4 Å-thick native oxide contained 21% In, 27% Ga, and 52% As oxides and was reduced to a 4.3±1.5 Å-thick oxide containing 91±7% As by aqueous HF. In contrast, the gas phase HF produced ~7 Å-thick mixed oxide and fluoride overlayer containing 30% In, 40% Ga, and 30% As.

Large reductions of substrate oxides were observed after the first TMA pulse on both liquid and gas phase HF-treated samples. The intensity of the O 1s XPS peak was constant but the peak shifted by 1 eV to higher binding energy (BE) due to the conversion of the oxide to Al2O3. On the gas phase HF-treated samples removal of In, Ga and As atoms in the fluoride-rich overlayer layer was also observed after the first TMA pulse. The intensity of the F 1s peak was reduced and the peak shifted by 2.2 eV to higher BE, indicating the etching of fluoride as well as the conversion of the bonding from substrate fluorides to Al-F.

Subsequent H2O and TMA pulses up to three cycles of TMA/H2O revealed a systematic peak shift of the overlayer atom signals. F 1s, O 1s and Al 2p peaks shifted 0.9 eV, 0.4 eV and 0.2 eV, respectively, towards lower BE after a H2O pulse and shifted back to their original positions after a TMA pulse. The systematic shifts could be attributed to the change in surface termination after every half-cycle reaction, methyl termination after the TMA pulse and hydroxyl termination after a water pulse. Understanding surface reactions involved in the nucleation phase and early cycles of ALD is important in achieving control of the III-V-dielectric interface.

Thin Film Division
Room: East Exhibit Hall - Session TF-TuP

Thin Films Poster Session

TF-TuP1 Spatially Varied Orientation Selective Epitaxial Growth of CeO_2(100) and (110) Areas on Si(100) Substrates by Reactive Magnetron Sputtering Utilizing Electron Beam Irradiation*, T. Inoue, S. Shida*, Iwaki Meisei University, Japan

Cerium dioxide is of great interest due to favorable properties as an electronic material, such as high dielectric constant of 26, high chemical stability, transmission in visible and infrared regions, and high efficient ultra-violet absorption. Epitaxial growth of CeO_2 layers on Si substrates has been studied making the best use of a close lattice parameter matching relation. Recently, we have found that orientation selective epitaxial (OSE) growth of (100) and (110) oriented CeO_2 layers on Si(100) is capable by controlling surface potential distribution in reactive magnetron sputtering. Non-polar CeO_2(110) grows on Si(100) with usual non-modified surface potential, whereas polar CeO_2(100) grows on Si(100) with adequately bent surface potential. We are studying two OSE control methods, one is substrate bias application[1] and the other is low energy electron beam irradiation.[2,3] The latter has the attractive possibility of spatially varied two dimensional control of OSE grown regions.[4] This paper describes experimental results of electron beam induced OSE growth with patterned scanning of 90 eV electron beams. The size and position of the electron beam irradiation area were controlled using absorbed electron current image observation. RHEED and XRD analyses proved the realization of two dimensionally controlled OSE growth of CeO_2(100) and (110) areas in electron beam irradiated and non-irradiated areas, respectively. Precise XRD peak profile measurements revealed that there are considerably wide transition regions in between the above two areas, which contain both orientation components. For the application to two dimensionally patterned hybrid orientation technology, the transition region width should be reduced significantly. Our experiments clarified that the width of the transition region reduces proportionally with the logarithm of underlying Si substrate resistivity, reflecting the surface spread of potential distribution. These results will lead to sophisticated microelectronics devices using hybrid orientation technology. This work was supported by KAKENHI (20560024). A part of this work were conducted at the AIST Nano-Processing Facility, supported by "Nanotechnology Network Japan" of the MEXT, Japan.

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TF-TuP2 Influence of Growth-Rate on the Epitaxial Orientation and the Crystalline Quality of CeO_2 Thin Films Grown on Al_2O_3(0001) by Molecular Beam Epitaxy*, M.I. Nandasiri,* Western Michigan University, *P. Nachimuthu, T. Varga, V. Shutthanandan, W. Jiang, S.V.N.T. Kuchibhatla,* ***S. Thevuthasan****,* Pacific Northwest National Laboratory*, S. Seal,* University of Central Florida*, A. Kayani*, Western Michigan University

Cerium oxide (CeO_2) is one of the extensively studied rare earth oxides; however, it continues to attract attention because of its potential use in medical biology, catalysis, intermediate temperature solid oxide fuel cells (IT-SOFC), and resistive oxygen gas sensors. Driven by the need for fundamental understanding of its unique properties, CeO_2 thin films grown on various substrates by different methods at different experimental conditions have been extensively studied. However, the influence of growth-rate on the orientation and the crystalline quality of the CeO_2 thin films is relatively unexplored. While understanding the influence of growth-rate, we evaluated the ability to tailor the orientation and the epitaxial quality of CeO_2 films on Al_2O_3(0001).

CeO_2 thin films were grown on Al_2O_3 (0001) substrates at 650°C with different growth-rates (1-10 Å/min) by oxygen plasma assisted molecular beam epitaxy (OPA-MBE). The growth rate induced epitaxial orientations and crystalline quality of CeO_2 thin films were studied by in-situ reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM), and x-ray diffraction (XRD) techniques. CeO_2 grows as three-dimensional (3-D) islands and two-dimensional (2-D) layers at growth-rates of 1-7 Å/min and ≥9 Å/min, respectively. AFM images show average surface roughness of 5-10 Å, indicating the high-quality surfaces of CeO_2 thin films. The formation of epitaxial CeO_2(100) and CeO_2(111) thin films occurs at growth rates of 1 Å/min and ≥9 Å/min, respectively. Glancing incidence XRD measurements have indicated that the films grown at intermediate growth rates (2-7 Å/min) consist of some polycrystalline CeO_2 along with CeO_2(100). As indicated by x-ray pole figure measurements, the CeO_2 thin film grown at 1 Å/min shows six in-plane domains, characteristic of well-aligned CeO_2(100) crystallites. When increasing the growth rate from 1 Å/min to 2-7 Å/min, poorly-aligned CeO_2(100) crystallites start to coexist along with well-aligned crystallites. The content of the poorly-aligned CeO_2(100) crystallites increases with increasing growth rate from 2 Å/min to 7 Å/min, and three out of six in-plane domains gradually decrease and eventually disappear. At growth rates ≥9 Å/min, CeO_2(111) film with single in-plane domain was identified. The formation of CeO_2(100) 3D-islands at growth rates of 1-7 Å/min is a kinetically-driven process unlike at growth rates ≥9 Å/min, which result in an energetically and thermodynamically more stable CeO_2(111) surface.

TF-TuP3 Influence of Target Type on Surface Texture-etched AZO Films Prepared by Magnetron Sputtering for Solar Cell Transparent Electrode Applications*, T. Minami,* ***T. Miyata****, T. Hirano, Y. Noguchi, J. Nomoto*, Kanazawa Institute of Technology, Japan

This paper describes the influence of sintered oxide targets on the surface texture formation as well as light management obtainable by wet-chemically etching transparent conducting Al-doped ZnO (AZO) thin films prepared by different types of magnetron sputtering depositions (MSD). For transparent electrode applications in thin-film solar cells based on $CuIn_{1-X}Ga_XSe_2$ and Si, transparent conducting AZO thin films require an appropriate surface texture to improve photovoltaic properties through induced light scattering and subsequent light trapping. It was found that the suitability of the light scattering characteristics for thin-film solar cell applications was considerably dependent on both the type of AZO target and the type of MS deposition used.

The surface texture-etched AZO thin films were prepared by a d.c.- or r.f. (13.56 MHz) power-superimposed d.c.- magnetron sputtering deposition (dc-MSD or rf+dc- MSD) with sintered AZO targets that was followed by a heat treatment with rapid thermal annealing (RTA) and a subsequent wet-chemical etch. Five types of commercially available high-density-sintered rectangular AZO targets were used. The suitability of the light scattering characteristics for thin-film solar cell applications was evaluated by carrying out surface texturing of the samples with wet-chemical etching in a 0.1% HCl solution conducted after the heat treatment with RTA (at a temperature of 300-500°C for 1-5 min in air). It was found that the obtainable surface texture as well as the haze value in the range from visible to near infrared were considerably affected by not only the AZO target used but also the type of MSD; the dc- and rf+dc-MSD were conducted using the five types of targets with properties that depended on the supplier. The surface-textured AZO thin films prepared by rf+dc-MSD and etched to an appropriate depth after RTA were found to exhibit a higher haze value and a lower resistivity than the values exhibited by equivalent films prepared by dc-MSD. It was also found from X-ray diffraction analyses that the as-deposited AZO thin films prepared by rf+dc-MSD exhibited better crystallinity than those prepared by dc-MSD; also, the crystallinity of AZO thin films, such as the c-axis orientation, was slightly improved by the RTA treatment. A high haze value generally above 70% in the range from visible to near infrared (at wavelengths up to 1200 nm), which is suitable for thin-film solar cell applications, was obtained in the best surface-textured AZO thin films: film thickness of 2 μm prepared by rf+dc-MSD with an appropriate AZO target and etched to a depth of approximately 300 nm after RTA at approximately 500°C for 5 min.

TF-TuP4 XPS and ToFSIMS Characterization of Laser Modified Films for Li-Ion Battery Cathodes*,* ***M. Bruns****, R. Kohler, J. Proell, C. Ziebert, W. Pfleging*, Karlsruhe Institute of Technology, Germany

The development of novel electrode materials for lithium-ion batteries has become subject of great interest in recent years due to the necessity of improved performance for future mobile applications and energy storage systems. Therefore, a great deal of effort has been spent to develop strategies for the enhancement of battery lifetime, capacity, and cyclability. A self-evident goal to improve the electrochemical properties of cathode materials is to enhance the lithium intercalation rate by increasing the surface to bulk ratio. For this purpose, a very promising approach is the laser-assisted surface modification and structuring of commonly as a cathode material used lithium cobalt oxide and lithium manganese oxide.

The present study focuses on the characterization of non-structured and laser modified films before and after electrochemical cycling using a

combination of complementary surface analytical methods. For this purpose rf magnetron sputtered lithium cobalt oxide and lithium manganese oxide were structured with laser radiation leading to a surface microstructure with increased active surface area. In particular, high repetition excimer laser radiation with a pulse width of 4-6 nm and 248 nm wavelength was used. Self-organized conical microstructures were formed using laser fluences between 0.5 J/cm² and 2.0 J/cm². A subsequent annealing process using high power diode laser radiation at 940 nm wavelength enables the adjustment of the required crystallinity.

X-ray photoelectron spectroscopy (XPS) provides the chemical composition in a non-destructive manner. The in-depth distribution of the electrode constituents and the solid electrolyte interface after cycling was studied by time-of-flight secondary mass spectrometry (ToFSIMS) and XPS sputter depth profiles. In addition, the conical topography was shown by scanning electron microscopy (SEM) and crystallinity was proven by X-ray diffraction.

TF-TuP5 Effect of Temperature on the Native Oxide Consumption during the ALD of Ta_2O_5 and TiO_2 on GaAs (100) Surfaces, ***L. Ye***, *T. Gougousi*, UMBC

Thermal ALD processes for the deposition of TiO_2 and Ta_2O_5 have been developed using amide precursors and H_2O as reagents. The TiO_2 films were deposited from tetrakis dimethyl amido titanium and H_2O and the Ta_2O_5 films were deposited from pentakis dimethyl amido tantalum and H_2O. The growth rate for both processes was ~0.6 Å/cycle at 200°C and 250°C respectively. These temperatures represent the so-called ALD minimum. At these temperatures the existence of a reaction that leads to the consumption of the surface native oxides during depositions on GaAs (100) surfaces has been confirmed using x-ray photoelectron spectroscopy and high resolution transmission electron microscopy. To investigate the effect of temperature on the native oxide consumption rate two sets of samples with thickness 2 and 3 nm have been prepared at temperatures ranging from 100 to 350°C. For both ALD chemistries a significant enhancement in the gallium and arsenic oxide consumption rate was observed for process temperatures above 300°C. For depositions performed at temperatures more than 50°C below the ALD minimum the consumption reaction is significantly slower.

TF-TuP7 Influence of Doped Al Content on Electrical Properties and Light Management Obtainable by Texture-etched AZO Films Prepared by DC Magnetron Sputtering, ***J. Nomoto***, *T. Miyata, T. Hirano, T. Minami*, Kanazawa Institute of Technology, Japan

Al-doped ZnO (AZO) thin films that would be suitable for transparent electrode applications in thin-film Si-based solar cells must necessarily attain not only a decrease of plasma resonance frequency by lowering the carrier concentration while retaining a resistivity on the order of 10^{-4} Ωcm, but also a significant scattering of light incident on the film by surface texturing. In this paper, we describe the influence of doped Al impurity content on the electrical properties as well as the light management obtainable by surface texture-etched AZO thin films that were prepared with various Al contents by a dc magnetron sputtering (dc-MS) deposition and wet-chemically etched after a rapid thermal annealing (RTA) treatment. In addition, the stability of the resulting electrical properties for practical use in various environments was investigated for these AZO films prepared with various Al contents.

Transparent conducting AZO thin films were prepared with a thickness up to 2μm by a dc-MS deposition using sintered AZO targets that had various Al contents. The basic sputter depositions were carried out on OA-10 glass substrates at a temperature of 200°C in a pure Ar gas atmosphere at a pressure of 0.4Pa and a power of 200W. Surface texturing of the AZO thin films was carried out by wet-chemical etching in a 0.1mol./l HCl solution after the thin films were heat treated with RTA at a temperature of 300-500°C for 1-5min in air. It was found that the obtainable surface texture and electrical properties in texture-etched AZO thin films were considerably affected by the RTA treatment conditions as well as the Al content doped into the films. The transmittance in the near-infrared region of the resulting AZO thin films exhibited a tendency to improve as the RTA temperature was increased. A high transmittance above 80% at a wavelength of 1.2μm was obtained in 1-μm-thick-AZO thin films prepared under the following conditions: an Al content (Al/(Al+Zn) atomic ratio) of approximately 0.5at.% when the thin films were heat treated without RTA and an Al content below 1.5at.% when the thin films were heat treated with RTA. In addition, when the thin films were heat treated with RTA at 500°C for 3-5min, increasing the Al content doped into the AZO films enhanced the transmittance in the near infrared region , irrespective of the film thickness. However, it should be noted that the optimal Al content doped into texture-etched AZO thin films that would be suitable for transparent electrode applications in thin-film Si-based solar cells was considerably dependent on the obtainable crystallinity in the films as well as whether the thin films were heat treated with RTA or not.

TF-TuP9 Structure and Photo-Functional Properties of N^+ Ion Irradiated TiO_2 Thin Film under Various Substrate Temperatures, ***H. Shukur***, *M. Sato*, Kogakuin University, Japan, *I. Nakamura*, Tokyo Metropolitan Industrial Technology Research Institute, Japan, *I. Takano*, Kogakuin University, Japan

Titanium dioxide (TiO_2) has been fundamentally used as a photocatalytic application to decompose environmental pollution materials. TiO_2 can generate active oxygen by exposing to sunlight and also is harmless to the environment and the low cost material, so that it is expected to use as an element of a clean energy system in the future .

TiO_2 shows relatively high reactivity and chemical stability under UV light whose energy exceeds the band gap of 3.2 eV for the anatase crystalline phase and 3.0 for the rutile crystalline phase. Many techniques has been examined to increase its activity under visible light region.

N^+ ion irradiation method has been used by many researchers because it can provide an activated TiO_2 in both of visible and UV light. However the collision between ion and film causes a defect in film structure as causing a decline in photo-functional property.

In this study structural, chemical and photo-functional properties of TiO_2 thin film with a rutile structure were studied after irradiation by various doses of N^+ ion beam under various temperatures. Reactive magnetron sputtering method was employed to prepare TiO_2 thin film on glass substrate (corning #1737). Ti-O was sputtered from Ti target in an Ar / O_2 gas and the substrate was hated at 300 ºC. The total film thickness was around 180 nm with a deposition rate of 0.025nm/sec. N^+ ion was irradiated to TiO_2 thin film under 15 keV in acceleration voltage, and 40 $\mu A/cm^2$ in ion current density with a various implantation doses. Substrate temperature was set at a room temperature (25 ºC), 100, 200 and 300 ºC through ion irradiation processes. The structure was determined by X-ray diffraction (XRD: MAC Science High quality XG M18XCE) with CuKα (0.154nm) radiation at an incident angle of 0.3º, and the composition was characterized by X-ray photoelectron spectroscopy. The photocatayst property was measured by a MB immersion test. The spectrophotometer (SHIMADZU UV-2550) was used to measure the difference in light absorption at a wave length of 665nm.

The increasing in the Full Wave Half Maximum (FWHM) of XRD measurements with N^+ ion irradiation under 25ºC refers to declining of the crystal structure of the TiO_2 thin film. On the other hand HMFW decreased by increasing the substrate temperature and closed to the value of the as-deposited film prepared under 300 ºC. Thus the improvement of photocatalytic property under visible light was increased from 9.1% at 25 ºC to 25.7% at 300 ºC under the same N^+ irradiation ($2.5x10^{15}ions/cm^2$).

TF-TuP11 Study of Electronic Structure in In-Ga-ZnO Amorphous Semiconductor Films, ***Y. Li***, *Z. Liu, X. Hu, J. Ren*, Xi'an Jiaotong University, China

Amorphous oxide semiconductor In-Ga-ZnO (IGZO) has unique electron transport properties such as large electron mobility (10-30 cm^2/Vs) and good uniformity for active-matrix flat panel display applications [1-2]. Theoretical studies indicate the high electron mobility in amorphous IGZO is due to spherically spread orbitals of metal cations forming unaffected electron transport path. It has been proposed amorphous IGZO has strong ionic electronic structure compared to the covalent electronic structure in amorphous Si [3]. However, the transport mechanism to result in high electron mobility in amorphous structure has not been experimentally explained yet. The focus of this study is to use surface probe, optical as well as Raman spectroscopic techniques to investigate the electronic structure in IGZO. Amorphous IGZO thin films are being grown at room temperature by pulsed laser deposition. Initial Hall effect measurements indicate that amorphous IGZO films have electron concentration of 9×10^{19} cm^{-3} with Hall mobility of 16.8 cm^2/Vs. Raman spectroscopy is being used to analyze the lattice arrangement, i.e. the amorphous state and the bonding properties in IGZO films. During film processing, hydrogen is being introduced into the material system to modulate the defect state levels and band gap structure in IGZO. X-ray photoelectron spectroscopy is being used to obtain the valence band spectrum of IGZO films. The energy state within the band gap is being analyzed using deep level transient spectroscopy. The correlation of growth parameters on optical properties as well as electronic structure will be described in this work.

[1] K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, H. Hosono, Science 300,1269 (2003).

[2] K. Hoshino, J.F. Wager, IEEE Trans. Electron Devices 31,818 (2010).

[3] T. Kamiya, H. Hosono, NPG Asia Mater. 2, 15 (2010).

Thin Film Division
Room: 110 - Session TF1+EM-WeM

ALD/MLD: Hybrid Organic Films
Moderator: Q. Peng, Duke University

8:00am **TF1+EM-WeM1 Vapor-Phase Fabrication of Organic-Inorganic Hybrid Thin Films Using Molecular Layer Deposition with Atomic Layer Deposition**, ***M.M. Sung***, Hanyang University, Korea **INVITED**

We report a vapor phase deposition method of high quality organic thin films, called molecular layer deposition (MLD). MLD is a gas phase process analogous to ALD and also relies on sequential saturated surface reactions which result in the formation of a self-assembled monolayer in each sequence. In the MLD method, the high quality organic thin films can be quickly formed with monolayer precision under ALD conditions (temperature, pressure, etc). The MLD method can be combined with ALD to take advantages of the possibility of obtaining organic–inorganic hybrid thin films. The advantages of the MLD technique combined with ALD include accurate control of film thickness, large-scale uniformity, excellent conformality, good reproducibility, multilayer processing capability, sharp interfaces, and excellent film qualities at relatively low temperatures. Additionally, a vast library of materials is accessible by ALD methods, ranging from single elements to compound semiconductors to oxides, nitrides, and sulfides. Therefore, the MLD method with ALD is an ideal fabrication technique for various organic-inorganic nanohybrid superlattices.

8:40am **TF1+EM-WeM3 Metalcone and Metalcone/Metal Oxide Alloys Grown Using Atomic & Molecular Layer Deposition Techniques**, ***B.H. Lee***, *V.R. Anderson, S.M. George*, University of Colorado, Boulder

A new class of films known as the “metalcones” can be grown using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques. Metalcones are hybrid organic-inorganic materials derived from the sequential, self-limiting reactions of metal and organic alcohol precursors. The first metalcones were the “alucones” based on trimethylaluminum and ethylene glycol (EG) and the “zincones” based on diethylzinc and EG. Other metalcones can be fabricated with various properties using different metal precursors together with organic alcohols. This talk reports new metalcones known as the “zircones” using zirconium tert-butoxide (ZTB) and EG. In addition, this talk will discuss two new tunable ALD:MLD films based on alloys of alucone MLD/Al2O3 ALD and zircone MLD/ZrO2 ALD. Zircone MLD films were grown by using zirconium tert-butoxide (ZTB) and EG. MLD growth was observed at temperatures ranging from 105 to 195°C. *In situ* quartz crystal microbalance and *ex situ* X-ray reflectivity (XRR) experiments confirmed linear growth of zircone MLD versus number of ZTB/EG reaction cycles. Zircone MLD growth rates decreased versus temperature and varied from 1.6 Å per cycle at 105°C to 0.3 Å per cycle at 195°C. A constant density of ~2.3 g/cm3 was measured for all growth temperatures. XRR measurement also showed that zircone MLD films were very stable under ambient conditions. The metalcones will have useful mechanical, optical and electrical properties that can be tuned by growing alloys of the metalcones and their parent metal oxides. For example, this tuning allows the density of alucone MLD/Al2O3 ALD alloys to be varied from 1.6 g/cm3 to 3.0 g/cm3. The density of zircone MLD/ZrO2 ALD alloys could also be varied from 2.3 g/cm3 to 4.0 g/cm3. The reflective index of zircone MLD/ZrO2 MLD alloys was also tuned continuously between 1.63 and 1.86. These new metalcone materials provide a tool set for engineering the functional properties of thin films. These materials can be grown with atomic control of thickness and excellent conformality. The metalcones and metalcone alloys can also be thermally annealed to remove the organic constituent and create porous metal oxide films.

9:00am **TF1+EM-WeM4 Sequential Vapor Infiltration and Atomic Layer Deposition on Surfactant Films for Mesoporous Metal Oxide**, ***B. Gong***, *D. Kim, G.N. Parsons*, North Carolina State University

Mesoporous materials are critical for applications such as catalyst support, energy storage and conversion, and chemical separations. Conventionally, solution based approaches are employed for the preparation of these materials, and amphiphilic molecules are widely used as templates to form well defined pore size and surface area. In these methods, the interaction between the hydrophilic block of the surfactant molecules and the metal oxide precursors direct the self-assembly of ordered micelles/metal oxide hybrid materials, and porous inorganic structures were recovered after removal of the organic template. Recently, this selective interaction was also discovered during vapor phase sequential vapor infiltration and atomic layer deposition (ALD) of metal oxide onto polymers, where precursor infusion and reaction depends strongly on the interaction between the precursor and polymer starting substrate. We therefore believe that sequential vapor infiltration or ALD on amphiphilc surfactant molecule films could also yield ordered inorganic/organic hybrid materials and porous metal oxides.

In this work, mesoporous aluminum oxide and titanium oxide materials were prepared by the vapor phase infiltration and ALD on two kinds of surfactants: the ionic cetyltrimethylammonium bromide (CTAB) and poly ethylene oxide based nonionic surfactant F127 (PEO-PPO-PEO). The nitrogen adsorption and desorption measurement was employed to measure the specific surface area and the pore size distribution of the resulted material. In-situ FTIR was used to monitor the chemistry change during the vapor infiltration, SEM TEM and XRD were used to characterize the structure and the morphology of the porous material.

We find that both sequential vapor infiltration and ALD produced mesoporous materials. However, the vapor phase infiltrated films show a relative higher specific surface area and narrower pore size distribution. This can be explained by the more uniform distribution of metal oxide into the surfactant layer compared to ALD. These results demostrate a new vapor phase approach for well defined mesoporous materials, which would potentially important for many advanced applications.

9:20am **TF1+EM-WeM5 Flexibility and Water Vapor Transmission Rates for Al-, Hf-, and Zr-based ALD Films and Nanolaminates Utilizing Water and Glycerol Co-Reactants**, ***M.J. Sowa***, *E.W. Deguns*, Cambridge NanoTech, Inc.

Organic electronics constructed on flexible substrates stand to revolutionize the display and lighting markets due to the low potential cost of manufacturing inherent to roll-to-roll manufacturing. A significant downside to organic electronics is their sensitivity to atmospheric oxygen and moisture. Various encapsulation techniques have been demonstrated, some of which have achieved Water Vapor Transmission Rates (WVTR) better than 1e-6 g/m^2/d, which has been suggested to be the maximum allowable rate to give a minimum usable lifetime of 10,000 hours for Organic Light Emitting Diodes (OLEDs). However, most of the encapsulation technologies that provide these low WVTRs lack the flexibility of the underlying plastic substrate or the organic electronics, limiting the actual flexibility of the final product.

Here we will report on the flexibility of aluminum-, hafnium-, and zirconium-based ALD films deposited on representative substrate material samples of polyethylene napthalate(PEN) at 115°C. Metal precursors used were trimethyl aluminum(TMA), tetrakis(dimethylamino)hafnium(TDMAH), and tetrakis(dimethylamino)zirconium(TDMAZ). Water was used as the ALD co-reactant for producing inorganic films while glycerol was utilized as the co-reactant for depositing hybrid organic films. Various nanolaminate combinations of the inorganic/organic materials were also investigated for their response to various levels of strain. Inorganic Al_2O_3 films subjected to 2% strain were observed to begin cracking at thicknesses below 27nm. A 2% strain did not cause any cracking on organic films deposited with TMA and glycerol to the thickest film studied at 245nm. Organic films were always observed to be more flexible than inorganic films of the same thickness. Nanolaminates were observed to have flexibility intermediate to their pure inorganic and organic constituents.

WVTR measurements were performed on inorganic, organic, and nanolaminate aluminum films. A WVTR of 6.1e-6 g/m^2/day was obtained for a 100nm inorganic Al_2O_3 film. A substantially more flexible 100nm TMA + glycerol film gave a WVTR of 9.2e-6 g/m^2/day.

The technical issues associated with uniformly delivering glycerol to a 115°C ALD reactor will also be discussed.

9:40am **TF1+EM-WeM6 Polymer Wires Containing Quantum Dots with Different Lengths Grown by Molecular Layer Deposition: Potential Applications to Sensitization in Photovoltaics**, ***T. Yoshimura***, *R. Ebihara, A. Oshima*, Tokyo University of Technology, Japan

[Introduction] Molecular layer deposition (MLD) grows tailored polymer wires with designated molecular arrangements by connecting different kinds of molecules with monomolecular steps. We grew polymer wires with quantum dots (QDs), called as “polymer multiple quantum dot (polymer

MQD)," by MLD using three kinds of molecules, terephthalaldehyde (TPA), *p*-phenylenediamine (PPDA) and oxalic dihydrazide (ODH), and proposed their potential applications to sensitized photovoltaic devices.

[Polymer MQDs] As a preliminary work, polymer MQDs of OTPTPT, OTPT and OT were grown. In OTPTPT, molecules are connected in a sequence of -ODH-TPA-PPDA-TPA-PPDA-TPA-ODH---. The region between two ODHs is a QD of ~3-nm long. In OTPT, ~2-nm-long QDs are constructed with a molecular sequence of -ODH-TPA-PPDA-TPA-ODH---. In OT, ~0.8-nm-long QDs are constructed by connecting ODH and TPA alternately. A polymer MQD with three kinds of QDs, "3QD-MQD," in which OT-like QD [OT], OTPT-like QD [OTPT] and OTPTPT-like QD [OTPTPT] are formed in one polymer wire, was grown with a sequence of -ODH-TPA-ODH-TPA-PPDA-TPA-ODH-TPA-PPDA-TPA-PPDA-TPA-ODH---. For polymer MQD growth, we used the carrier-gas type MLD, where carrier gas of nitrogen was employed to give molecular gas blows onto substrates through valves for molecular gas switching.

[Light Absorption Spectra] Light absorption measurements revealed that the peak energy of the absorption spectra shifts toward the high energy side with decreasing the QD length, namely, in the order of OTPTPT, OTPT, and OT. This effect is attributed to the quantum confinement. The absorption spectrum of 3QD-MQD is broad extending from ~480 nm to ~300 nm, which is a superposition of the spectra of [OTPTPT], [OTPT], and [OT]. This result indicates that the polymer MQD with different QD lengths could be an efficient sensitizer. In addition, the molecular orbital calculation confirmed that the electron density is high in the QD regions of 3QD-MQD.

[Proposal of Polymer MQD Sensitization] In the polymer MQD sensitization, polymer MQD is on a ZnO surface as a sensitizer. QDs exhibit narrow absorption bands comparing with bulk semiconductors like Si due to their zero-dimensional characteristics. The absorption peak energy can be adjusted by QD lengths. Therefore, polymer MQD containing different-length QDs enables us to divide the wavelength region for light absorption into narrow regions. Each QD absorbs lights of wavelengths matched to its own energy gap, and injects the excited electrons into ZnO. This might suppress the energy loss arising from the heat generation in the light absorption process. The structure is regarded as a molecular tandem structure.

10:40am **TF1+EM-WeM9 Hybrid Materials by Vapor Phase Infiltration**, ***M. Knez***, Max-Planck-Institut für Mikrostrukturphysik, Germany **INVITED**

Atomic layer deposition (ALD) is a thin film deposition technique which was developed in the 1970s to meet the needs for processing thin film electroluminescent displays (TFEL). Technically and chemically it is similar to chemical vapor deposition (CVD). However, in contrast to CVD, ALD incorporates as a specific feature the separation of the chemical reaction into two half-reactions. The ALD is not only able to perform thin film coatings of inorganic materials, but also allows coatings with organic-inorganic hybrid materials and, due to the separated exposure of the substrate to the precursors, infiltration of soft matter.

This talk will show top-down approaches to hybrid organic-inorganic and bio-inorganic materials obtained by infiltration with metals from the vapor phase. With tiny amounts of metals infiltrated, biological materials, such as spider silk or collagen, can positively change their mechanical properties after being treated with pulsed vapors of metal-organic precursors. The improvement of mechanical properties is related to changes in the molecular structure of the protein-based materials. However, not only biopolymers undergo changes after infiltration. With the example of some synthetic polymers, analogous routes to modify their mechanical properties will be shown.

11:20am **TF1+EM-WeM11 Titanicone Molecular Layer Deposition Using $TiCl_4$ and Sugar Alcohols and Porous TiO_2 Films Produced by Annealing**, ***R.A. Hall***, *A.I. Abdulagatov, S.M. George*, University of Colorado, Boulder

Metalcone molecular layer deposition (MLD) can be performed using metal precursors and organic diols or triols. The first metalcone MLD films were the alucones and zincones grown using trimethylaluminum and diethylzinc, respectively, with ethylene glycol (EG). In this work, we report the growth of titanicone MLD films using $TiCl_4$ and two sugar alcohols: EG and glycerol (GL). The titanicones may have useful photocatalytic properties and may form valuable porous TiO_2 frameworks upon annealing to remove the organic constituent. Titanicone films were grown using $TiCl_4$ and EG at temperatures between 90-135°C. Quartz crystal microbalance (QCM) measurements observed a growth rate of ~83 ng/cm^2-cycle from 90 to 115°C before decreasing significantly at 135°C. X-ray reflectivity (XRR) studies obtained a growth rate of 4.5 Å/cycle with a density of 1.84 g/cm^3 at 115°C. Titanicone films were grown using $TiCl_4$ and GL at higher temperatures between 130-210°C. The GL is believed to lead to more cross-linking that stabilizes the MLD film. QCM measurements observed growth rates that varied slightly with temperature from 49 ng/cm^2-cycle at 130°C to 34 ng/cm^2-cycle at 210°C. XRR studies yielded a growth rate of 2.2 Å/cycle at 150°C. QCM measurements revealed that the surface chemistry for titanicone MLD was self-limiting. XRR studies indicated that the titanicone films were stable in air. The titanicone films were absorptive in the ultraviolet and consistent with an optical bandgap of ~3.5 eV. Annealing the titanicone films removed the carbon component and yielded porous TiO_2 films. Ultraviolet exposures also appear to be able to produce porous TiO_2 films. The ability to deposit conformal porous TiO_2 films on high surface area substrates could produce "super" high surface area substrates. These substrates may serve as TiO_2 scaffolds for dye-sensitized solar cells or photocatalytic membranes.

Energy Frontiers Focus Topic
Room: 103 - Session EN1+TF-WeA

Thin Film Chalcogenide Solar Cells (CIGS, CZTS, CdTe and Related Materials)
Moderator: L.W. Rieth, University of Utah

2:00pm **EN1+TF-WeA1 Comparative Study of Structure and Morphology of $CuIn_{1-x}Ga_XS_2$ and $CuIn_{1-x}Ga_XSe_2$ Thin Film Absorbers Using EBSD**, ***A. Kaul***, *E. Schneller, N.G. Dhere,* Florida Solar Energy Center, *H.R. Moutinho*, National Renewable Energy Laboratory

Electron backscatter diffraction (EBSD) in scanning electron microscopy (SEM) is a powerful technique that allows crystallographic information such as the grain orientation, grain boundaries and also the grain size to be obtained. Crystalline maps are formed in EBSD while the electron beam of a SEM scans the sample surface providing information about crystalline orientation of individual grains as well as features such as twin boundaries. This study relates to EBSD investigation of $CuIn_{1-x}Ga_XSe_2$ (CIGSe) and $CuIn_{1-x}Ga_XS_2$ (CIGS2) samples that were prepared by a two stage process which is easily scalable to large area manufacturing. Since sample polishing is very critical for generation of very good quality Kikuchi pattern formed by back scattered electrons, the earlier work was focused on optimizing the sample polishing technique. Efforts were also made to develop a database to facilitate proper indexing and corresponding accurate determination of preferred orientation of the pseudo-quaternary compound absorber films. Eventually, high quality Kikuchi patterns and EBSD maps have been obtained. It is essential for the research and development of the chalcopyrite thin film absorbers to elucidate the effect of variation of processing conditions (temperature, time and composition) on the growth and development of microstructure. Therefore, in the current work, CIGSe and CIGS2 absorber films were synthesized under different processing conditions and their EBSD maps and patterns are being compared in terms of grains size, grain orientation and grain boundaries as a necessary and vital step prior to undertaking the study of the still more complex compound $CuIn_{1-x}Ga_XSe_{2-y}Se_y$ (CIGSeS) being used in large-volume production of photovoltaic solar cells and modules.

2:20pm **EN1+TF-WeA2 Improving the Damp-Heat Stability of Copper Indium Gallium Diselenide Solar Cells**, ***B.S. Tosun***, University of Minnesota, *R.K. Feist,* The Dow Chemical Company, *S.A. Campbell, E.S. Aydil*, University of Minnesota

While copper indium gallium diselenide (CIGS) thin film solar cells with laboratory efficiencies exceeding 20 % have been reported, these high efficiencies may degrade with time as the devices are exposed to humid environments. It is well known that grain boundary diffusion of water through the ZnO to the CIGS-CdS interface is implicated in long-term degradation of the solar cell performance.[1] This penetration must be reduced or stopped to increase the solar cell lifetime. Herein, we show that amorphous tin dioxide (SnO_2) layers deposited by radio frequency (RF) magnetron sputtering on top of the completed CIGS solar cells can significantly increase the device lifetime by forming a barrier against water diffusion. Specifically, with approximately 0.2 micron and thicker SnO_2 layers deposited on top of the completed CIGS solar cells we have demonstrated that initially 11.1 % efficient CIGS solar cells lose less than 7 % of this peak efficiency and still exhibit efficiencies greater than 10 % (factor of 10%) after 150 hours at 85 ^oC and 85 % relative humidity. In comparison, under identical test conditions, the solar cells without the SnO_2 layer lost nearly 80 % of their initial efficiency within 24 hours after commencing the test. We studied the effects of deposition conditions and film thickness for different film structures on the solar cell stability in damp-heat tests. The deposited SnO_2 films tend to be amorphous when deposited at room temperature or when the films are thin, but show increased crystallinity for thicker films and films deposited at 150 ^oC. We found that solar cells coated with polymorphous SnO_2 films exhibit better damp-heat stability than those coated with polycrystalline films. By polymorphous we mean films that consist of nanocrystalline SnO_2 embedded in amorphous SnO_2. We attribute this difference to the lack of grain boundary diffusion in polymorphous SnO_2 films. Replacing the crystalline ZnO window layer with a SnO_2 film can provide further protection of the CIGS solar cells. We demonstrate a 8.2±0.2 % efficient CIGS solar cell with a SnO_2 window layer. Same solar cell fabrication process and CIGS film with ZnO window layer resulted in 8.2±0.6 % overall efficiency. The open circuit voltages of the two cells were the same indicating that the band alignment with the SnO_2 film is suitable for CIGS. These SnO_2 films were deposited using magnetron sputtering at 5 mTorr and 150-250 W RF power using Ar as the sputtering gas without substrate heating.

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[1]R. Feist et al, IEEE Photovoltaic Specialist Conference, 2009.

2:40pm **EN1+TF-WeA3 Progress Towards a High-Efficiency Cu-Zn-Sn-S-Se Thin-Film PV Technology**, ***D.B. Mitzi***, *O. Gunawan, T.K. Todorov, D.A.R. Barkhouse, S. Bag, R. Haight, T. Gokmen, T. Goislard de Monsabert, S.J. Chey, S. Thiruvengadam*, IBM T.J. Watson Research Center **INVITED**

A key criteria for achieving terawatt-compatible photovoltaic (PV) technology is the ability to fabricate high power conversion efficiency (>10%) solar cells using a low-cost process (< $1/watt) and readily available, abundant and preferably non-toxic materials. The kesterites, $Cu_2ZnSn(S,Se)_4$ (CZTSSe), are considered a promising PV technology for meeting this goal because of similar electronic properties to the two leading thin-film chalcogenide technologies, CdTe and $Cu(In,Ga)(S,Se)_2$ (CIGSSe), achieved while employing low-cost, readily-available constituents. This talk will discuss recent developments that have enabled the demonstration of the first CZTSSe solar cells with certified power conversion efficiencies of over 10%, using a glass/Mo/CZTSSe/CdS/i-ZnO/ITO structure and a simple liquid-based deposition approach. We also present a device characterization study that compares the CZTSSe devices with higher-performing CIGSSe analogs, elucidating some of the key performance bottlenecks in CZTSSe cells, including dominant buffer-absorber recombination, high series resistance and a relatively short minority carrier lifetime. These studies help to elucidate key areas for improvement for the CZTSSe cells in the effort to develop a high performance pervasive technology.

4:00pm **EN1+TF-WeA7 Solar Cells from Colloidal Dispersions of Cu2ZnSnS4 Nanocrystals**, ***A. Khare***, *Y. Li, B. Chernomordik, B.S. Tosun, A.W. Wills, D.J. Norris, E.S. Aydil*, University of Minnesota

Copper zinc tin sulfide (Cu_2ZnSnS_4 or CZTS) is emerging as a promising photovoltaic material for thin film solar cells. CZTS has a band gap of ~1.4 eV, the ideal value for converting the maximum amount of energy from the solar spectrum. In addition, CZTS has a high absorption coefficient (> 10^4 cm^{-1} in the visible region of the electromagnetic spectrum) and its constituent elements are all abundant in the earth's crust and are non-toxic. We have synthesized CZTS nanocrystals from metal dithiocarbamate complexes. The diameter of the nanocrystals can be varied from 2-7 nm by changing the temperature and synthesis time. A suite of methods including Raman spectroscopy, optical absorption, electron energy loss spectroscopy and X-ray diffraction were used to characterize these nanocrystals and show that they are phase-pure CZTS. Nanocrystals with diameters less than 3 nm exhibit quantum confinement. These quantum dots were used to assemble quantum dot solar cells. In a second approach to making solar cells, thin films of CZTS nanocrystals are annealed to form thin films with large grains. Nanocrystals melt at temperatures much less than the bulk temperature and recrystallize to yield larger CZTS grains. These films were then used for making conventional thin film solar cells.

4:20pm **EN1+TF-WeA8 Surface Structure of Pyrite Thin Films Grown by MOCVD**, ***M. Cheng***, *Y. Liu, N. Berry, A. Margarella, J.C. Hemminger, M. Law,* University of California, Irvine, *H. Bluhm, Z. Liu*, Lawrence Berkeley National Laboratory

Iron pyrite (FeS2) has been considered one of promising materials for use in solar cells due to its large absorption coefficient, suitable band gap and elemental abundance. In-lab X-ray photoelectron spectroscopy and tunable-energy synchrotron X-ray photoelectron spectroscopy were used to explore the surface structure of pyrite thin films grown by metal organic chemical vapor deposition (MOCVD). The influence of sodium diffusion on the growth of pyrite thin films on glass substrates was examined. By using synchrotron X-ray photoelectron spectroscopy, the different types of sulfur chemical states on the surface of pyrite thin films were resolved. The mechanism of pyrite oxidation after exposure to different oxidizing environments indicated that the surface monosulfide species were oxidized first. In addition, the band gap of pyrite thin films was determined by combining valence band spectroscopy with X-ray absorption spectroscopy compared to traditionally ultraviolet-visible absorption spectroscopy. The discrepancy between the two measurement techniques will be discussed.

4:40pm **EN1+TF-WeA9 Effect of the Use of a c-CdS Nanocrystalline Layer on the Photovoltaic Characteristics of the Screen Printed CdS/CdTe Heterostructure**, *L.G. Rangel-Chavez,* UAM-Azcapotzalco, Mexico, *M. Garcia-Aguirre, F.A. Cuevas-Ortiz,* Cinvestav-IPN, Mexico, *M.I. Neria-Gonzalez,* Instituto Tecnologico de Estudios Superiores de Ecatepec, Mexico, ***M.A. Melendez-Lira***, Cinvestav-IPN, Mexico

The fact that the efficiency for the CdS/CdTe system has remained without any change for several years until now requires employing new approaches in order to increase it. In this work it is reported the effect on the photovoltaic characteristics of the CdS/CdTe system by employing as source of the CdS the one obtained as a by-product from bio-remediation of heavy metals in residual waters. By using a novel sulfate-reducing bacterium (*Desulfovibrio alaskensis* 6SR) particles of the CdS semiconductor are obtained. Structural and optical characterization by XRD, UV-vis, Raman and photoluminescence spectroscopies shown that nanoparticles of cubic CdS are obtained. The nanoparticles of cubic CdS are deposited on CdTe films by screen printing and then subject to a mild thermal treatment. It is expected that the employment of CdS with cubic rather than hexagonal crystal structure will reduce the number of defects at the CdS/CdTe interface improving the transport of minority carriers through it. We will report the effects on the spectral response and filling factor obtained for the CdS/CdTe heterostructure by employing nanostructured cubic CdS as compared to those obtained employing hexagonal CdS.

*: Work partially supported by CONACyT-Mexico.

5:00pm **EN1+TF-WeA10 Surface Structure and Chemistry of $AgInSe_2$ Studied by Scanning Tunneling Microscopy**, ***P. Peña Martin***, *J.W. Lyding, A. Rockett*, University of Illinois at Urbana-Champaign

Chalcopyrite semiconductors such as $(Cu,Ag)(In,Ga)(S,Se)_2$ show great promise in thin film solar cells as they exhibit high optical absorption and excellent performance even as polycrystalline layers. The alloy $AgInSe_2$ (AIS) is a promising candidate for solar applications, as it has a nearly ideal energy gap (1.2 eV), high absorption coefficient, and shows sharper photoluminescence emissions than do the Cu-containing alloys. The surface of the material forms the heterojunction and determines many aspects of device performance. These semiconductors also contain a large number of intrinsic point defects, which are probably responsible for minority carrier recombination in the depletion region. Therefore understanding the surface and near surface nanostructure and nanochemistry are critical to device optimization. To characterize the structure and buried point defects near the surface, we used ultra high vacuum scanning tunneling microscopy (UHV-STM) to obtain atomic-scale topographic and electrical information.

We report the first atomically-resolved STM images and current-voltage profile measurements of AIS. Epitaxial layers were grown on epi-ready substrates of p-GaAs(111)A by hybrid technique, in which Ag and In are sputtered concurrently with effusion cell evaporation of Se. The resulting film was transported in a N_2 ambient to the STM laboratory, mounted under normal lab air as quickly as possible, and introduced to vacuum, with a total atmosphere exposure of about 20 minutes. The sample was degassed at ~100°C to drive off water and other contaminants. Electrochemically-etched W tips were used for scanning. The STM measurements were carried out in a home-built system with a base pressure of $1.2x10^{-8}$ Pa ($9x10^{-11}$ Torr). Topographic images reveal atomically-resolved regions on the surface with the periodicity expected for the polar metal-terminated [112] plane, 0.34 and 0.36 nm along rows oriented 60° from each other. This indicates that the surface does not reconstruct, unless by swapping one type of metal atom for another. Current-voltage spectra confirm that the material exhibits n-type behavior with an energy gap close to the bulk value of 1.2 eV. Some regions exhibit more fluctuations in the bandgap for a series of current spectra taken along a different line, indicating that there are variations in the electronic properties due to defects. We attempt to correlate these with topographic features in order to identify the defect responsible. Understanding and controlling these defects should lead to improved device performance, and some of the results may even carry over to CIGS devices.

5:20pm **EN1+TF-WeA11 Imaging and Phase Identification of Cu_2ZnSnS_4 Thin Films using Confocal Raman Spectroscopy**, *A.-J. Cheng,* ***M. Manno***, *A. Khare, C. Leighton, S.A. Campbell, E.S. Aydil*, University of Minnesota

Copper zinc tin sulfide (Cu_2ZnSnS_4 or CZTS) is a potential candidate for next generation thin film solar cells because it contains abundant and nontoxic elements and exhibits high light absorption. Thin films of CZTS are typically synthesized by sulfidizing a stack of zinc, copper and tin films. In addition to CZTS, a variety of binary and ternary metal sulfides can form and distinguishing among phases with similar crystal structure can be difficult. Herein, we show that confocal Raman spectroscopy and imaging can distinguish between CZTS and the other binary and ternary sulfides [1]. Specifically, Raman spectroscopy was used to detect and distinguish between CZTS (338 cm^{-1}), Cu_2SnS_3 (298 cm^{-1}) and Cu_4SnS_4 (318 cm^{-1}) phases through their characteristic scattering peaks. Confocal Raman spectroscopy was then used to image the distribution of coexisting phases and is demonstrated to be a useful tool for examining the heterogeneity of CZTS films. We show that, during sulfidation of a zinc/copper/tin film stack, ternary sulfides of copper and tin, such as Cu_2SnS_3 form first and are then converted to CZTS. The reason for formation of Cu_2SnS_3 as an intermediary to CZTS is the strong tendency of copper and tin to form intermetallic alloys upon evaporation. These alloys sulfidize and form copper tin sulfides first, and then eventually convert to CZTS in the presence of zinc. As a consequence, films sulfidized for 8 hours at 400 °C contain both CZTS and Cu_2SnS_3 while films sulfidized at 500 °C contain nearly phase-pure CZTS. In addition, using Cu *Ka* radiation, we identify three CZTS X-ray diffraction peaks at 37.1° [(202)], 38° [(211)] and 44.9° [(105) and (213)], which are absent in ZnS and very weak in Cu_2SnS_3.

[1] A.-J. Cheng, M. Manno, A. Khare, C. Leighton, S. A. Campbell, and E. S. Aydil, J. Vac . Sci. Technol. A, *in press* (2011).

5:40pm **EN1+TF-WeA12 Synthesis of CZTS Solar Cells using Non-Toxic Sulfur Precursor**, ***P. Vasekar***, *L. Ganta, D. Vanhart, T. Dhakal, C.R. Westgate*, The State University of New York at Binghamton

Thin film solar cells based on $Cu(In,Ga)(S,Se)_2$ and CdTe have demonstrated significant improvement in last few years and they are also being transferred to production level. However, both CIGS and CdTe based thin film solar cells are hindered by potential environmental hazard issues and scarcity issues associated with the constituent elements , mainly Te, In, Ga and to some extent Se. Recent research trends are moving towards finding alternatives based on earth-abundant and non-toxic elements. An alternative material $Cu(Zn,Sn)(S,Se)_2$ is being explored these days by the thin film photovoltaics community which contains earth abundant materials like Zn and Sn. CZTS structure can be derived from $CuInS_2$ chalcopyrite structure by replacing one half of the constituent indium atoms by zinc and other half by tin. The resulting bandgap varies in the range of 0.8 eV for a selenide structure to 1.5 eV for a sulfide structure. Copper and sulfur in earth's crust are 50 and 260 ppm respectively and while abundance of zinc and tin is 75 and 2.2 ppm in respectively. As compared to this, indium in earth's crust is 0.049 ppm and selenium 0.05 ppm. CZTS also has a large absorption coefficient in the order of 10^4 cm^{-1}. There are vacuum-based as well as non-vacuum based approaches for the synthesis of CZTS solar cells. Among vacuum based approaches, generally sulfurization in H_2S atmosphere is carried out on sputtered CuZnSn precursors. However, there are toxicity issues involved with the use of H_2S gas. We subscribe to the philosophy of sticking to a non-toxic approach of synthesizing thin film solar cells and for the first ever time introduced a non-toxic sulfur precursor called di-tertiray-butyl-disulfide (TBDS) for the sulfurization of CZT layer. Initial results are quite encouraging and device quality CZTS cells are already being synthesized. The CZTS cells are characterized using materials characterization techniques such as SEM, XRD, XPS and photovoltaic parameters are being extracted under AM 1.5 conditions and also analyzed using quantum efficiency measurement. This is the very first attempt to successfully synthesize CZTS solar cells using a non-toxic sulfur source.

Energy Frontiers Focus Topic
Room: 106 - Session EN2+TF-WeA

Thin Films for Solar Fuels
Moderator: A.J. Muscat, University of Arizona

4:00pm **EN2+TF-WeA7 N-doped $SrTiO_3$(100) Epitaxial Films for Fundamental Studies of Visible Light Active Photocatalysts**, ***T. Luttrell***, *M. Batzill*, University of South Florida

N-doping of photocatalysts, in particular TiO_2, has been extensively studied for its ability to increase visible light activity. However, the solubility of N in TiO_2 is limited to ~ 2% and thus limits the visible light absorption. One reason for the low solubility of nitrogen is the different preferred charge state of nitrogen (3-) compared to the substituted oxygen (2-) anions. Here, we investigate the less studied perovskite $SrTiO_3$, which has similar photocatalytic activity to TiO_2. Because a wide range of oxides crystallize in the perovskite structure, we anticipate that charge compensating co-doping in N:$SrTiO_3$ can be more easily accomplished than in TiO_2. Such co-doping may result in a higher achievable N-concentration. In our studies, the stability of N-doping in $SrTiO_3$ and the effect of co-doping have been investigated in thin films. High quality pure and N-doped epitaxial films of $SrTiO_3$ have been grown on $LaAlO_3$(100) substrates by pulsed laser deposition (PLD). The structural and electronic properties have been investigated, by x-ray and UV photoemission spectroscopy (XPS and UPS) and ex-situ atomic force microscopy (AFM). N-doping was accomplished by deposition in an ammonia atmosphere. N^{3-} ions are substituting for O^{2-}

ions in the $SrTiO_3$ matrix and thus cause a charge imbalance that is compensated for in pure films by formation of oxygen vacancies. To avoid this defect formation, substitution of the quadrivalent cations in $SrTiO_3$ by co-doping with La^{5+} is investigated. La co-doping allows a higher nitrogen solubility in $SrTiO_3$. Nitrogen doping causes a band gap narrowing due to formation of filled N-2p states at the top of the valence band and thus an increase in visible light adsorption. The UV and visible light photocatalytic activity is assessed by decomposition of methyl orange.

4:20pm **EN2+TF-WeA8 Photoelectrochemical Water Splitting by Hematite Nanostructures Prepared by Chemical Bath Deposition**, ***R. Morrish***, Colorado School of Mines, *M. Rahman, J.M.D. MacElroy,* University College Dublin, *C.A. Wolden*, Colorado School of Mines

Hematite (a-Fe_2O_3) is a promising material for sustainable generation of H_2 due to its low cost, widespread availability, chemical stability, and ability to absorb a significant fraction of visible light. However numerous challenges remain in order for this material to approach its theoretical potential of 15% solar to hydrogen efficiency. Nanorod geometries are an ideal configuration for this material, decoupling the different length scales required for photon absorption and efficient carrier transport. Unfortunately such structures have historically yielded poor photoelectrochemical performance (<5 mA/cm^2).[1] We recently demonstrated that nanorods synthesized by chemical bath deposition (CBD) could be activated through the use of appropriate annealing treatments.[2] Photocurrents >500 mA/cm^2 were achieved at 1.23 V versus RHE, and the photoanodes displayed low onset potentials. These changes were correlated with significant amount of tin diffusion from the underlying FTO substrate into the Fe_2O_3 matrix occurs during high temperature annealing process. The benefits of this process may include enhanced conductivity as well as improvement of the FTO/ Fe_2O_3 interface. Despite these advancements, significant room remains for further improvement. In this paper we describe a number of strategies to reach this goal. First, the nanostructure of the hematite can be further improved. This is explored by varying the CBD chemistry, optimizing the post-deposition annealing conditions, and through subtractive processing. A second issue is electron transport at the hematite/FTO interface, and this is explored through the use of novel treatments of the FTO prior to deposition. Finally, the addition of an electrocatalyst can further reduce the onset potential. Each of these three strategies has demonstrated enhanced photocurrent over our previous results. We plan to integrate these advancements in order to maximize performance. Detailed characterization of the structure, composition, and electrochemical changes observed with these processes will be used to provide fundamental insight into the mechanisms underlying the improvements.

References

[1] N. Beermann, L. Vayssieres, S.-E. Lindquist & A. Hagfeldt, "Photoelectrochemical Studies of Oriented Nanorod Thin Films of Hematite", 2456-2461, (2000).

[2] R. Morrish, M. Rahman, J. M. D. MacElroy & C. A. Wolden, "Activation of hematite nanorod arrays for photoelectrochemical water splitting", 474-479, (2011).

4:40pm **EN2+TF-WeA9 Nanostructured Thin Films for Solar Water Splitting**, ***K. Sivula***, Ecole Polytechnique Federale de Lausanne, Switzerland **INVITED**

Solar energy can be converted to chemical energy stored in hydrogen through water splitting using a photoelectrochemical device. However, decades of research have failed to identify one semiconducting electrode material that can perform the water splitting reaction with adequate efficiency, stability and material cost. Here I present a system that overcomes the limitations of conventional materials to afford direct solar hydrogen production by taking inspiration from natural photosynthesis and using two photosystems in tandem. In addition, to reach the terawatt energy scale needed to have a global impact, I describe the use of abundant and inexpensive semiconducting materials. Specifically, progress developing hematite (Fe_2O_3) photoanodes and cuprous oxide (Cu_2O) photocathodes will be presented. I will show that our water splitting tandem cell, using these materials and inexpensive processing techniques, is capable of solar-to-hydrogen conversion efficiencies of over 5 % at standard conditions. I will further detail how the progress in developing the electrode thin films has been enabled by exploiting recently developed techniques like aerosol–assisted chemical vapor deposition and atomic layer deposition.

5:20pm **EN2+TF-WeA11 TiO_2 N-doped Nanofibers Deposited by Electrospinning for Photocatalytic Applications**, *D. Di Camillo, F. Ruggieri,* ***L. Lozzi****, S. Santucci*, University of L'Aquila, Italy

Titanium dioxide (TiO_2), thanks to its interesting properties as nontoxicity, low cost and high chemical stability, has been extensively investigated for several application in which, following light absorption, the generated charges can be usefully applied, as for photovoltaic applications or for photocatalytic devices. However, due to the wide intrinsic energy gap of TiO_2 (between 3.0 and 3.2 eV, depending on the crystalline structure), only a small fraction of the solar spectrum can be used to promote the light absorption [6]. In the photocatalytic devices one of the most important goal of the recent research is to be able to prepare photocatalyst which can be active by absorbing the visible light, in order to increase the application of TiO_2-based system in poor regions (where it could be difficult to use UV light sources) or to reduce the application cost . In order to increase the fraction of the solar spectrum that can be absorbed, different approaches have been used, mainly by doping TiO_2 with metals or anions.

One of the most studied doping is using nitrogen. TiO_2 doped with nitrogen atoms can be prepared in different ways, as powders, as thin films by sol-gel or reactive sputtering.

In this paper we will show the photocatalytic results obtained depositing TiO_2 N-doped nanofibers (NF) prepared by means of electrospinning (ES) and near-field electrospinning (NF-ES) techniques for the photo-degradation of methylene blue (MB) in water under visible light. The ES preparation technique allows a quick deposition of fibers on wide surfaces using a cost-effective system. Instead NF-ES method allows the growth of a well ordered NF net, with a spacing lower then few microns.

The NFs were deposited using different deposition and post-deposition parameters (solution composition, annealing temperature and atmosphere) and have been characterized by using X-ray photoemission spectroscopy (XPS), X-ray diffraction (XRD) and Secondary Electron Microscopy (SEM). The photocatalytic properties have been studied recording the variation of the optical absorption of MB when the sample is illuminated by an halogen lamp (visible spectrum).

The annealing process determines a partial loss of nitrogen and the formation of the Anatase crystalline phase. The TiO_2 N-doped NFs have shown interesting degradation properties, which are much better than those observed when TiO_2 NFs are used.

5:40pm **EN2+TF-WeA12 Fabrication of Palladium Nanoscale Structures for Hydrogen Sensing Applications**, *D. Rodríguez-Vindas,* University of Puerto Rico at Río Piedras, *C. Ortiz, V. Pantojas,* University of Puerto Rico at Cayey, ***W. Otaño***, University of Puerto Rico at Cayey and Institute for Functional Nanomaterials

Palladium (Pd) metal is one of the most prominent materials studied for the detection of hydrogen gas. Hydrogen rapidly dissociates on its surface and diffuses into subsurface layers forming palladium hydride with consequent changes in optical, mechanical and electrical properties that are easily detected. Materials with nanoscale morphologies are promising to improve sensor performance as they provide large surface areas for adsorption, and smaller crystallite size reducing the time needed for “bulk” diffusion. The amount of sites available for hydrogen adsorption per Pd atom is also higher in the surface and subsurface layers resulting in higher sensitivity. In this project, Pd nanoribbons and nanoshells are prepared by magnetron sputtering deposition on top of the mat of polymer fibers, which act as a template that shapes the morphology of the palladium being deposited while providing support to the metallic scaffold that is created. Sputtering is a line-of-sight deposition process and the fibers become a variable angle-substrate for the incoming Pd flux. A larger amount of palladium is deposited on top of the fiber where the incoming flux is perpendicular to the surface compared to the sides where the flux is incident at a glancing angle. The top and sides of the fibers shadow their bottom parts closer to the substrate preventing any substantial deposition there. The end result of the deposition is the formation of Pd nanostructures, thicker in the middle region than at the edges, with a large void network. Process parameters such as deposition time, sputtering pressure, and power can be used to produce nanoshells with different thickness and crystallinity. The high sensitivity and response time shown to 1% or less of hydrogen in nitrogen is understood to result from the reduced dimensions combined with this unique nanostructure. A description will be given of the conductance changes with hydrogen concentration as result of the competing mechanisms of percolation and scattering. This work shows the use of nanotechnology combined with unique processing approaches to produce new sensor geometries with different behavior and morphology than simple thin film or wire approaches.

Thin Film Division
Room: 109 - Session TF1+EM-WeA

Nonvolatile Memory
Moderator: T. Karabacak, University of Arkansas at Little Rock

2:00pm **TF1+EM-WeA1 Application of Amorphous Zinc Tin Oxide for Memristor Devices**, ***G.S. Herman****, J.S. Rajachidambaram, S. Murali, J. Conley,* Oregon State University*, S.P. Sanghavi, P. Nachimuthu, V. Shutthanandan, T. Varga, S. Thevuthasan*, Pacific Northwest National Laboratory

Amorphous zinc tin oxide semiconductor materials have been studied primarily as the active semiconducting material for thin film transistors with applications including transparent and flexible electronics. Due to the amorphous nature of these materials excellent uniformity can be obtained over a large area, while still having reasonably high electron mobilities (>10 cm^2/Vs). Furthermore, considerable control over the electrical properties can be maintained, where insulating, semiconducting, and conductive properties can be obtained by varying the processing conditions. We have recently used sputter-deposited zinc tin oxide as a bipolar switching element in memristor devices. Memristors are a two-terminal nonvolatile data memory device that is very promising for the replacement of silicon-based Flash. A significant benefit is that memristors can be manufactured with high areal densities with potentially low manufacturing costs. A variety of oxide-based materials are being evaluated for memristors, however many of these are nanocrystalline which can lead to non-uniformity of devices. We have found that the switching properties of zinc tin oxide are closely related to the process conditions, the electrical test conditions, and the electrode materials. In this presentation we will discuss the physical and electrical characterization of the zinc tin oxide films and the switching mechanisms for these materials.

2:20pm **TF1+EM-WeA2 PE-MOCVD of GeTe Materials for Phase Change Memory Applications**, ***E. Despiau-Pujo****, L. Dussault, C. Vallée,* LTM/CNRS-UJF, France*, E. Gourvest,* ST Microelectronics, France*, D. Jourde, S. Maitrejean, P. Michallon*, CEA Leti Minatec Campus, France

Phase-Change Random Access Memories (PCRAM) are very promising candidates for next generation of non-volatile memories. Those devices store information using the high electrical contrast between the amorphous and crystalline phases of chalcogenide alloys such as $Ge_2Sb_2Te_5$ (also called GST) which are mainly deposited by physical vapor deposition (PVD) [1]. However, two important drawbacks have to be overcome: a too short archival life for GST at high operating temperatures and a too high power consumption. The binary compound GeTe seems to be a promising candidate for high temperature applications since it has an estimated archival life up to ten years at 110°C. A pronounced increase in thermal stability of N- and C-doped GeTe was also demonstrated [2].

Concerning the power consumption, it was shown that a way to reduce the high operating currents is to confine the material. In this way, several groups try to develop a new deposition process to achieve the gap filling of the confined structure. Atomic Layer Deposition (ALD) of GST has shown very good step coverage but the deposition rate remains very low. Therefore, we proposed to study the deposition of GeTe in a shower-head type 200mm plasma-enhanced pulsed liquid injection CVD reactor (AltaCVD200). Ge and Te liquid precursors are introduced into the deposition chamber as vapours through a pulsed injection system and an evaporating furnace. A capacitively-coupled RF plasma is applied between the shower head and the substrate heater to decompose the precursors. Chamber walls are maintained at 70°C to avoid condensation of precursors vapours. The deposition chamber is mounted on a cluster tool which allows quasi *in situ* analysis of the deposited films by angle-resolved XPS while the plasma is analyzed by optical emission spectroscopy (OES).

In this paper, we investigate the optical emission spectra of high pressure (2-20 Torr) Ge- and Te-containing plasmas. Reference UV-visible emission spectra (200-800 nm) are recorded for various conditions of RF power, pressure, and flow rate. The role of electrons and H atoms in the decomposition of Ge and Te precursors is discussed by correlating the OES of the plasma with the chemico-physical properties of the deposited material. It is shown that H atoms induce a competitive effect between deposition (due to the decomposition of the precursors) and etching of Ge and Te atoms at the growing film surface. Role of C contamination in the phase change properties is also discussed and phase transitions of plasma deposited GeTe-C materials are compared with sputtered GeTe-C.

[1] G. W. Burr et al, J. Vac. Soc. Technol. B 2010, 28 (223)

[2] A. Fantini et al, IEDM 2010

2:40pm **TF1+EM-WeA3 Embedded HfO_2 based 1T1R Cells for Future RRAM Applications**, ***Ch. Wenger****, T. Bertaud, Ch. Walczyk, D. Walczyk, M. Malgorzata*, IHP, Germany **INVITED**

The integration of various functionality to (Bi)CMOS circuits is in the focus of the "More than Moore" approach. Here, we demonstrate the incorporation of nonvolatile memories (NVM) into the Back end of line (BEOL) of Bi(CMOS) circuits. The added functionalities open new technological possibilities for high value microelectronics systems.

Embedded nonvolatile memories (NVM) with high-density, high-speed, and low-power are attractive for a growing number of applications. One promising candidate for next-generation nonvolatile memories is based on the electrically switchable resistance change between a high (OFF-state) and a low (ON-state) resistive state of a metal-insulator-metal (MIM) structure. This approach is often termed resistance random access memory (RRAM) technologies. Due to the cost effectivity and BEOL compatibility with (Bi)CMOS technologies, this approach is highly attractive. By combining the MIM devices (R) with selection transistors (T), the 1T-1R cells offer good scalability, long retention time, and rapid read/write times. In this letter, the reliable bipolar resistive switching of $TiN/HfO_2/Ti/TiN$ devices embedded into 1T-1R cells is demonstrated.

The current-voltage (I-V) characteristics of the $TiN/HfO_2/Ti/TiN$ diodes and 1T-1R cells were studied by DC voltage sweep measurements. By applying a positive voltage at the top electrode, the resistance is reduced for $V > V_{Set}$. The device can be switched back into the OFF-state when a negative voltage is applied beyond V_{Reset}. In case of the 1T-1R cell, the forming and set processes can be controlled by changing the gate voltage (V_G) of the select transistor.

4:00pm **TF1+EM-WeA7 Synthesis and Characterization of Multiferroic Oxides by Radical Enhanced Atomic Layer Deposition**, ***C.D. Pham****, J.H. Choi, J.P. Chang*, University of California Los Angeles

Multiferroic materials exhibit two or more forms of ferroic order such as (anti)ferroelectricity, (anti)ferromagnetism, ferroelasticity, or ferrotoroidicity. Materials containing both ferroelectricity and ferromagnetism will exhibit some amount of magnetoelectric coupling which is a desirable aspect for the future of non-volatile memory, as these materials could potentially be used for devices that will be written magnetically and read electronically or vice versa, as well as the prospect of four-state memory devices. Materials which exhibit magnetoelectric coupling have been well studied, however, the synthesis methods may not easily translate into large scale integration.

One possible route for synthesis on a commercial scale, atomic layer deposition (ALD) is a thin-film processing technique which involves alternatively flowing non-self reacting precursor vapors or gases onto a substrate. As a result of the self limiting reaction, the precursors only form a single monolayer per cycle. The sequential and self-limiting nature of the deposition is used to deposit thin films with good compositional control, high conformity, high uniformity, and excellent thickness control.

To create multiferroic crystal structures, a 1:1 stoichiometric ratio between cations is desired with low contamination by organic ligands in order to form the crystal phases that permit multiferroicity. Therefore, in this work, multiferroic $YMnO_3$ and $BiFeO_3$ on various substrates are synthesized by radical enhanced atomic layer deposition (RE-ALD) using $Y(tmhd)_3$ (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), $Mn(tmhd)_3$, $Fe(tmhd)_3$, and $Bi(tmhd)_3$ as metal precursors and oxygen radicals as the oxidizer. By varying the cycle sequences, controlled composition is demonstrated and verified through XPS. Growth rates are shown on a thickness per cycle basis as a function of deposition temperature, precursor pulse times, and substrate. The crystal structure as well as atomic environment are examined by XRD and extended x-ray absorption fine structure spectroscopy (EXAFS) respectively and are accompanied by TEM micrographs. Finally, magnetic measurements made by a super conducting quantum interference device (SQUID) magnetometer, zero-field cooled and field cooled (ZFC-FC) M vs. T and M vs. H, are shown on 1:1 $YMnO_3$ stoichiometric films showing a Néel temperature T_N = ~45 K and a coercive magnetic field H_C = 130 Oe for Si(111) and H_C = 300 Oe for YSZ(111).

4:20pm **TF1+EM-WeA8 Perpendicular Magnetic Tunnel Junctions based on Thin CoFeB Free Layer and Co-based Multilayer SAF Pinned Layers**, ***A. Natarajarathinam****, S. Gupta*, University of Alabama

We have previously reported on fully perpendicular Co/Pd multilayers (ML)-based CoFeB/MgO/CoFeB magnetic tunnel junctions (MTJ's)1, 2. However, Co/Pd ML-based MTJ's have rarely exhibited TMR ratios greater than about 10%. This has been attributed to the inability to pull a sufficiently thick CoFeB layer perpendicular on top of MgO, as well as the incomplete bcc templating of CoFeB from MgO owing to the adjacent fcc Co/Pd ML's3. Recent results3-7 have generated great interest in MTJ's with pinned perpendicular synthetic antiferromagnets (SAF), of the form AP1/Ru/AP2 where AP1 and AP2 are Co-based multilayers, for instance,

Co/Ni or Co/Pd. We report on fully perpendicular MTJ's with a thin CoFeB free layer and a Co/Pd(Pt) ML-based SAF pinned layer. For Co/Pd ML SAF's, strong antiferromagnetic coupling was seen at tRu of 1.1nm, with a coupling strength of 0.017 mJ/m2. For Co/Pt ML SAF's the optimum antiferromagnetic coupling was found at slightly higher Ru thickness of 1.3 nm, with a coupling strength of 0.013 mJ/m2. Improved MTJ properties are expected from using a thin Ta-seeded CoFeB bottom free layer, along with a thin, amorphous Ta layer used to transition from bcc CoFeB to fcc Co/Pd(Pt) for the top pinned layer6. The full stack is of the form: bottom lead/Ta (2)/CoFeB(1)/MgO(1.6)/CoFeB(0.8)/Ta(0.3)/[{Co(0.3/Pd(1)}5/Co(0.3) or {Co(0.5)/(Pt(2)}5/Co(0.5)/Ru1.1 or 1.3/[Co(0.3/Pd(1) or Co(0.5)/(Pt(2)]9/top lead. CIPT measurements indicated TMR values as high as 20% for as-deposited stacks. Magnetometry of blanket stacks showed a large separation in the switching fields of free and pinned layers, with free layer switching close to zero field and pinned layer switching at 0.8-1.8 kOe (Fig.1). This symmetric extended plateau of constant magnetization offers a large dynamic range over which the magnetic configuration remains stable7. The stacks were patterned into MTJ's, annealed at 240◦ C in an in-plane field of 0.5 T, and characterized magnetically and electrically.

Acknowledgements:

This work is partially supported by a U.S. Department of Defense DARPA-MTO STT-RAM Universal Memory contract, and Grandis Technology, Milpitas. Dr. David Abraham of IBM is gratefully acknowledged for CIPT measurements.

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4:40pm **TF1+EM-WeA9 Characterizing the Effects of Processing on Materials for Phase Change and Spin Torque based Non-Volatile Memory Technologies***, **E.A. Joseph**, R.M. Martin, J.S. Washington, D.W. Abraham, S. Raoux, J.L. Jordan-Sweet,* IBM T.J. Watson Res. Ctr.*, D. Miller,* IBM Almaden Res. Ctr.*, H.-Y. Cheng,* Macronix International Co., Ltd, Taiwan, R.O.C.*, M.C. Gaidis, M. Gajek, M. Breitwisch,* IBM T.J. Watson Res. Ctr.*, S.-C. Lai,* Macronix International Co., Ltd, Taiwan, R.O.C.*, Y. Zhu, R. Dasaka, R. Sawant, D. Neumayer,* IBM T.J. Watson Res. Ctr.*, R.M. Shelby,* IBM Almaden Res. Ctr.*, H.-L. Lung,* Macronix International Co., Ltd, Taiwan, R.O.C.*, C.H. Lam, N.C.M. Fuller*, IBM T.J. Watson Res. Ctr. **INVITED**

Phase change memory (PCM) and spin-torque magnetic random access memory (ST-MRAM) have recently garnered significant interest for future non-volatile memory applications due to their promise for scalability beyond that of conventional DRAM and flash memory technologies. In addition, both PCM and ST-MRAM have potential to enable improvements in programming speed, low voltage operation and high endurance, as compared to current devices. However, the introduction of each technology not only brings with it new device challenges, but the fabrication process itself can also alter the properties of the materials, leading to performance degradation. In this work, we explore the effects of integration and processing on $Ge_2Sb_2Te_5$ (GST) and CoFeB for PCM and ST-MRAM devices respectively, with relevance towards scaling to the 14nm node and beyond. Using multiple analysis techniques including time resolved laser reflectivity and X-ray diffraction, we determine that exposure to various etch and ash plasma chemistries can cause a significant reduction in the (re)crystallization speed of GST, while concurrently increasing the transition temperature from the rocksalt to the hexagonal phase. Furthermore, by utilizing optical emission spectroscopy, X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) we are able to link the changes in crystallization to etch-induced modification of the GST stoichiometry. For CoFeB materials, vibrating sample magnetometry is used to determine the effect that plasma exposure (as used for both patterning and encapsulation) has on the magnetic moment. We find that even when relatively thick capping layers are present, magnetic moment can still be significantly degraded. The severity of this effect is heavily dependent on plasma chemistry. Further results of process-induced material modification and device degradation as a function of etch, encapsulation, and thermal processing will be presented, focusing primarily on the impact on scaling of these technologies. Finally, potential integration and processing solutions to circumvent these issues will also be discussed.

Thin Film Division
Room: 110 - Session TF2+EM-WeA

Nanostructuring Thin Films
Moderator: A.V. Melechko, North Carolina State University

2:00pm **TF2+EM-WeA1 Templated Solid-State Dewetting for Patterning of Films***, **C.V. Thompson**, J. Ye, A.L. Giermann*, Massachusetts Institute of Technology **INVITED**

Most crystalline thin films are metastable in the as-deposited state, and will dewet to form islands when they are heated to temperatures that lead to sufficiently high atomic mobilities. This can happen well below the melting temperature of the film, so that the material remains in the form of a crystalline solid throughout the dewetting process. When unpatterned films dewet on flat substrates, the resulting islands have widely varying sizes and spacings. However, we have shown that substrate patterning can be used to control the solid-state dewetting process and to produce ordered arrays of monodispersed and crystallographically aligned islands from polycrystalline films. Recent experiments on patterned single-crystal films have allowed independent study of the various mechanisms that control structure evolution during solid-state dewetting. These include fingering instabilities, edge faceting, corner instabilities, pinch-off processes, and Rayleigh-like instabilities. Surface energy anisotropy plays a very important role in these processes, and for single-crystal films, leads to the formation of crystallographically aligned complex patterns of lines and islands that can be reproducibly controlled through pre-patterning.

2:40pm **TF2+EM-WeA3 Dynamics of Solid Thin-Film Dewetting in the Silicon-On-Insulator System***, **E. Bussmann**, F. Cheynis, F. Leroy, P. Müller*, CINaM-CNRS, France

Thin-film dewetting is a process wherein a film on a substrate spontaneously agglomerates into 3D islands, which in some instances are ordered. A detailed understanding of the mechanism and dynamics of dewetting is crucial, either to avoid the agglomeration, or to engineer organized arrays of nanostructures. Silicon-on-Insulator (SOI) films, which are promising substrates for microelectronics, undergo dewetting when annealed at >700°C under ultrahigh vacuum conditions. The Si film spontaneously transforms into an assembly of ordered nano-sized Si islands. Previous *ex-situ* studies of dewetted SOI films provided a qualitative description of the dewetting process [1-4]. However, the dewetting dynamics, as well as the thermodynamic driving forces and atomistic mechanisms at work, remained largely unclear. We simultaneously measure the real-time dewetting dynamics and the motion of surface atomic-steps (surface self-diffusion) using low-energy electron microscopy (LEEM) [5]. We observe the following scenario: (i) dewetting voids nucleate at defects in the Si(001) layer. In the early stages of dewetting, the area of the opening voids grows linearly with time, and the Si ejected from the voids accrues into a rim surrounding the dewetted area. (ii) As dewetting progresses, the rim undergoes an instability that leads to the formation of elongated Si fingers. Once the first fingers have formed, the void area grows as the square of time. (iii) Finally, the Si fingers undergo a Plateau-Rayleigh instability, breaking apart into 3D Si nano-islands. We compare our measurements of the morphological evolution of dewetting to a simple analytical model for dewetting void growth (based on surface diffusion, nucleation on the top of the 3D structures, and mass-conservation), and to Kinetic Monte Carlo simulations. The KMC simulations reproduce the qualitative features of the complex void shape evolution in detail, while the analytical model of void growth allows us to connect the void growth rate with the dewetting driving force. These approaches unambiguously show that the SOI dewetting process is surface-diffusion-limited and driven by surface and interface free-energy-minimization.

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3:00pm **TF2+EM-WeA4 Self and Directed Assembly of Thin Metallic Films by Pulsed Laser Induced Dewetting**, ***Y. Wu***, University of Tennessee, *J.D. Fowlkes,* Oak Ridge National Laboratory, *L. Kondic,* New Jersey Institute of Technology, *J. Diez,* Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Argentina, *N.A. Roberts, P.D. Rack*, University of Tennessee

The synthesis and assembly of functional metallic nanomaterials is critical for realizing many important applications of nanoscience and nanotechnology, and metallic thin film dewetting has been an effective and low-cost approach to this end. In this study, we investigated dewetting of metal thin films via pulsed nanosecond laser melting. We also explore the dewetting and nanopattern formation of nanolithographically pre-patterned thin films of various shapes to understand initial and boundary conditions in guiding the assembly. More recently, nanolithography was used to impose the perturbation which ultimately led to an organized nanoparticle array. Specifically, liquid–phase pulsed laser induced dewetting (PLiD) was used to transform metallic thin film strips into nanoparticle arrays. We demonstrated that the assembly accuracy and precision could be drastically improved by merely imposing a synthetic sinusoidal perturbation onto the lateral surfaces of the thin film strip. The synthetic perturbations in the strip translated into an unstable varicose oscillation on the rivulet during retraction – a precise nanoparticle diameter and pitch emerged thereby superseding the otherwise naturally evolving modes predicted by the modified Rayleigh-Plateau instability. A nanoscale, synthetic perturbation was usefully imposed to "nudge" the natural, self–assembly dispersion toward significantly higher order.

4:00pm **TF2+EM-WeA7 Directed Self-Assembly of Ge Heteroepitaxial Quantum Dots with sub-35nm Spacing**, ***C. Petz***, University of Virginia, *D. Yang, J. Levy,* University of Pittsburgh, *J.A. Floro*, University of Virginia

Artificially ordered Ge quantum dot (QD) arrays, where confined carriers can interact via spin coupling, may create unique functionalities such as spintronic bandgap systems. Development of such arrays for quantum computing requires fine control over QD size and spatial arrangement on the sub-35 nm length scale. We employ fine-probe electron-beam irradiation to locally decompose ambient hydrocarbons onto a bare Si (001) surface. These carbonaceous patterns are annealed in UHV, forming ordered arrays of nanoscale SiC precipitates that serve as templates for subsequent Ge quantum dot nucleation via strain-induced self-assembly during heteroepitaxy. The nanoprecipitates effectively reduce the critical thickness for Ge QD formation to below the 3-4 monolayers typical of Stranski-Krastanov growth in the Ge/Si (001) system. Thus, Ge QDs in the SiC-patterned regions nucleate prior to formation of randomly located QDs in the unpatterned areas. It is critically important to ascertain the variability in Ge QD size and placement, and ultimately to determine the crystalline quality and interface properties of these ultrasmall Ge dots on SiC nanoprecipitates. Using atomic force microscopy and cross-sectional transmission electron microscopy, we investigate the patterned surface morphology and internal structure of patterned QDs to develop a fundamental understanding of the Ge adatom behavior in the vicinity of local high lattice-mismatch nanoprecipitates. We find that Ge self-assembly at SiC sites depends on QD spacing and that the QD size is surface diffusion limited, suggesting that local alteration of the intermediate Si surface may repel Ge to higher lattice mismatched SiC sites. Support from the DOE Office of Basic Energy Sciences is gratefully acknowledged under grant number: DE-FG02-07ER46421.

4:20pm **TF2+EM-WeA8 Surface Functionalization of Zeolites and Nanoparticles: Understanding and Applying Plasma Modification Strategies for Unusually Shaped Particles**, ***J.C. Shearer***, *E.R. Fisher*, Colorado State University

Unusually shaped micron- and nanometer-sized particles are becoming key components in catalytic and biological applications. Zeolite particles are typically modified for ion-exchange and catalytic applications. Fe_2O_3 nanoparticles are widely used in biological applications such as MRI imaging and site-specific drug delivery, thereby creating a need for surface functionalization techniques to ensure biocompatibility. Plasma processing can effectively modify and implant functional groups onto flat substrates, and is non-directional. Thus, the primary focus here is on applying these plasma processes to unusually shaped materials and understanding the gas-phase chemistry and surface reactions that make these coatings viable. Previous work in our lab employed plasma-enhanced chemical vapor deposition to create composite SiO_2/TiO_2 nanoparticles. Here, we use plasma processing methods for the modification of zeolite surfaces and functionalization of Fe_2O_3 nanoparticles. Compositional and morphological data demonstrate that the conformal treatment of particles was achieved and that the use of PECVD methods allowed for advanced control over surface modification and specific tailoring of the structure, composition, and growth characteristics of any deposited film. Insight into the modification and deposition process is provided by actinometric optical emission spectroscopy (AOES) and laser induced fluorescence spectroscopy (LIF), which allow characterization of the gas-phase species and their energetics (i.e. internal energies) for each system. To further investigate the functionalization of nanoparticle surfaces, additional studies explore the contributions of gas-phase OH radicals to the creation of SiO_2/Fe_2O_3 composite nanoparticles. Scatter coefficients and gas-phase density measurements derived from our imaging of radicals interacting with surfaces technique (IRIS) provides additional insight on the molecular-level chemistry occurring at the interface between gaseous plasma species and nanoparticle substrates. The operation and design of an in-house rotating drum reactor will be discussed as a potential method for adapting the composite nanoparticle fabrication to an industrial scale.

4:40pm **TF2+EM-WeA9 Role of Ion Flux on Alignment of Carbon Nanofibers Synthesized by DC Plasma on Transparent Insulating Substrates**, ***R.C. Pearce***, North Carolina State University, *A.W. Vasenkov,* CFD Research Corporation, *D.K. Hensley, M.L. Simpson, T.E. McKnight,* Oak Ridge National Laboratory, *A.V. Melechko*, North Carolina State University

A key factor to the implementation of vertically aligned carbon nanofibers (VACNFs) in devices is a more fundamental understanding of how to control fluctuations in the growth direction of the fibers. It has previously been hypothesized that the electric field is the primary factor in determining the orientation of fibers grown catalytically using plasma enhanced chemical vapor deposition (PECVD). Here we present results of carbon nanofiber synthesis on insulating substrates by dc plasma in the vicinity of grid electrodes. To perform these observations, VACNFS were synthesized on a fused silica substrate using direct current PECVD. To maintain continuous glow discharge above the substrate, a metal grid electrode layer (Cr) was deposited over silica with windows of exposed silica ranging in size from 200 µm to 1 mm. Observed trends in nanofiber alignment at the window-electrode interface suggests that the alignment is governed by the direction of the ion flux rather than the electric field at the substrate level. The proposed alignment mechanism is that ion sputtering of the carbon film on a catalyst particle the growth direction of the nanofibers. With this development, fiber growth direction can be better manipulated through changes in ionic flux direction, opening the possibility for growth of nanofibers on substrates with unique geometries.

5:00pm **TF2+EM-WeA10 High-Performance Poly-3-alkylthiophene-Carbon Nanotube Composites for Transparent Electrodes**, ***S.L. Hellstrom***, *R.Z. Jin, R.M. Stoltenberg, Z. Bao*, Stanford University

Flexible transparent electrodes are crucial for flat panel display and solar cell technologies. While carbon nanotube network electrodes show promise, their fabrication often involves insulating surfactants which worsen conductivity. As an alternative, we show that small amounts of conjugated semiconducting polymer added to nanotube dispersions enables straightforward solution deposition of uniform electrodes by spin-coating or drop casting. After doping, electrodes as good as 120 ohm/sq with 81% transmittance at 550 nm are obtained. Tuning system chemistry and deposition parameters allows control of tube bundle size, density, and alignment, and these may be correlated with electrode performance.

We also employ the selectivity of P3HT:CNT composites in wetting of and adhesion to different dielectric surfaces, to simultaneously fabricate and pattern organic electrodes with unprecedented nanotube density gradients and excellent feature resolution. We employ these to drive pentacene and C_{60} transistors that are competitive with those made using Au electrodes. We thereby suggest that this material system and fabrication technique has promise in applications requiring flexible, semitransparent, low-cost complementary circuits.

5:20pm **TF2+EM-WeA11 SiGe Nanomembranes: Defect-Free Single-Crystalline Growth Substrates for High- Quality Strained Epitaxial Materials**, ***D.M. Paskiewicz***, *B. Tanto, D.E. Savage, M.G. Lagally*, University of Wisconsin Madison

Silicon-Germanium semiconductor alloys are important in improving Group IV opto- and microelectronics. Typically, SiGe is used as a stressor to introduce strain into Si, thereby altering the electronic band structure [1, 2] or changing optical properties [3]. The SiGe stressor can be incorporated locally to strain small areas of Si uniaxially [2], or relaxed SiGe can be used as a substrate for growth of biaxially strained Si over large areas [1]. We will focus on the latter: using relaxed SiGe to induce global biaxial strain in Si. Conventional methods for creating relaxed SiGe substrates involve epitaxial growth on Si substrates and relaxation of the alloy *via* dislocations. The density of defects that reach the top relaxed SiGe layer can be limited though various techniques [4], but strain inhomogeneities and surface roughness created by the dislocations remain. We demonstrate the fabrication of SiGe nanomembranes (NM): fully *elastically* relaxed,

smooth, single-crystalline sheets of SiGe alloy. A thin SiGe layer (less than the kinetic critical thickness for dislocation formation) is grown on a silicon-on-insulator (SOI) substrate with molecular beam epitaxy (MBE), followed by a Si capping layer of similar thickness to the Si template layer of the SOI. The SiO_2 layer of the SOI is selectively etched away, leaving the Si/SiGe/Si trilayer heterostructure free to strain share [5]. The Si layers of the trilayer are then selectively etched away, leaving a fully elastically relaxed SiGe NM. These SiGe NMs can be transferred to new handling substrates, bonded, and used as templates for growth of new defect-free materials.

A specific application involving strained Si/relaxed SiGe heterostructures is fabrication of 2-dimensional electron gas devices (2DEGs) that can be patterned and gated to confine individual electrons into quantum qubits with long spin coherence times [6]. These devices are very sensitive to changes in the electrostatic potential and thus require superb material quality. We compare the material quality of strained Si/SiGe heterostructures grown on SiGe NMs with those created on SiGe substrates relaxed *via* dislocations.

Research supported by DOE. Facilities support from NSF-MRSEC is acknowledged. DMP is supported by a NSF Graduate Research Fellowship.

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5:40pm **TF2+EM-WeA12 Multilayer Barrier Coatings for Organic Photovoltaics**, ***A.M. Coclite***, *K.K. Gleason*, Massachusetts Institute of Technology

Barrier coatings, which prevent the permeation of water into OPV devices fabricated on flexible plastic substrates, are essential to extend the device lifetime. Such protective coatings are made of multilayer stacks where multiple dense, inorganic layers are alternated with soft, organic ones. The inorganic layer contains inevitably some pinholes and defects. The roles of the organic layer are (i) creating a tortuous and longer path among the defects of two successive inorganic layers (ii) filling the pores of the inorganic underlayer limiting the propagation of defects from one inorganic layer to the other and (iii) smoothening the substrate surface roughness.

In the past, we obtained good barrier properties (WVTR= 10^{-2} $g/cm^2/day$) with a hexalayer obtained by coupling initiated CVD (iCVD) and plasma enhanced CVD (PECVD). iCVD layers resulted in effective defect decoupling and good planarization of the substrate.[1]

Now a similar approach is investigated for the multilayer deposition in a large-area reactor (0.16 m^3), maintaining the same organosilicon precursor and the same reactor configuration for both deposition of silica-like and organosilicon layers.

SiO_x layers were deposited through PECVD in MW plasma at high power and high oxygen dilution. The silanol and organic groups were not detectable by IR spectroscopy, resulting in denser film if compared with the previous results.

A new process was used for the formation of organosilicon polymers with enhanced monomer structure retention compared to a conventional plasma deposition and faster deposition rate if compared to conventional iCVD processes from organosilicon monomer. We demonstrate that the monomer molecule remains substantially preserved in fact the C/Si ratio calculated from XPS data on the polymer was 4.3, close to the 3.7 C/Si elemental ratio of the monomer molecule.

The deposition of smoothening organic layers is demonstrated by depositing the coating on the top of a microsphere (1 µm in diameter) monolayer deposited over silicon wafers. Increasing the thickness of the coating, the degree of planarization (DP), both local (DLP) and global (DGP), increases. The DLP increases much faster than the DGP: when the coating is 1µm-thick the DLP is already 99%, for the global planarization instead a 1.8µm-thick-coating is needed to reach DGP= 99%.

The high density of the inorganic layer, the smoothness and planarization properties of the organic one make this approach particularly promising for the deposition of effective multilayer barrier coatings.

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Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-ThM

Spectroscopic Ellipsometry of Biological Materials and Organic Films

Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands, K.G. Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **EL+AS+EM+MS+PS+TF-ThM1 Application of Various Spectroscopic Ellipsometry Techniques for In Situ Studies of Thin Polymer Films on Solid Substrates**, ***K.-J. Eichhorn***, Leibniz-Institut für Polymerforschung Dresden e.V., Germany **INVITED**

Thin films of functional polymers are not only widely integrated into modern micro- and nanoelectronic devices, but also used to modify solid surfaces for biosensor, biomedical and antifouling applications.

Therefore, in the first part I will report on improved temperature-dependent spectroscopic Vis-ellipsometry experiments to study confinement effects on the polymer dynamics in thin films to address a question which is controversially discussed in the polymer physics community for a long time past: Is there really a significant change of the glass transition temperature Tg of polymers when confined in nanoscopic films (studied here down to about 10 nm thickness)? We compared well-known linear polystyrenes of different molecular weights /1/ and hyperbranched polyesters having different architectures and functional groups /2/. Films of different thickness were prepared by spin-coating on silicon wafers, carefully equilibrated and measured in dependence on temperature (up to 250°C) in an inert gas atmosphere. The Tg data were determined from the ellipsometric results and discussed.

In the second part, “smart” surfaces will be presented which can be used for controlled adsorption and release of biomolecules. For that, different types of stimuli-responsive polymer brushes were prepared on solid substrates by a “grafting-to” procedure. The brush properties (e.g. swelling/collapsing) as well as the resulting adsorption/desorption of model proteins (e.g. Human Serum Albumin, Chymotrypsin) can be switched in an appropriate aqueous medium with temperature (PNIPAAM) and/or pH (PAA-P2VP). The corresponding processes at the solid-liquid interface were studied in-situ by spectroscopic Vis- and IR-ellipsometry /3,4/.

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8:40am **EL+AS+EM+MS+PS+TF-ThM3 Hard Matter Meets Thin Polymer Films-Spectroscopic Ellipsometry as a Versatile Tool to Investigate Properties of Responsive Poly(N-isopropylacrylamide) Systems with Incorporated Magnetic Nanoparticles**, ***S. Rauch***, Leibniz-Institut für Polymerforschung Dresden e. V., Germany

Responsive polymer systems designed by using polymer brushes or hydrogels are interesting systems, which can exhibit reversible or irreversible changes in their physical and structural properties to special environmental conditions (e.g. temperature or magnetic fields). The temperature responsive poly(*N*-isopropylacrylamide) (PNiPAAm) is one of such polymers. It undergoes a phase transition in aqueous solution at its lower critical solution temperature (LCST) of 32 °C which induces an increase in hydrophobicity. Combined with the properties of magnetic nanoparticles (NP) (e.g. Fe_3O_4 or $CoFe_2O_4$) these systems can lead to new surface functionalities with new interesting properties for many applications, as sensing, wettability or (bio)adhesion.

For the design of such thin film systems a basic knowledge of the film characteristics is essential. Therefore it is first necessary to know how much nanoparticles are inside or attached to the system. By using spectroscopic Vis-Ellipsometry (SE) it is not only possible to investigate optical properties of these films but also the composition of it, e.g. volume fraction of Fe_3O_4-NP.

We studied two types of films and present results for a thin NP-composite film prepared by pre-mixing of the PNiPAAm with hydrophobic Fe_3O_4-NP, spin-coated and grafted to a silicon substrate (System 1) and a film prepared by adsorption of hydrophilic functionalized Fe_3O_4-NP onto PNiPAAm brushes (System 2). The former system was chosen to develop an optical model starting from a simple two component effective-medium-approach (Maxwell-Garnett-EMA) using the optical constants of the pure polymer measured by SE and of Fe_3O_4 with averaged data taken from three different publications. The SE best fit-results were validated against scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

After transferring this optical model to System 2, the adsorption of hydrophilic functionalized Fe_3O_4-NP onto PNiPAAm brushes was investigated and will be discussed with additional results obtained from contact angle (CA) and phase transition (LCST) measurements.

9:00am **EL+AS+EM+MS+PS+TF-ThM4 The White Scarab Beetle *Cyphochilus insulanus* –Scattering and Polarization Properties**, ***C. Akerlind***, Swedish Defence Research Agency / Linköping University, Sweden, *H. Arwin*, Linköping University, Sweden, *T. Hallberg, H. Kariis,* Swedish Defence Research Agency, Sweden, *J. Landin, K. Järrendahl*, Linköping University, Sweden

Three methods were used to characterize the optical properties of the light scattering white scarab beetle *Cyphochilus insulanus*. Spectral directional hemispherical (DH) reflectance measurements in the wavelength region 250 nm to 25 µm were performed using integrating spheres. The general spectral appearance shows a relatively strong reflectance band in the range 400 - 1600 nm. The Bidirectional Reflection Distribution Function (BRDF) was measured over a semi-circle in the plane of incidence at the wavelengths 633 nm and 3.39 µm, using s- and p-polarized light. In the visible the BRDF data shows a near Lambertian behaviour with a constant BRDF for most angles, *i.e.* the light is diffusely scattered. For large incident angles and in the infrared the BRDF is more specular. Full Mueller-matrix spectroscopic ellipsometry (MMSE) measurements were performed in the wavelength range 250 - 1000 nm at angles of incidence between 45° and 75° using a dual rotating compensator ellipsometer. The Mueller data show that the reflected light in general has a high degree of polarization *P* even for nonpolarized incident light. The angular dependence of *P* was pronounced for incident p-polarized light and was very low near the Brewster angle. In comparison, *P* was high for all measured angles for incident s-polarized light. Close to the Brewster angle, the reflected light showed a high ellipticity for incident p-polarized light. The optical data is used to model the structure and optical response of the beetle cuticle. With input from the DH and BRDF-data analysis of the Mueller Matrix data was made using Fresnel-based layer modelling. 2-, 3- and n-phase models are compared. The obtained optical properties are also used to calculate color data in terms of chromaticity and whiteness. The scattering properties of the *Cyphochilus insulanus* cuticle are also discussed by combining the BRDF and MMSE data as well as recently obtained Mueller matrix imaging polarimetry results.

9:20am **EL+AS+EM+MS+PS+TF-ThM5 Real-time Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation Characterization of Biomolecule Adsorption within Sculptured Thin Films**, *T. Kasputis, D. Schmidt,* ***K.B. Rodenhausen***, *H. Wang, A.K. Pannier, M. Schubert*, University of Nebraska - Lincoln

Recent improvements in nanofabrication strategies have led to the development of precisely crafted nanostructures with intricate features. Incorporating biomolecules such as proteins, DNA, drugs, and even whole cells could allow for functionalization of nanostructured surfaces for biological applications including biosensing, tissue engineering scaffolds, and drug and gene delivery. Along with the nanofabrication of biological devices, there is a need to develop instrumentation capable of probing and characterizing the dynamic evolution of these bio-functionalized interfaces. Spectroscopic ellipsometry combined with quartz crystal microbalance with dissipation (SE/QCM-D) is a non-destructive optical/mechanical characterization technique that reveals dynamic properties, including average film thickness (with sub-angstrom resolution), adsorbed mass, and porosity.

Nanostructures in the form of sculptured thin films (STF) were fabricated by glancing angle deposition via electron beam evaporation of titanium onto gold-coated quartz sensors. The sensors were then mounted within an SE/QCM-D liquid cell, and proteins of varying sizes were deposited and characterized, *in-situ*. Protein adsorption was detected shortly after introducing the protein solutions by SE and QCM-D as a change in the optical response and decrease of vibration frequency, respectively. QCM-D reported greater adsorbed mass for larger proteins (fibronectin) than smaller

proteins (bovine serum albumin). The adsorbed mass of proteins within the nanostructured scaffold exceeded that of proteins on flat surfaces, confirming that the STFs are capable of trapping proteins. Analysis of the anisotropic optical response from the nanostructures, which is very sensitive to environmental changes, adds complementary information on protein adsorption; the optical quantification is in agreement with QCM-D results. In addition, the adsorption of other biomolecules, such as cells and DNA complexes, has also been accomplished. The use of combinatorial SE/QCM-D to characterize and monitor the attachment of biomolecules on complex nanotopographies will improve the design and fabrication strategies for a wide array of biotechnological devices.

9:40am **EL+AS+EM+MS+PS+TF-ThM6 Characterization of Multilayer Organic Thin Film for Use as an Aptamer Biosensor with Hybrid Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation**, ***J.Y. Gerasimov***, *K.B. Rodenhausen, H. Wang, R.Y. Lai, M. Schubert*, University of Nebraska - Lincoln

DNA aptamer molecules passivated by alkanethiols can be used for biological detection and screening. Through the use of spectroscopic ellipsometry (SE, optical) and quartz crystal microbalance with dissipation (QCM-D, mechanical) techniques, selective binding of analytes to chemisorbed aptamer probes can be observed *in-situ*. The system analyzed consists of a gold-coated quartz substrate, a multilayer organic thin film (containing aptamer probe, alkanethiol, and single-stranded DNA analyte), and physiological buffer solution. The attachment and detachment of material, the hybridization efficiency of the aptamer probes, and changes in the porosity of the multilayer organic thin film were all determined by SE/QCM-D.

In this contribution, we present the real-time SE/QCM-D characterization of (a) the formation of the aptamer probe layer, (b) the subsequent chemisorption of alkanethiol, and (c) the interrogation of single-stranded DNA that is non-complementary or complementary to the sequence found on the aptamer probe. The aptamer DNA sequence encodes codon 12 of the *K-ras* gene; mutations of this gene are frequently found among pancreatic cancer patients. We found that introduction of either complementary or non-complementary DNA caused increases of the multilayer organic thin film thickness. However, our SE/QCM-D analysis showed that the porosity of the multilayer organic thin film responded differently depending on the compatibility of the DNA analyte. The SE/QCM-D technique provides evidence for different surface attachment mechanisms and can be useful in characterizing biological interfaces.

10:40am **EL+AS+EM+MS+PS+TF-ThM9 Contamination Processes of EUV Optics Characterized by Spectroscopic Ellipsometry**, ***L.J. Richter***, *C. Tarrio, S. Grantham, S.B. Hill, T.B. Lucatorto,* National Institute of Standards and Technology*, N.S. Faradzhev*, University of Virginia

Extreme ultraviolet (EUV) lithography using 13.5 nm light is emerging as a viable tool for semiconductor fabrication at design rules below 32 nm. Tool performance critically depends on limiting and mitigating degradation of the EUV optical elements. A primary degradation mechanism is the EUV induced deposition of carbon from ambient species originating from outgassing of the unbaked vacuum system and/or outgassing from the EUV irradiation of the resist. Using the high brightness of the Synchrotron Ultraviolet Radiation Facility (SURF-III) at NIST both fundamental studies of EUV induced contamination and practical (“witness plate”) studies of resist out gassing are performed. Typical deposits are hydrogenated amorphous carbon features with peak thicknesses of about 1 nm and nominal lateral extent of 1 mm. Both ex-situ, small spot mapping spectroscopic ellipsometry (SE) and in situ single-wavelength imaging nulling-ellipsometry are used for rapid, sensitive, contamination metrology. Fundamental studies of contamination by admitted gases indicate that the process is a complex function of both gas pressure and photon dose. Correlations between SE and XPS are suggestive that, at high EUV fluxes, densification can occur resulting in spatial variation in the deposit dielectric function. The use of principal component analysis of the SE images to highlight the spatial diversity will be discussed.

11:00am **EL+AS+EM+MS+PS+TF-ThM10 Characterization of Organic Solar Cells Materials and Structures by Spectroscopic Ellipsometry**, *J.P. Piel,* ***L. Kitzinger***, *A. Bondaz, C. Defranoux*, SEMILAB-SOPRALAB, France

Spectroscopic Ellipsometry (S.E) is a well known optical technique widely used for the characterisation of all types of thin films for determination of film thickness and optical indices on glass or plastic substrates.

S.E. is also being applied to the characterization of materials and multilayer structures of organic materials like organic light-emitting diodes (OLEDs) or Organic Solar Cells.

We present the determination of the refractive indices of organic Solar Cells materials like P3HT, PCBM, Pentacene, Perylene, and their blends. Complex organic materials can be analyzed accurately and fully characterized from their absorption bands in the visible and UV range (190nm to 900nm).

Transmission and absorption can be also measured at the same time and be used to determine the optical properties of these materials.

Using these refractive indices, analysis of real multi-layer stacks can be done. The refractive indices can be used afterwards to automatically optimise and balance the energy flow dissipation Q inside an organic solar cell composed of a thin film stack. We present an example performed on a single cell and on a tandem bi-layer cell structure.

Since these materials are sensitive to moisture and pollution, it can be necessary to measure their optical properties and thickness values through an encapsulated media. We will demonstrate how we can measure single layer properties and multi-layer stacks, through encapsulated samples, from the back side of the substrate. This technique can be applied to test structure or real Organic Solar Cell monitoring. Backside measurement combined with a water vapour cell used for ellipsometry porosimetry is used to test the efficiency of the thin film encapsulation.

We also present the characterization of ITO and ZnO transparent electrodes by S.E. and how near infra-red ellipsometry is used to determine the ITO resistance, without contact, by using the Drude behaviour on encapsulated samples.

Electronic Materials and Processing Division
Room: 210 - Session EM+TF-ThM

Hybrid Electronic Materials and Interfaces
Moderator: A.J. Muscat, University of Arizona

8:00am **EM+TF-ThM1 Chemical Modification of Surfaces for Biological Applications**, ***W.G. McGimpsey***, Kent State University **INVITED**

The chemical and physical characteristics of surfaces can have profound and useful effects on the behavior of biological systems. We describe here several methods for modifying the surfaces of a variety of biocompatible materials, including metals, glass and polymers, in order to produce desired chemical and physical properties. The effects of surface chemistry and surface morphology on the growth and proliferation of mammalian cells as well as bacteria are also reported. Applications investigated include control of the growth of microbial biofilms, the growth of three-dimensional tissue assemblies, the patterned growth of neurons and other cell types and the functionality of primary neurons deposited on surfaces.

8:40am **EM+TF-ThM3 Modification of Oxide-Free Silicon Surfaces with Phosphonic Acid Self-Assembled Monolayers**, ***P. Thissen***, *T. Peixoto, A. Vega, Y.J. Chabal*, University of Texas at Dallas

Phosphonic acid self-assembled monolayers (SAMs) are being considered as versatile surface modification agents due to their ability to attach to surfaces in different configurations, including mono-, bi- or even tri-dentate arrangements. Different chemical strategies for grafting SAMs on oxide-free silicon have been developed. Recently, a novel method for preparing OH-terminated, on otherwise oxide-free silicon has been reported [1] and further expanded for this work. This atomically flat surface contains precisely 1/3 OH and 2/3 H termination groups.

Using this model surface, we demonstrate that the phosphonic group of organic molecules can be chemically grafted to the OH group on the surface using a single chemical step, leaving the Si-H termination unaffected, without oxidation of the Si surface. We also show that the nature of solvents is important as they can act as a catalyst. The perfection of the surface (that remains atomically flat throughout the modification) makes it possible to use first principles DFT-based calculations to model the IR and XPS data obtained for this surface. Thus, a detailed structure for the SAMs can be derived on an atomic level. It is found that phosphonic acids are chemically attached to the Si(111) surface as mono-dentate via Si-O-P bond upon reaction with the OH groups. The remaining groups of P=O and P-OH are further oriented by forming a 2D network of hydrogen bonds.

[1] D. J. Michalak, S. R. Amy, D. Aureau, M. Dai, A. Esteve and Y. J. Chabal, Nanopatterning Si(111) surfaces as a selective surface-chemistry route, NATURE MATERIALS, Vol. 9, March 2010

9:00am **EM+TF-ThM4 Competing Effects of Interfacial Organic Layers on the Nucleation of Inorganic Thin Films Deposited Via Atomic Layer Deposition**, *K.J. Hughes,* ***J.R. Engstrom***, Cornell University

Over the past several years a number of groups have been investigating the use of interfacial organic layers (IOLs) in the form of self-assembled monolayers (SAMs) and/or surface grown or bound oligomers to promote the subsequent growth of inorganic thin films. Work in our group has initially focused on determining the relative importance of the type, density and dimensionality of the organic functional groups present in IOLs on the subsequent growth of the thin film, particularly via ALD[1]. Here we shall report on two perhaps less well-studied aspects concerning the use of SAMs or IOLs to promote nucleation and growth via ALD: (*i*) the effects of the underlying substrate on the IOL, and its ability to promote growth; and (*ii*) given the same IOL|substrate combination, the effects on ALD for a series of inorganic thin film deposition processes. To examine these systems we have made use of a variety of experimental tools, including a conventional viscous flow ALD tool, and also an ultrahigh vacuum (UHV) molecular beam based ALD process, where we employ *in situ* x-ray photoelectron spectroscopy. Concerning the first of these, we have examined the effect of a thin (< 10 Å) organic layer, poly(ethylene-imine) (PEI) on the ALD growth of TaN_x, where the underlying substrate is a chemically oxidized SiO_2 thin film, or a porous SiO_2 based low-κ dielectric thin film. Here we observe essentially the same result from conventional viscous flow, and molecular beam UHV ALD: PEI acts to attenuate TaN_x ALD on SiO_2, while it enhances growth on a low-κ dielectric thin film. From a practical point of view, most importantly, we find that PEI stops infiltration/penetration of the TaN_x ALD thin film into the porous low-κ dielectric. Concerning the second major issue, we have examined the effect of PEI on the subsequent growth via ALD of a series of inorganic thin films, namely: Al_2O_3, HfO_2, Ta_2O_5, and TaN_x. Here PEI has the effect of attenuating growth to different degrees depending on the subsequently grown ALD thin film, leading to no attenuation of growth for Al_2O_3, but significant incubation periods, in increasing order, for Ta_2O_5, HfO_2 and TaN_x. The length of the incubation time is found to correlate with both the total enthalpy change of the overall ALD reaction, as well as the net internal energy change of a single ligand exchange reaction representative of the second half of the ALD reaction, suggesting that these factors associated with the ALD process play a key role in determining the length of the incubation period caused by PEI.

[1] K. J. Hughes and J. R. Engstrom, J. Vac. Sci. Technol. A **28**, 1033-1059 (2010)

9:20am **EM+TF-ThM5 Towards Molecular Electronics: Solution-Based Methods for Selective Deposition of Metals and Semiconductors**, *Z. Shi, J. Yang, P. Lu,* ***A.V. Walker***, University of Texas at Dallas

Robust methods for the chemically selective deposition of metals, semiconductors, biomolecules and other substances are developed and applied in the construction of complex two- and three-dimensional structures. This work has important applications in molecular and organic electronics, sensing, biotechnology and photonics. These methods are easily parallelized, afford precise nanoscale placement and are compatible with photolithography. Two examples are discussed in detail: the chemical bath deposition (CBD) of CdSe on functionalized self-assembled monolayers (SAMs), and the electroless deposition of Ni nanowires on micron-scale patterned surfaces.

CBD is a solution-based method for the controlled deposition of semiconductors. The formation of CdSe nanocrystals are of particular interest for a wide range of applications because their photoluminescence spans visible wavelengths. Using CdSe chemical bath deposition (CBD) we demonstrate the selective growth and deposition of monodisperse nanoparticles on functionalized self-assembled monolayers (SAMs). On –COOH terminated SAMs strongly adherent CdSe nanoparticles form via a mixed ion-by-ion and cluster-by-cluster mechanism. Initially, Cd^{2+} ions form complexes with the terminal carboxylate groups. The Cd^{2+}-carboxylate complexes then act as the nucleation sites for the ion-by-ion growth of CdSe. After a sufficient concentration of Se^{2-} has formed in solution via the hydrolysis of selenosulfate ions, the deposition mechanism switches to cluster-by-cluster deposition. On –OH and $–CH_3$ terminated SAMs monodisperse CdSe nanoparticles are deposited via cluster-by-cluster deposition and they do not strongly to the surface. Thus under the appropriate experimental conditions CdSe nanoparticles can be selectively deposited onto -COOH terminated SAMs. We illustrate this by selectively depositing CdSe on a patterned -COOH/$-CH_3$ terminated SAM surface.

Our approach for the construction of Ni nanowires begins with a single SAM layer deposited and UV-photopatterned using standard techniques. We exploit the different deposition rates of nickel electroless deposition on $–CH_3$ and –OH terminated SAMs to deposit nanowires. The deposited nanowires are long (centimeters) and uniform in diameter, and can be patterned in arbitrary shapes. SAMs are ideal for the construction of nano- and micro- structures since their surface chemistry can be easily tuned to form the needed structures. Further the micron-scale UV photopatterning of SAMs does not require a clean room or expensive lithography equipment.

9:40am **EM+TF-ThM6 Sensing Mechanism for Peroxide and Hydroperoxide Vapors in Phthalocyanine Thin Film Transistors**, ***J. Royer****, E. Kappe, W. Trogler, A.C. Kummel*, University of California San Diego

Organic thin-film transistors (OTFTs) are promising candidates for selective chemical sensors due to numerous chemical and electrical parameters which govern sensor response. Analyte selectivity can be obtained using multiparameter electrical monitoring of a single OTFT which is sensitive to changes in mobility, I_{on}/I_{off} ratio, and/or threshold voltage. The present study demonstrates selective hydrogen peroxide and organic peroxide sensors based on irreversible metal-phthalocyanine (MPc) OTFT threshold voltage shifts. The irreversible threshold voltage shift is not evident with non-oxidizing analytes such as di-methyl methylphosphonate (DMMP) and common background analytes such as water vapor. Furthermore, the threshold voltage shift responds linearly to the dose time which permits dosimetric sensing analysis. A proposed mechanism for peroxide sensing is determined using simultaneous monitoring of mobility and threshold voltage. The data reveal reversible mobility and irreversible threshold voltage response. Mobility response time is fast and saturates quickly whereas threshold voltage response is dosimetric, and irreversible, suggesting an accumulation of uncompensated positive charge in the MPc film. The results are consistent with a dual response adsorption/decomposition mechanism in which the peroxide reversibly decreases mobility through a molecular chemisorption event and irreversibly shifts threshold voltage due to electron transfer from the MPc to peroxide. The electron transfer from the MPc to peroxide dissociates the peroxide to form hydroxyl products and leaves an uncompensated MPc^+. This detection method is exclusive for the OTFT platform and permits high selectivity at low peroxide concentrations.

10:40am **EM+TF-ThM9 Organic/Oxide Hybrid Thin-Film Applications for Photo-detector Cells and Complementary Inverters**, ***S.I. Im***, Yonsei University, Republic of Korea **INVITED**

Due to the distinct advantages and functionalities, oxide and organic devices on glass or flexible substrates have extensively been studied in such basic forms as thin-film transistors (TFTs) and light emitting diodes. As a more revolutionary approach to realize advanced thin-film devices using both oxide and organic layers, organic/inorganic hybrid layer techniques were also employed, so that hybrid p-n diodes, image sensors, nonvolatile memory, and complementary inverters have recently been demonstrated. *These hybrid approaches are an interesting and attractive way to extract a unique device performance which may not be possible with organics or with inorganics alone, compensating some weakness of organics with inorganics or vice versa*. The most representative example among the organic/inorganic hybrid devices may be complementary thin-film transistor (CTFT) inverters with an organic p-channel thin-film transistor (TFT) and an oxide n-channel TFT. In particular, a vertically stacked CTFT (VS-CTFT) inverter for logic operation on a glass substrate is very impressive since the vertical stacking of organic p-TFT on oxide n-TFT improves device integration or device area reduction. For the VS-CTFT inverter for logic and photo-gating, we used a thermally-evapotated p-channel pentacene layer, sputter-deposited n-channel GaZnSn-based oxide (GZTO), and atomic layer deposited (ALD) Al_2O_3 dielectric. Our VS-CTFT inverter nicely displays effective photo- and electrical-gating with a high voltage gain, dynamically operating in the low-voltage regime of 3, 5, and 8 V (the thin pentacene channel receives blue photons). As a more advanced hybrid approach, we have successfully fabricated transparent image pixels that operate at 3 V as composed of pentacene thin-film transistor (TFT) and semitransparent pentacene/ZnO photodiode with a transparent top electrode in the interest of a light detectable smart functional windows. Our transparent pixels was equipped with an additional 6,13-pentacenequinone phosphor layer as deposited on the pentacene/ZnO photodiode. The organic phosphor transmits most of visible photons but absorbs ultra-violet (UV) photons to convert them to yellow-green photons, so that the emitted yellow-green lights excite the pentacene/ZnO diode under a reverse bias state. Our approach to the transparent pixel adopting such an organic phosphor layer certainly makes the pixel operations efficient under not only visible photons but also UV, protecting the organic pentacene from direct UV.

11:20am **EM+TF-ThM11 Near-ideal Schottky-Mott Behavior of n-Si / Hg Diodes with Hydroquinone-Alcohol Monolayers**, ***A. Vilan****, R. Har-Lavan, O. Yaffe, P. Joshi, R. Kazaz, D. Cahen*, Weizmann Institute of Science, Rehovot Israel

The Schottky-Mott model predicts that the eventual energy barrier formed when metal and semiconductor are brought into intimate contact, will be equal to the difference between the metal work function and the

semiconductor's electron affinity (for n-type). 60 years of extensive experiments have clearly shown that this ideal picture, that seems to hold for wide bandgap ionic semiconductors such as ZnO, GaS etc., is far from being adequate for the more covalent narrow bandgap Si, Ge, InP, and GaAs. Following Bardeen, who attributed this deviation from the model to surface states energetically located within the semiconductor's forbidden gap, different explanation were raised as for the source of those surface states.

One commonly used model for surface states formation at the interface of semiconductor and metal is the intrinsic Metal Induced Gap State (MIGS) model, stating that gap states are inevitably formed due to the decay of metal electronic states' wavefunction into the semiconductor's bandgap.

We have examined the presence of such MIGS using Hg, which is one of the few metals that doesn't interact chemically with Si, as an electrode. Furthermore, in order to eliminate surface states which are just due to Si dangling bonds, we have used state of the art mixed molecular monolayers of hydroquinone and alcohols that were shown to be the best chemical passivation for Si surfaces.

Using alcohols of different alkyl chain lengths we succeeded to effectively change the electron affinity of the Si over 400 mV range while maintaining firm surface passivation. Current-voltage measurements of diodes formed that way, with Hg on organically modified n-Si surface, demonstrated near ideal Schottky-Mott characteristics with index of interface behavior S=0.9 (compared to a common value for Si S=0.1).

11:40am **EM+TF-ThM12 Electroless Deposition of Metals on SiO_2 Surfaces Modified by a Self-Assembled Monolayer**, ***R. Jain***, *A. Ng, A.J. Muscat*, University of Arizona

Self-assembled monolayers (SAMs) are used to both chemically activate and deactivate semiconductor surfaces. For instance, octadecyltrichlorosilane prevents atomic layer deposition of high-k films, and 3-aminopropyltriethoxysilane promotes metal deposition. The formation of a uniform and defect free monolayer is essential for nano-scale device fabrication. SAMs could serve as an adhesion layer, which is required for the electroless deposition of metals on some dielectric surfaces. Electroless deposition processes in particular are known to be sensitive to the surface termination and are not robust. In this work, the thickness and density of an aminosilane SAM formed on a SiO_2 surface were monitored as a function of solvent, concentration, and time, and the metal to N ratio was quantified.

A 3-aminopropyltrimethoxysilane (APTMS) SAM was formed on a well-hydroxylated SiO_2 surface. SAM formation was studied as a function of solvent (methanol and toluene), APTMS concentration (5.72 mM and 57.2 mM), immersion time, solution agitation (stirring and sonication), and post-deposition rinsing in methanol or chloroform depending on the solvent used. The thickness of the APTMS SAM using ellipsometry was 7.8±0.2 Å after 15 min when prepared by stirring an APTMS-methanol solution. This thickness corresponds to the expected length of an APTMS molecule. The roughness was 0.3±0.1 nm measured over 2×2 μm^2 regions using atomic force microscopy. These thickness and roughness values indicate that thin, uniform layers were formed using this method. The absence of a peak for methoxy groups in the high resolution C 1s x-ray photoelectron spectroscopy (XPS) spectrum suggests that all of the methoxy groups were hydrolyzed on the APTMS molecules that reacted with the surface. A single peak in the N 1s spectrum at 399.7 eV indicates the presence of a primary amine when the SAM was prepared in methanol. A second peak was also observed at 400.4 eV corresponding to a hydrogen-bonded amine when the SAM was prepared in toluene. These results suggest that all the SAM molecules were bonded to the surface by siloxane (Si-O-Si) linkages and that amine groups were directed away from the surface with the methanol solvent. Based on XPS peak areas, the molecular density in the SAM layer was 5.4±1.9 molecules/nm^2. A layer of Pd atoms was successfully deposited by immersing the APTMS SAM surfaces in an 80 mM $PdCl_2$-HCl solution for 2 min, yielding one Pd atom bonded to two amine groups based on XPS peak areas. These results demonstrate that an adhesion layer can be formed that will bind metal. Future work will be done to determine how strongly the metal layer adheres to the SAM.

Plasma Science and Technology Division
Room: 202 - Session PS+TF-ThM

Plasma Deposition and Plasma Enhanced ALD
Moderator: S.-P. Tay, Mattson Technology Inc.

8:00am **PS+TF-ThM1 High Quality SiNx by Microwave RLSA Plasma Enhanced Atomic Layer Deposition**, ***T. Karakawa***, *M. Oka, N. Fukiage, H. Ueda, T. Nozawa*, Tokyo Electron Technology Development Institute, INC., Japan

Shrinking critical dimensions of Ultra Large Scale Integration (ULSI) and optical device structures continue to drive advances in semiconductor fabrication processes. Three dimensional (3D) and metal gate structures for example, require low temperature dielectric layers (e.g., SiO2 and SiNx) with dimensions and film quality that may be met only by Plasma Enhanced Atomic Layer Deposition (PEALD) [1]. In addition to film quality and conformality, minimizing plasma damage in the PEALD process sequence is imperative. Prior to this work we characterized PEALD SiO2 deposition in a Radial Line Slot Antenna (RLSA) plasma source using bis-tertiaryl-buthyl-amino-silane (BTBAS) as a precursor [2]. In this study, we determined RLSA ALD process conditions favorable for SiNx film formation. The Si ALD precursor was dichlorosilane (DCS) and nitridation employed a NH3, N2 and Ar RLSA plasma. The wafer temperature was controlled below 400°C during the ALD process. Precursor adsorption time, process temperature, nitration time, plasma power were varied in order to determine the RLSA Plasma conditions resulting in the best SiNx ALD film quality. We obtained very high quality SiNx films having almost the same HF wet-etching rate as thermal LP-CVD SiNx (720°C) film. In this presentation, the results of Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) analyzed RLSA ALD deposited SiNx films will be presented. We found that the sub-nitride bonding ratio of the SiNx film was strongly correlated with the HF wet-etching rate, a measure of the film quality. The lower sub-nitride bonded SiNx film such as Si3N4 was created by the RLSA plasma at low temperature with low plasma damage. The reason so little damage occurs is the low rate of ion bombardment on new Si3N4 surfaces during plasma nitridation.

[1] S. Yokoyama et al., Applied Surface Science 112 (1997) 75-81

[2] Y. Osawa et al., Proceedings DPS-2009, 2-P51

8:20am **PS+TF-ThM2 Composition, Morphology and Optical Dispersion of Plasma Polymerized Titanium Oxide Derived Using PECVD**, ***L. Sun***, General Dynamics Information Technology, *A. Reed,* Air Force Resarch Laboratory, *H. Jiang,* General Dynamics Information Technology, *J.T. Grant,* University of Dayton Research Institute, *R. Jakubiak*, Air Force Resarch Laboratory

In this work plasma-polymerized (PP-) TiO_xC_y films derived from titanium (IV) isopropoxide (TTIP) were deposited onto Si and KBr substrates using remote, room temperature plasma enhanced chemical vapor deposition (PECVD). The composition and morphology of the films was varied by systematically changing the ratio of Ar to O_2 in the carrier gas. Chemical compositions were investigated by FTIR and X-ray photoelectron spectroscopy (XPS). Morphological data derived atomic force microscopy (AFM) and scanning electronic microscopy (SEM) studies showed that the morphology was strongly dependent on the ratio of oxygen to total carrier gas composition. The films grown with Ar as the majority carrier gas have a featureless, smooth, one phase 3-D crosslinking morphology due to the incomplete oxidation of Ti to the most stable Ti^{4+} valence state during deposition in an oxygen poor environment. As the mixture of carrier gas became more O_2 rich a second phase evolved that had a columnar structure attributed to TiO_2. This increase in oxidation was also noted in high resolution XPS measurements where a peak corresponding to a carboxyl group in the C 1s spectrum increases with increasing O_2 concentration. Development of the structured second phase was also noted in the optical dispersion obtained by spectroscopic ellipsometry. In order to fit the data, an anisotropic model has to be used that took into account the surface roughness determined from the AFM and SEM studies.

8:40am **PS+TF-ThM3 Plasma Deposition of Carbide-Based Composite Membranes for Hydrogen Purification**, ***C.A. Wolden***, Colorado School of Mines **INVITED**

We introduce a new class of composite membranes based on transition metal carbide as economical alternatives to palladium for high temperature purification of H_2. In this talk we describe two membrane concepts that were synthesized using plasma-enhanced chemical vapor deposition (PECVD) and magnetron sputtering. The first is a surface diffusion membrane comprised of nanostructured Mo_2C deposited on porous ceramic supports. Stoichiometric Mo_2C was fabricated using a two step synthesis

process. Dense molybdenum oxide films were first deposited by plasma-enhanced chemical vapor deposition (PECVD) using mixtures of MoF_6, H_2, and O_2. Oxide films 100 – 500 nm in thickness were then converted into molybdenum carbide using temperature programmed reaction using mixtures of H_2 and CH_4. Permeation testing of these membranes showed very high flux, but limited selectivity. To address this issue we describe a counterflow PECVD approach that we are developing which is used to both modify the pore size of the original supports as well as to repair pinholes that develop during the carburization.

The second strategy is to produce dense composite membranes comprised of Mo_2C layers sputtered onto BCC metal foils. BCC metals (V, Ta, Nb) and their alloys have extremely high permeability for atomic hydrogen, but negligible catalytic activity for hydrogen dissociation. Platinum group metals have been used as catalysts, particularly palladium, but at elevated temperature they alloy with the underlying metal and rapidly lose their activity. In contrast, the Mo_2C/V membranes described in this work displayed no change in permeability when operated at high temperature for >160 hours, and transmission electron microscopy confirmed that negligible interdiffusion occurs between these materials during testing. Hydrogen dissociation is the primary factor limiting hydrogen transport, as evidenced by the sensitivity of performance to carbide morphology. Sputter parameters were systematically varied to optimize the crystal structure and morphology. These composite membranes are perfectly selective to H_2, with permeability values approach and in fact exceed that of pure palladium. These findings demonstrate the potential of low cost group V metals for H_2 separations with simultaneous carbon capture at temperatures compatible with the processes used for H_2 generation.

9:20am **PS+TF-ThM5 Quantum Dot Sensitized Solar Cells using Nanoparticles of Si Compounds Fabricated by Multihollow Discharge Plasma CVD**, ***M. Shiratani**, G. Uchida, M. Sato, Y. Wang, K. Koga, N. Itagaki*, Kyushu University, Japan

Quantum dot sensitized solar cells using semiconductor nano-particles have attracted much interest because they are expected to have a high efficiency and a low manufacturing cost. Narrow band-gap semiconductors such as CdS, PbS, and CdSe are employed as sensitizers, and they transfer photo-generated electrons in them to large band-gap semiconductors such as TiO2 under light excitation. Our interest has been concerned with quantum dot solar cells using Si coumpound nano-particles because Si is abundant and has little toxicity. We have succeeded in producing Si nano-particles of a narrow size dispersion using a multi-hollow discharge plasma CVD method [1], and have applied them to Si quantum dot sensitized solar cells [2]. In our CVD system, discharges were sustained in 8 small holes of 5 mm in diameter at SiH4 and H2 flow rates of 2 and 448 sccm. Si nano-particles were nucleated, grew in SiH_4/H_2 plasma produced inside small holes, and were transported to the downstream region by neutral gas flow. We also performed surface nitridation of Si nano-partciles to terminate dangling bond of the surface. Our experiments clearly demonstrated advantages of nitridation of Si nano-particles on the device performance; the short circuit current of Si QDs sensitized solar cells showed 1.3 times higher value by the nitridation and a photon to current conversion efficiency (PCE) achieved a high value of 40% at short wavelength of 350nm [3, 4]. Moreover, quantum dot sensitized solar cells using FeSi nanoparticles show better performance than those using Si nanoparticles. We will compare characteristics of three kinds of quantum dot sensitized solar cells using Si, Si/SiN core shell, and FeSi nanoparticles and discuss relationship between optical and electrical properties of the nanoparticles and the device performance.

[1] T. Kakeya, et al.: Thin Solid Films 506-507 (2006) 288.

[2] Y. Kawashima, et al.: Trans. Mater. Res. Soc. Jpn. 35 (2010) 597.

[3] G. Uchida, et al.: Phys. Status Solidi C, (2011) at press.

[4] G. Uchida, et al.: submitted to Jpn J. Appl. Phys.

9:40am **PS+TF-ThM6 Structure of Organosilicon Polymeric Films Obtained by Expanding Thermal Plasma Chemical Vapor Deposition**, ***P.H. Tchoua Ngamou**, M.C.M. van de Sanden, M. Creatore*, Eindhoven University of Technology, the Netherlands

Organosilicon polymeric thin films (SiCxHyOz) have attracted considerable interest due to their wide range of applications such as interlayers in gas/moisture diffusion multi-layer systems, low dielectric constant interconnect materials in microelectronic circuits and biocompatible coatings for medical implants, to name a few. An accurate control of the microstructure and composition of the films is generally required to meet specific requirements in the above-mentioned applications.

In this contribution, we report on the control of the composition and structure of films deposited in Ar/organosilicon precursor mixtures by using a remote plasma, i.e. the expanding thermal plasma, CVD process. The characterization of the deposited layers has been carried out by means of Fourier-transform infrared spectroscopy (FTIR), spectroscopic ellipsometry and X-ray photoelectron spectroscopy (XPS). The characterization of thin films showing a tunable chemical composition and optical properties has allowed identifying the main dissociation paths of the deposition precursor as controlled by the argon ions and electrons emanating from the plasma source, i.e. a cascaded arc, in the downstream region, where the monomer is injected. In particular, Ar ions are responsible for the charge exchange reaction with the monomer and electrons participate to the dissociative recombination with the molecular ions generated in the first reaction, as already proven in the case of other molecular gases [1]. An optimum in the monomer structure retention of 35 % has been observed under conditions of low plasma reactivity, i.e. high monomer flow-to-(Ar+,e-) flow rate ratio.

[1] M. Creatore, Y. Barrell, J. Benedikt, M.C.M. van de Sanden, Plasma Sources Science & Technology 15 (2006) 421-431.

10:40am **PS+TF-ThM9 Impact of VUV Photons and Ions on Metal Oxide Films Prepared by Plasma-Assisted ALD with Substrate Biasing**, ***H.B. Profijt****, *M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The interest in plasma-assisted atomic layer deposition (ALD) has increased rapidly over the last

years, since it has been demonstrated that the presence of a plasma step can improve material

properties and ease processing conditions. Although it is known from other plasma-based techniques that

the photons and ions can play an important role during processing, their presence and influence have not

systematically been addressed so far for the specific case of plasma-assisted ALD. In this contribution,

we present a detailed investigation of the impact that VUV photons and energetic ions can have on the

properties of metal oxide thin films prepared by plasma-assisted ALD. We will demonstrate the

detrimental impact that VUV photons can have on electrical properties and we show that structural

material properties can be controlled by tuning the ion energy through substrate biasing. Optical

emission, retarding field energy analyzer, and Langmuir probe measurements were carried out in three

R&D plasma-assisted ALD reactors. In the O_2 plasmas employed, vacuum ultraviolet (VUV) photons with

energies up to 9.5 eV were detected and these photons were found to be able to generate electronic

defects at thin film interfaces. This was demonstrated by experiments in which Al_2O_3 passivated Si(100)

samples were exposed to O_2 plasmas. By exposing the samples through quartz and MgF_2 windows, the

role of ions was excluded and the specific role of the high energy VUV photons was confirmed

unambiguously. Furthermore, during regular ALD conditions, an ion energy of ~30 eV was measured.

This energy is sufficient to contribute to the ALD process by, e.g., the displacement of lattice atoms and

enhancement of the ALD surface reactions, however, it is low enough to prevent substantial damage to

the deposited layers. The impact of the ions was further explored by enhancing the energy of the ions

through the implementation of substrate biasing, either through substrate self-biasing or by RF biasing.

By enhancing the ion energy up to 230 eV, these experiments demonstrated that at 300°C the crystallinity

of TiO_2 films can be changed from the anatase to the rutile crystalline phase. Moreover, at a substrate

temperature of 200°C the rutile phase can be obtained when employing substrate biasing while normally

amorphous TiO_2 is obtained. These results are particularly significant as generally the deposition of rutile

* Coburn & Winters Student Award Finalist

TiO_2 is difficult to achieve by ALD due to substrate temperature limitations imposed by the precursors

used. It is therefore evident that substrate biasing is a promising method to extend the possibilities of ALD.

11:20am **PS+TF-ThM11 Plasma Enhanced Atomic Layer Deposition and Plasma Etching of Gadolinium Oxide High-k Gate Dielectrics**, ***S.A. Vitale***, MIT Lincoln Laboratory, *C. Hodson*, Oxford Instruments Plasma Technology, UK

Lanthanide series oxides are being evaluated as second-generation high-k gate dielectric materials. In addition to improving transistor electrostatics by reducing the equivalent oxide thickness (EOT), using lanthanide series gate oxide capping layers allows the effective metal gate workfunctions to be tuned toward the silicon band edges, providing the correct transistor threshold voltages. However these non-traditional CMOS materials have several integration challenges that must be overcome, including depositing a thermally-stable, high quality film with low fixed charge and high-k, without damage to the underlying layers of the gate stack. In addition, in some gate-first and gate-last approaches, the oxide must be etched from the source/drain regions prior to silicidation.

In this work, plasma-enhanced atomic layer deposition (PE-ALD) of gadolinium oxide is reported for the first time. Using $Gd(iPrCp)_3$ as the organometallic precursor and a pure O_2 plasma as the oxygen source, Gd_2O_3 growth is observed from 150°C to 350°C, though the optical properties of the film improve at higher temperature. True layer-by-layer ALD growth of Gd_2O_3 does not occur under all conditions, in fact only a relatively narrow window of self-limiting ALD growth of 1.4 Å/cycle was observed at 250°C and below under certain precursor dose conditions. As the temperature increases, high-quality films are deposited, but the growth mechanism appears to become CVD-like. At 250°C, the refractive index of the film is stable at ~1.80 regardless of other deposition conditions, and the measured dispersion characteristics are comparable to those of bulk Gd_2O_3. The electrical characteristics of the films, such as fixed charge and dielectric constant, are extracted from C-V measurements using TiN metal gate capacitors, and will be reported.

The plasma etching rate of the ALD Gd_2O_3 film in a high-density helicon reactor is very low. Little difference is observed in etching rate between Cl_2 and pure Ar plasmas, suggesting that physical sputtering dominates the etching at high bias power. A threshold bias power exists below which etching does not occur, thus it may be possible to etch a metal gate material and stop easily on the Gd_2O_3 gate dielectric. The threshold bias power is lower in a Cl_2 plasma compared to an Ar plasma, which suggests there is a small ion-enhanced chemical component to the etching as well.

*This work is sponsored by the Department of the Air Force under Air Force Contract #FA8721-05-C-0002. Opinions, interpretations, conclusions and recommendations are those of the author and are not necessarily endorsed by the United States Government.

11:40am **PS+TF-ThM12 Nano- & Micro-Hybrid Materials by a Novel Plasma Deposition Method**, *M. Gulas, A. Felten,* Research Center in Physics of Matter and Radiation (PMR) Facultés Universitaires Notre-Dame de la Paix (FUNDP), Belgium, *A. Mansour, J. Guillot,* Centre de Recherche Public - Gabriel Lippmann, Luxembourg, *N. Claessens,* Université Libre de Bruxelles, Belg

A novel low temperature plasma method using organometallic precursors has been tested and optimised to produce various hierarchical nano-hybrid and micro-hybrid materials. Very fast, operating at low or ambient temperature, this original "one pot" physical method is extremely simple, not requiring any pre- or post-treatment. The plasma-based technique can use any kind of electric discharge (direct current, radio or microwave frequency), does operate at low pressure or at the atmosphere, and can be combined with a large choice of plasma gases and organometallic precursors. Examples of the versatility of the method will be shown, including Pt and Ni-decorated carbon nanotubes (CNTs), Ag and Ti-decorated latex beads, and Pd-decorated clay sheets.

One focus of the presentation will be the preparation and full characterisation of bimetallic Pd/Rh - CNT hybrids. The x-ray diffraction (XRD) and TEM (EDX) analyses were used to confirm that the deposited nano-particles are indeed truly Pd/Rh bimetallic, excluding the possibility of a simple physical aggregate/mixture of the two metals ; complementary analytical tools such as x-ray photoelectron spectroscopy (global information) and scanning transmission x-ray microscopy (truly local information) reveal that the particles contain a metal/oxide ratio depending of the processing gas; they testify also of the possibility of a nano-particle core-shell structure and of a reorganisation of its structure depending of the processing gas.

Thin Film Division
Room: 109 - Session TF1-ThM

Post-Deposition Processing and Characterization of Thin Films
Moderator: C. Vallée, LTM/CNRS-UJF, France

8:00am **TF1-ThM1 Protrusions, Surface Grains and Extended Single-Crystalline Plates**, ***A. González González,*** Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Spain, *G.M. Alonzo Medina, A.I. Oliva,* Centro de Investigaciones y de Estudios Avanzados del IPN, CINVESTAV Unidad de Mérida, Mexico, *C. Polop,* Universidad Autónoma de Madrid, Facultad de Ciencias, Spain, *E. Rodríguez Cañas, J.L. Sacedón, E. Vasco*, Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Spain

The processes controlling shape transformations during post-deposition treatments attract great interest due to their technological implications. As an example, residual stress relaxation during thermal annealing could influence component lifetime and performance in applications ranging microelectronics to mechanical coatings, affecting their functional properties [1]. In this work, we investigate the morphology evolution during thermal annealing at 0.2 $T_{melting}$ in polycrystalline Au(111) films using atomic force [scanning electron] (AFM [SEM]) microscopies and x-ray diffraction in order to follow both shape and structural transformations of surface features for different annealing times. Before annealing, a high density of round-like surface grains —which are surface components of an underlying competitive columnar microstructure—, is observed. During annealing, surface grains merge together into "multigrain" structures that expand laterally up to a saturation size, suggesting a size-dependent phenomenon controlling surface recrystallization. By comparison with Au polycrystalline growth fronts for the same temperature range [2] (T zone of the zone models [1]), we can relate the annealing–generated multigrain structures to the incipient formation of extended sub-micrometric-sized plates that are observed for thinner films. They contain many small surface grains with low-angle or no inner grain boundaries [2]. The small amount of material to be recrystallized for each component favors the multi-component extension of recrystallized zone. Interestingly, results here reported concerning the recrystallization phenomenon are discussed on the basis of local interactions between surface grains triggering plausible elastic/plastic mechanisms of stress accommodation (grain zipping and shear strain) and relaxation by surface diffusion processes [1,3], which in principle seems not be very different from those expected in the coalescence stage at the T zone.

[1] L. B. Freund and S. Suresh, *Thin Film Materials: Stress, Defect Formation and Surface Evolution* (Cambridge University Press, Cambridge, England, 2003) and references therein.

[2] C. Munuera *et al.*, J. Vac. Sci. Technol. A **22**, 1767 (2004)

[3] A. González-González *et al.*, "*Morphology evolution of thermally annealed polycrystalline thin films*" (submitted)

8:20am **TF1-ThM2 Characterization of Mg Acceptors in GaN:Mg Grown by Metal Modulated Epitaxy and MOCVD**, ***J.E. Lowder***, *M.W. Moseley, B. Gunning, W.A. Doolittle,* Georgia Institute of Technology, *M.E. Zvanut, J. Dashdorj*, University of Alabama

Acceptor doping of III-Nitrides has been the subject of many studies due to the relativity low hole concentration (~10^{17}-10^{18} cm^{-3}) material commonly grown in contemporary devices. This limitation is thought to be one of the contributing factors to efficiency droop in LED's. Recently, extremely high hole concentration ($p>4x10^{19}$ cm^{-3}) material with very high (>50%) ionization efficiency (see Fig. 1) has been demonstrated by metal modulated epitaxy (MME), an application of MBE where surface chemistry is controlled via shuttering of the source material [J. Appl. Phys. 106, 014905]. The samples in this study are characterized by temperature dependent Hall measurement to elucidate the reduction in the acceptor activation energy. Electron paramagnetic resonance spectroscopy (EPR) was used to show the microscopic view of the Mg acceptor without influence of the surrounding crystal as well as the effect of annealing temperature on the EPR signal. It is found that the primary transport mechanism is likely due to impurity band conduction, consistent with a distributed acceptor band as opposed to an isolated acceptor energy level as is generally observed in p-type GaN. Likewise, the interaction of the Mg with hydrogen shows different annealing behavior when compared to MOCVD p-type GaN.

The samples analyzed by EPR were annealed at various temperatures in forming gas (H_2:N_2). Fig. 2 shows the relative intensity from the EPR signal of the neutral Mg acceptor as a function of forming gas anneal temperature.

It is clear that there is a sharp decrease in signal for the MME grown samples (doped $>10^{20}$ Mg as seen in fig. 1) at 525 °C as compared to the drop observed at 750 °C for the MOCVD grown samples (doped $\sim 10^{19}$ Mg). The exact nature of this temperature dependent decrease in signal is not fully understood, however it is suggested the different growth kinetics and resulting surface leads to a change in H_2 transport. A second mechanism may be the formation of Mg-H complexes with varying activation energies.

Preliminary temperature dependent Hall results (Fig. 3) show an as-grown activation energy of 70 meV in the MME samples as well as $5x10^{18}$ cm^{-3} holes remaining at cryogenic temperatures. This extremely low activation energy and lack of carrier freeze out is evidence of impurity band conduction and shows the degenerative nature of the material. The full effect of the annealing temperature on this degenerative material will be presented in further detail as it pertains to device processing.

8:40am **TF1-ThM3 Post Deposition Annealing Effects on Thin Film Material, Process, and Device Properties**, ***Y. Kuo***, Texas A&M University **INVITED**

Thermal annealing is a critical but often neglected step in semiconductor production. It has been routinely used to activate the ion implanted dopant and at the same time, to restore the single crystal structure. However, it is also a powerful tool in repairing damages in bulk films as well as at film-film interfaces, which are caused by the plasma-related deposition or etching process. In addition, the thermal annealing step can change film characteristics, which affects the subsequent process result. In this talk, the author will review some of his recent work related to thermal annealing, which involves three types of solid-state devices and thin films. First, an example on repairing the RIE damaged a-Si:H TFT with a low temperature thermal annealing process will be given. This step reduced defects in the bulk a-Si:H and SiNx layers as well as at the gate-dielectric interface. This result has been interpreted in all TFT LCD productions around the world. In the second example, it will be shown that the thermal annealing step changed the grain size of the sputter deposited copper thin film. It resulted in the change of the copper-Cl reaction mechanism and therefore, the copper consumption rate. This is critical to a new plasma-based copper etch process that has been interpreted in large-area TFT LCDs and BiCMOS chips. In the third example, it will be shown that the post deposition annealing (PDA) condition is the key to the realization of a new type of nonvolatile memory device, i.e., the nanocrystals embedded high-k capacitors or MOSFETs. Furthermore, an addition low temperature annealing step removed the defects generated in the gate and back-contact sputtering processes. In summary, the thermal annealing effects are non-negligible because they are directly involved in product reliability and yield.

(1) Y. Kuo, "TFT and ULSIC – Competition or Collaboration," Jpn. J. Appl. Phys., 47(3), 1845-1852 (2007).

(2) G. Liu, Y. Kuo, S. Ahmed, D. N. Buckley, and T. Tanaka-Ahmed, "Grain Size Effect on Plasma-based Copper Etch Process," J. Electrochem. Soc., 155(6) H432-H437 (2008).

(3) Y. Kuo, "Status Review of Nanocrystals Embedded High-K Nonvolatile Memories," ECS Trans. 35(3), 13-31(2011).

9:20am **TF1-ThM5 Semiconductor Thin Film Metrology using Coherent Acoustic Phonon Spectroscopy**, ***A.D. Steigerwald***, *K. Varga, A.B. Hmelo,* Vanderbilt University*, L. Feldman,* Rutgers University*, N.H. Tolk*, Vanderbilt University

Here we discuss the use of coherent acoustic phonon spectroscopy as a noninvasive and nondestructive measurement tool for semiconductor thin films. Specifically we emphasize its usefulness in studying the optoelectronic structure of materials with various types of structural defects. We discuss in-depth studies of ion-implanted GaAs, demonstrating that the technique may be used to quantitatively determine depth profiles of lattice disorder. Our optoacoustic measurements are shown to be 2-3 orders of magnitude more sensitive in defect concentration than channeling techniques, and establish a quantitative dependence between the change in optical response and defect concentration between 10^{18}-10^{21} defects/cm^3. Further, we demonstrate the entire range over which the coherent acoustic phonon technique is applicable in defect studies, and show results ranging from no noticeable change in optical response to complete damping of the phonon wave. We also discuss the electronic nature of the CAP response, which can provide insight into the interplay between lattice disorder and electronic structure.

9:40am **TF1-ThM6 On the Phase Formation of Reactively Sputtered ZrO_2 Thin Films**, ***R. Snyders***, *G. Geumez, S. Konstantinidis*, UMons, Belgium

ZrO_2 is a material used as thin films in numerous applications. One of the applications with the highest added value is its use as ionic conductor in, for example, fuel cell devices. Nevertheless, only the tetragonal and cubic polymorphs of ZrO_2 exhibit these ionic conduction properties. Therefore, effort have to be made in order to synthesis phase pure tetragonal or, ideally, cubic ZrO_2 thin films. It has been demonstrated that these polymorphs are generated when about 10% of oxygen vacancies are introduced in the material lattice. Recently, some works have demonstrated that it was possible to synthesize, by reactive high power impulse magnetron sputtering, cubic HfO_2 (a compound very close to ZrO_2) containing, as for cubic ZrO_2, 5% of oxygen vacancies when working in the transition region of the poising curve. This implementation of this strategy was possible thanks to the smoothness of this transition using this peculiar sputtering technology.

In this work, we aim to apply such a strategy to grow tetragonal (or cubic) ZrO_2 by reactive DC magnetron sputtering. Due to the very sharp metallic-to-poisoned mode transition, we used a plasma monitoring system (PEM) to work in stable conditions in that region.

A pure Zr metallic target is sputtered at constant current (0.2 A) at 10 mTorr in Ar/O_2 mixtures using a DC magnetron sputtering source with an unbalanced magnetic field configuration. A PEM system is implemented in order to grow films in the transition region. The Zr line at 340 nm is monitored in real time. The deposited films were characterized by grazing angle X-Ray diffraction (GAXRD) and X-Ray photoelectron spectroscopy (XPS).

Discharge parameters (voltage, current) and XPS data reveal that the transition occurs for $4\% < \%O_2 < 6\%$. For $\%O_2 < 4\%$, the films are under-stoichiometric with a metallic character. In the transition, we measure a stoichiometry of about $ZrO_{1.8.}$ Finally, $\%O_2 > 6\%$, the films are stoichiometric. In term of phase constitution, it has been demonstrated that working in the poisoned mode, the monoclinic phase is synthesized while in the transition, for which the compound is under-stoichiometric, the tetragonal (and maybe cubic) phase is grown. These data support, for the first time, the theoretical assumption about the oxygen vacancies-generated tetragonal (or cubic) phase of ZrO_2. Finally, the thermal stability of the coatings has been studied: the as-grown samples have been annealed up to 1200°C. For annealing temperature up to 600°C, no modification of the phase constitution is observed while for an annealing temperature of 1200°C, the films experience a phase transition towards the monoclinic structure.

10:40am **TF1-ThM9 Effect of 10 keV X-rays on Silicon Oxidation**, ***S. Bhandaru***, *S.M. Weiss, E.X. Zhang, D.M. Fleetwood, R.A. Reed, R.A. Weller, B.R. Rogers, R.R. Harl*, Vanderbilt University

In the past few decades, studies have been conducted to investigate photon assisted oxidation of silicon substrates. Most of these efforts have focused on understanding and modeling the oxide growth mechanism using photon energies spanning the visible (1.55 eV – 3.0 eV) to the UV range (3.0 eV – 6.5 eV). In this work, we study the influence of higher energy x-rays (10 keV) on silicon oxidation. We found that x-ray irradiation of silicon substrates, performed at ambient temperature and atmospheric pressure conditions, can significantly affect the formation of silicon oxide. The oxide formation is influenced by the dose rate and total dose of x-ray irradiation, as well as the initial silicon surface preparation.

Boron doped silicon samples (0.01 Ω-cm - 0.02 Ω-cm) were irradiated at dose rates ranging from 5.8 krad(SiO2)/min to 31.5 krad(SiO2)/min using a 10 keV x-ray source (ARACOR Model 4100). The samples were cleaned in dilute HF acid to remove the initial native oxide and obtain a clean surface prior to irradiation. The resulting silicon oxide thickness was estimated using spectroscopic ellipsometry (J. A. Woolam M-2000). Different models for the optical properties of the surface layer were evaluated. Oxide growth on the irradiated samples was compared to oxide growth on control samples, which were placed in ambient air at room temperature. The ellipsometry analyses suggest that the oxide growth on the irradiated samples was greater than that on the control samples. Initial XPS analysis showed that the oxide layers on the irradiated and control samples were chemically different, suggesting that differences observed in the ellipsometry analyses may be due, in part, to differences in the optical properties of the oxide layers and not purely due to a change in thickness.

We will present the results of the oxidation study in addition to XPS and AES characterization of the resulting oxide films. The impact of heating the silicon substrate up to 150°C during x-ray irradiation will also be discussed. A mechanism to explain the experimental observations is proposed based on ozone concentration measurements performed during irradiation. The possible generation of atomic oxygen, due to dissociation of molecular oxygen, by the high energy x-rays is suggested as a key factor in the observed x-ray irradiation induced silicon oxidation.

Acknowledgement: This work was supported in part by the DTRA Basic Research Program (Grant No. HDTRA1-10-0041).

11:00am **TF1-ThM10 Investigating the Local Physical Structure of Amorphous Hydrogenated Boron Carbide**, ***M.M. Paquette****, W. Li, M.S. Driver, S. Karki, N.A. Oyler, A.N. Caruso*, University of Missouri - Kansas City

The unique physical structure of boron-rich carbides, based on an extended molecular network of covalently bound icosahedral cages, has distinguished this material with an exceptional set of thermal, electrical, and mechanical properties. Technologically, boron carbide has generated interest for applications in solid-state neutron detectors, interlayer low-*k* dielectrics for ultra-large-scale integrated circuits, and high-temperature thermoelectric power convertors. A method that has proven amenable to thin-film heterostructure device fabrication is the plasma-enhanced chemical vapor deposition (PECVD) of high-resistivity amorphous hydrogenated boron carbide (a-B_xC:H_y; $x \approx 2$–5) from the single-source precursor orthocarborane ($C_2B_{10}H_{12}$). However, although the physical structure of bulk crystalline boron carbide (e.g., $B_{4.3}C$) is nowadays well-understood, the short-range physical structure of the hydrogenated material (e.g., the number and types of atoms/bonds) has remained unsatisfactorily characterized, likewise for the intermediate-range physical structure of the amorphous lattice (e.g., how molecular subunits are bound together and arranged on a short sub-nm length scale)—structural modifications which have important consequences on the properties of the a-B_xC:H_y films. Herein, we investigate the short- and intermediate-range physical structure of a-B_xC:H_y films using solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) and Fourier transform infrared (FTIR) spectroscopies, backed by density functional theory (DFT) molecular structure calculations. The comparison of experimentally observed spectral features with theoretical predictions for model molecular compounds provides valuable insight into the different local chemical environments and intermediate-range networks that make up the a-B_xC:H_y films. We demonstrate how applying these combined analyses provides an important stepping stone to understanding and optimizing the chemical, electrical, and mechanical properties of a-B_xC:H_y films for next-generation device fabrication.

11:20am **TF1-ThM11 Characterization of Amorphous and Nanocomposite Nb-Si-C Thin Films Deposited by dc-Magnetron Sputtering**, ***N. Nedfors***, Uppsala University, Sweden, *O. Tengstrand,* Linköping University, Sweden, *A. Flink,* Impact Coatings AB, Sweden, *A.M. Andersson,* ABB AB, Corporate Research, Sweden, *P. Eklund, L. Hultman,* Linköping University, Sweden, *U. Jansson*, Uppsala University, Sweden

Thin films of Me-Si-C (Me = early transition metal) have interesting multifunctional properties, see, e.g., [1]. We have in the present study investigated thin films in the Nb-Si-C system deposited by dc-magnetron sputtering using elemental targets. The microstructure and composition of the films have been characterized with x-ray diffraction, x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy. Nanoindentation and atomic force microscopy were used to investigate the mechanical properties of the thin films while the electrical contact resistance was measured using a four wire set-up with an Au-coated probe pressed against the film surface.

Our results show that films with a silicon content less than 20 at.% exhibit a nanocomposite (nc-NbC/a-SiC) structure with nanocrystalline NbC grains embedded in an amorphous matrix phase. The size of the carbide grains decrease with the carbon content increase. A transition to a completely amorphous structure occurs with a Si content above 20 at.%. The transition in microstructure is reflected in the properties of the films with an abrupt increase in contact resistance (from 30 mΩ to 200 mΩ at 1 N) and a change in the mechanical behavior of the thin films. The XPS spectra show a change of chemical bonding from mainly C-Nb to a significant amount C-Si bonds as the Si and C content increase in the films. This results in harder films and an increase in the electrical resistivity. The amorphous films can be described as a metal carbide-based glass and the formation of this type of structures in sputtered Me-Si-C films will be discussed.

[1] J. Lauridsen et al., Surf. Coat. Technol., 205, 299-305, 2010

11:40am **TF1-ThM12 Evaluation of Mn-based Cu Barriers for Interconnect Applications**, ***E. Van Besien****, N. Jourdan,* IMEC, Belgium, *L. Zhao,* Intel assignee at IMEC, Belgium, *K. Croes, Y.K. Siew, S. Van Elshocht, Zs. Tőkei*, IMEC, Belgium

Diffusion barrier layers with a uniform thickness and good step coverage in narrow lines are needed to enable the continuing scaling of Cu interconnects. Since physical vapor deposition (PVD) processes have limitations in respect of conformality, atomic layer deposition (ALD) and chemical vapor deposition (CVD) might become the preferred alternatives. Among others, Mn-based CVD barriers have been proposed [1], but up to now, Cu barrier properties for such films have not been proven electrically.

In this study, MnOx layers were deposited by CVD, on top of an O3/TEOS SiO2 layer. Deposition was done at two different temperatures: 200 °C and 350 °C. The effect of a post-plating anneal of one hour at 300 °C or 430 °C was studied. A test structure based on planar capacitors was used, in which first wide areas were patterned, followed by the deposition of the oxide and CVD MnOx layers, metallization, and CMP, respectively [2]. After passivation, voltage ramp (at 25 °C and 100 °C) and TDDB measurements (at 100 °C) were conducted. The electrical data were compared with those from a known good TaN/Ta-barrier reference system.

Voltage ramp measurements at 25 °C show a similar behaviour for all Mn-based films under study, except for the one deposited at 350 °C, with a post-plating anneal at 430 °C. For the latter a leakage current of about 1 order of magnitude lower is found, comparable to the leakage current of our TaN/Ta reference. For the film deposited at 200 °C, and annealed at 430 °C, voltage ramp measurements only showed shorts.

TDDB lifetimes were in all cases higher than for a reference without barrier, but lower than for a TaN/Ta reference. For the Mn-based films deposited at 350 °C, a post-plating anneal at 430 °C clearly improved the reliability properties. In this case, the extrapolated lifetime at user conditions (using the E-model), is above 10 years. A γ value of -3.4 cm/MV was found. However, for the films deposited at 200 °C, an anneal at 300 °C already degraded the reliability properties.

In conclusion, voltage ramp and TDDB measurements on planar capacitors structures show that, with optimised processing, CVD Mn-based barriers are promising candidates as Cu barriers in advanced interconnects.

[1] K. Neishi, S. Aki, K. Matsumoto, H. Sato, H. Itoh, S. Hosaka, J. Koike, Appl. Phys. Lett. 93 (2008) 032106

[2] L. Zhao, Zs. Tökei, G. Giai Gischia, M. Pantouvaki, K. Croes, G. Beyer, IEEE International Reliability Physics Symposium, 2009, 848-850

Thin Film Division
Room: 110 - Session TF2-ThM

Modeling and Analysis of Thin Films
Moderator: P.D. Rack, University of Tennessee Knoxville

8:00am **TF2-ThM1 Aluminum Molecular Model for DSMC Simulations of Thin Film Deposition**, *A. Venkattraman,* ***A. Alexeenko***, Purdue University

The direct simulation Monte Carlo (DSMC) technique has been shown to be able to predict various properties of thin films grown using vacuum deposition methods such as CVD, PVD, EBPVD. Such simulations can also provide information about the energy distribution and orientation of vapor molecules striking the substrate which are critical inputs to the prediction of the grain size, residual stress and other properties of the deposited films. One of the most important inputs to a DSMC simulation is the molecular model that determines the interaction between the simulated particles. The variable hard sphere (VHS) model that is widely used due to its combination of simplicity and accuracy is typically determined by fitting to viscosity data obtained from experiments. In the absence of direct measurements of transport coefficients for metal vapors such as Aluminum, one needs to resort to other techniques to determine a set of accurate molecular model parameters. In this work, we compare DSMC simulations with Aluminum thin film deposition experiments to determine the VHS model parameters. The growth rate of the thin films at the substrate location depends strongly on the transport properties of the metal vapor – viscosity being one of the most important – and hence can be compared with the DSMC simulations to determine a suitable molecular model. In a similar analysis for copper published earlier, we used experimental data available in literature while the experiments for this study are performed in the electron-beam evaporator in the Birck Nanotechnology Center at Purdue University.

8:20am **TF2-ThM2 ISSG Chemistry Modeling to Understand Uniformity Issues in RTP**, ***S. Gupta****, U. Kelkar*, Applied Materials, Inc.

This paper describes three-dimensional flow/thermal/chemistry modeling efforts to study the silicon oxidation using In-Situ Steam Generation (ISSG). This 3D model incorporates 27 step gas phase reaction mechanism which is responsible for ISSG chemistry. The complex 3D geometry, supersonic flow, detailed chemistry pose major challenges to the model convergence and results in unrealistic results due to H2 and O2 exothermic

reaction. Complex 3D geometry causes CFD model mesh size to become more than a million cells. The computational times to include all chemical reactions on a 3D complex flow problem are exorbitant. Thus a simple 2D RTP chamber model was built to examine the validity of gas phase reaction mechanism by comparing in-house simulation results with Professor Robert J. Kee, Colorado School of Mines [1] and to set the solver control parameters for stable solution in 3D. After a working 2D model, simple representative 3D model was built with very good quality structured mesh and the further geometric complexity was added in steps. The oxygen radical distribution predicted from the model matched very well with the oxide growth uniformity over a wide range of chamber pressure, gas flow rate, hydrogen fraction, and gas distributor geometry. At 5 torr, temperature distribution is dominated by wafer temperature as gas phase reaction is weak. At higher pressure exothermic gas phase reaction causes higher temperature above the wafer. There is weak gas phase reaction at 5 torr, resulting in low O atom number density. The O radicals diffuse in the chamber due to higher velocity at 5 torr where they recombine. At higher pressure flame ignites right at the edge of the wafer due to higher residence time resulting in very high O atom number density at the edge. This well calibrated simulation model was used in understanding and expanding process space by optimizing on several hardware and process variables using virtual prototyping before building the hardware.

8:40am **TF2-ThM3 Composition and Finite Size Effects in Thin Magnetic Films for Data Storage Applications: Magnetic and Transport Properties**, ***O.N. Mryasov***, University of Alabama **INVITED**

Scaling of magneto-resistance (MR) and resistance area product (RA) with thickness is one of a critical materials specific properties of hard disk drive sensors. We consider fundamental aspects of MR-RA scaling with two planar FM/NM/FM hetero-structures: (i) Fe/MgO/Fe tunneling junctions and (ii) all Heusler alloy giant-magneto-resistance (GMR) spin valves [1-3]. In both cases we focus on the electronic structure contributions to RA(MR). Third example motivated by rapidly decreasing grain size of data storage media where material specific finite size effects originate from magnetic interactions of 3d-5d(4d) elements [4,5]. First, we show that calculated within the QSGW theory [6] decay constant controlling thickness dependence of RA are consistent with experiment [7]. We also present results of direct spin dependent electronic transport simulations for two types of GMR structures (i) non-magnetic Heusler alloy spacers [1,2] and (ii) Ag spacer [3]. The (110) textured Co_2MnGe (CMG) and Rh_2CuSn (RCS) [1] have been used to build test hard disk drive reader and yielded MR of about 7 % and DRA of about 4.0 mW-mm^2 [2]. The (001) textured FM Co_2Fe(Ge-Ga) with Ag spacer yielded MR values in excess of 45 % and DRA of 9.5 mW-mm^2 [3]. Ab-initio electronic structure methods used to account for composition effects are shown to reproduce experimentally observed trends [1-3]. Finally we investigate finite size effects in the recording media granular films using model of magnetic interactions proposed to explain temperature dependence of magnetic anisotropy energy (MAE) observed in highly order $L1_0$ FePt thin films [4]. We discuss measurements protocol to quantify single vs. two ion contributions to MAE responsible for particular contributions to finite size effects in of 3d-5d(4d) thin films.

References:

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[5]. U. Nowak, O. N. Mryasov, R. Weiser, K. Guslienko, R.W. Chantrell , Phys. Rev. B, v. 72 p.172410, (2005).

[6]. S. Faleev, O. Mryasov and T. Mattsson, Phys. Rev. B., v.81, p. 205436 (2010) and references therein

[7]. S. Yuasa and D.D. Djayaprawira, J. Phys.D: Appl. Phys. v40, R337 (2007).

9:20am **TF2-ThM5 Large Scale TiN Thin Films Growth Simulations via Improved Modified Embedded Atom Parameterization**, *D.G. Sangiovanni,* ***V. Chirita****, L. Hultman,* Linkoping University, Sweden*, I. Petrov, J.E. Greene*, University of Illinois at Urbana Champaign

Significant advancements within the last decade in the Modified Embedded Atom Method (MEAM) formalism, present the opportunity to perform, previously not possible, realistic large scale simulations of important model material systems such as TiN. The currently limited number of TiN MEAM parameterizations yield reasonable description of general bulk/surface properties of the material. However, to perform Molecular Dynamics (MD) simulations of TiN thin films growth, a number of critical nucleation and diffusion phenomena have to accurately be accounted for in addition to basic properties. Herein, an improved TiN MEAM parameterization is reported, which not only correctly predicts bulk/surface properties, but also reproduces the experimentally observed trends in the diffusion of single species (Ti, N), Ti-N dimers and other complexes, on most representative, (100) and (111), steps/surfaces for TiN growth. The calculated activation energies for diffusion, and the all-important Ehrlich-Schwoebel (ES) step-edge barriers, are in good agreement with ab-initio calculations and experimental observations. To demonstrate the potential of this MEAM parameterization for simulations of TiN thin films growth, illustrative case simulation studies are presented, which successfully reproduce experimentally documented crucial processes in the initial stages of TiN nucleation, known to dramatically affect growth modes, and ultimately, properties of thin films. The implications of these results, and perspectives for large scale simulations of this extremely important material model system, are discussed.

9:40am **TF2-ThM6 Hard, yet Tough, Transition Metal Nitride Thin Films by Alloying and Valence Electron Concentration Tuning**, ***D.G. Sangiovanni****, V. Chirita, L. Hultman*, Linkoping University, Sweden

Improved toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure during ***in-use*** conditions, in modern applications. Based on the successful approach and results obtained for TiN- and VN-based ternary thin films [1,2], we expand our Density Functional Theory (DFT) investigations to TiAlN-based quarternary thin films. (TiAl)1-xMxN thin films in the B1 structure, with $0.06 \le x \le 0.75$, are obtained by alloying with M = V, Nb, Ta, Mo and W, and results show significant ductility enhancements, hence increased toughness, in these compounds. Importantly, these thin films are also predicted to be hard/superhard, with similar and/or increased hardness values, compared to TiAlN. For (TiAl)1-xWxN these results have experimentally been confirmed recently [3]. As previously demonstrated [1], the ductility increase originates in the enhanced occupancy of d-t2g metallic states, induced by the valence electrons of substitutional elements (V, Nb, Ta, Mo, W). This effect is more pronounced with increasing valence electron concentration (VEC), and, upon shearing, leads to the formation of a layered electronic structure, consisting of alternating layers of high and low charge density in the metallic sublattice. This, in turn, allows a selective response to tetragonal and trigonal deformation: if compressive/tensile stresses are applied, the structure responds in a “hard” manner by resisting deformation, while upon the application of shear stresses, the layered electronic arrangement is formed, bonding is changed accordingly, and the structure responds in a “ductile/tough” manner as dislocation glide along the {110}<1-10> slip system becomes energetically favored [2].

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[2] D. G. Sangiovanni et. al. Acta Mater. 59 (2011) 2121.

[3] T. Reeswinkel et. al. Surf. Coat. Technol. (2011) in press.

10:40am **TF2-ThM9 Using Crystallographic Space Group-Subgroup Relations to Analyze Phase Selection and Transition in HfO_2 and Hf-based Ternary Oxide Films**, ***C.R. Aita***, University of Wisconsin-Milwaukee

HfO_2 and Hf-based ternary oxides are important candidates for ultrathin high permittivity dielectric applications. However, technological aspects of their use in actual devices far outstrips our knowledge of the fundamental science that governs phase selection and transition in these materials. The latter is important for predicting both initial device performance and long term stability. One big issue is that pure HfO_2 readily forms nanocrystallites in thin films. These crystallites exhibit finite size effects on two different length scales: (1) *Two* metastable phases initially form in crystallites < ~ 7nm in size [1] and transform to monoclinic (m) HfO_2, the standard state, as crystallites grow. (2) Upon transformation from the metastables, m-HfO_2 nanocrystallites whose size is <~ 11 nm exhibit a lattice expansion concurrent with surface dipole repulsion [2]. A second issue involves the stability of Hf-based ternaries that are either intentionally grown or inadvertently form as a result of cation mixing during thermal processing or heating upon device use. These questions are being addressed from an experimental viewpoint through controlled isochronal and isothermal annealing studies. In this paper, we use crystallographic space group-subgroup analysis to examine phase selection and transition in three sputter deposited nanolaminates, HfO_2-Al_2O_3, HfO_2-TiO_2, and HfO_2-ZrO_2. The goal is demonstrate how this tool connects phase transitions between seemingly unrelated structures by symmetry considerations. We show that several important transitions observed in these materials are 2nd order and can be described by a simple relation between a parent group of higher symmetry and a daughter group of lower symmetry. Using the suite of programs in the Bilbao Crystallographic Server [3], first, conjugacy classes associated with

the parent → daughter transition are identified, and then using the operations within each class, the general atom positions of the parent are decomposed into cosets of symmetry elements expressed the daughter's basis. Symmetry elements that are "lost" in the decomposition are used to identify a twin domain structure in the daughter resulting from the transition. Using these formalisms, we discuss metastable phase→m-HfO_2 transition in pure HfO_2, the robustness of an entropy-stabilized HfAl-oxide phase, and the initiation $HfTiO_4$demixing.

Support from UWM Foundation Catalyst Grant / Rockwell Automation Charitable Trust.

[1] E.E. Hoppe et al. APL 91, 203105 (2007); APL 92, 109903 (2008).

[2] M.C. Cisneros-Morales et al., APL 96, 191904 (2010).

[3] M.I. Aroyo et al., Z. Kristallogr. 221, 15 (2006); M. Nespolo, Acta Crystall. A64, 96 (2008).

11:00am **TF2-ThM10 Experimental and Theoretical Investigations Using SiO_2 Nanotemplates to Relieve Stress Caused by Thermal Expansion Coefficient Mismatch in Epitaxial Germanium Grown on Silicon**, ***S. Ghosh***, *D. Leonhardt, S.M. Han*, University of New Mexico

High-quality Ge-on-Si (GoS) heterostructures are pursued for many applications, including near-infrared photodetectors, high-mobility devices with Si-based integrated circuits, and virtual substrates for III-V multijunction solar cells. Growing low-dislocation-density GoS and subsequently integrating III-V layers present two significant engineering challenges: lattice mismatch and thermal expansion coefficient mismatch. The materials engineering solutions to circumvent the lattice mismatch include metamorphic growth, graded buffer layers, selective epitaxial overgrowth, aspect ratio trapping (ART), and a variety of defect filtering strategies. The ART technique, in particular, utilizes high-aspect-ratio holes or trenches etched through dielectric films to trap dislocations, greatly reducing the dislocation density. However, one shortcoming of ART is that it has been demonstrated to be effective only for small holes or narrow strips with dimensions less than 1 μm. In this study, we demonstrate that a combination of ART with selective epitaxial growth can produce large areas of high-quality GoS. We focus on the use of SiO_2-based templates with nanoscale windows placed on GoS to relieve the thermal stress. We observe that voids form around the top and sidewalls of SiO_2 template deposited by chemical vapor deposition, further relieving the thermal stress. The same templates also filter threading dislocations propagating from the underlying Ge-Si interface. The Ge layer grown and coalesced over the template is analyzed by transmission electron microscopy and etch pit density measurements. When the template is used, the threading dislocation density near the Ge film surface is approximately $<10^7$ cm^{-2}, while the twin defect density is approximately $<5x10^7$ cm^{-2}. Finite element modeling based on a commercial software package COMSOL is used to calculate the thermal stress occurring in the epitaxial Ge due to differences in thermal expansion coefficients among Ge, Si, and SiO_2. The simulation results, comparing Ge grown on Si with and without SiO_2 templates, show that the nanoscale templates can effectively reduce the thermal stress. The resulting stress results obtained using the simulation model corroborate the experimental observations. In summary, the simulation results suggest that the SiO_2 nanotemplates can reduce the stress caused by the thermal expansion coefficient mismatch, while simultaneously reducing the lattice-mismatch-induced dislocations in Ge grown on Si.

11:20am **TF2-ThM11 Controlling Heteroepitaxy through Surfactant-Enabled Growth: An *Ab Initio* Thermodynamics Study**, *B.E. Gaddy, E.A. Paisley, M.D. Losego, J.S. Tweedie,* North Carolina State University*, R. Collazo,* North Carolina State Univeristy*, Z. Sitar,* ***D.L. Irving****, J.-P. Maria*, North Carolina State University

We demonstrate that surfactant-assisted epitaxy is a useful method for stabilizing the growth of {111} CaO films on (0001) GaN. Surface free energies, calculated by ab initio thermodynamics, for configurations of CaO surfaces with varying surfactant coverage will be presented. These results explain the recent experimental observation that incorporating water vapor during CaO deposition produces a hydroxylated surface. Hydroxylation changes the preferred habit of CaO from (001) to (111), which enables layer-by-layer growth of (111) CaO on (0001) GaN. Together with experiment, these results demonstrate a new approach, applicable to numerous materials systems, where chemical boundary conditions are engineered to regulate the growth mode. Unique opportunities to integrate highly heterogeneous materials of dissimilar structure and symmetry are consequently available.

11:40am **TF2-ThM12 Deposition and Modeling of Nanoscale Organic Porous Polymeric Layers and their Characterization with Visual and Electrical Methods***,* *G. Franz,* ***F. Schamberger***, Munich University of Applied Sciences, Germany

To act as long-term antibacterial coating on the interior of hollow implants like artificial bladders or flexible pipes which can act as urethrae, silver layers have to be partly protected against aggressive solutions of the human body, e.g. urine or gall. One of these organic polymers is poly-p-xylylene, commonly known as polyparylene. In order to control this process of dissolution from metallic silver to silver ions which is responsible for the toxic impact, the layers should exhibit an adjustable hole density. This requires the growth control of very thin layers between zero and about 250 nm. By application of the conventional Gorham method, only thicknesses beyond 2 microns are accessible. We present a completely new method to control the growth of these very thin layers with defined porousity for which exact knowledge of vapor pressure and evaporation rate is required which have been measured and modeled using statistical rate theory (SRT) [1]. Applying a digital evaluation procedure of the micrographs gained with AFM, the hole density is correlated with the breakdown voltage and the capacitance which can both easily applied to the samples. Whereas the coating of open surfaces is controlled by flow, this mechanism is not applicable for coating of narrow holes which takes place as a diffusive process with losses due to deposition. In a series of experiments, the growth behavior in thin, narrow pipes with an aspect ratio between 10 and 30 has been obtained, and a theoretical model is presented which reflects the crossover of these two transport mechanisms as function of chamber pressure and temperature. [1] C.A. Ward, and G. Fang, Phys. Rev. E59, 429 (1999)

Actinides and Rare Earths Focus Topic
Room: 207 - Session AC+TF-ThA

The Structure, Properties and Chemistry of Thin Films of Actinides and Rare Earths
Moderator: L. Havela, Charles University, Czech Republic

2:00pm **AC+TF-ThA1 Plutonium Sorption and Reactivity at the Solid/Water Interface**, ***M. Schmidt***, *P.A. Fenter, S.S. Lee, R.E. Wilson, L. Soderholm*, Argonne National Laboratory **INVITED**

Reliable long-term predictions about the safety of a potential nuclear waste repository must be based on a sound, molecular-level comprehension of the geochemical behavior of the radionuclides. We apply *in situ* crystal truncation rod (CTR) measurements and resonant-anomalous X-ray reflectivity (RAXR) in combination with alpha-spectrometry to elucidate the sorption behavior of tetravalent actinides on muscovite under varying solution conditions.

Key retention mechanisms, particularly in clay formations, are surface mediated processes. In order to be able to understand these processes analytical techniques that allow selectively probing the mineral/water interface and elucidating processes at the interface under *in situ* conditions are required. X-ray reflectivity techniques (CTR, RAXR) have proven to be valuable tools for geochemical studies concerning the sorption behavior of metal ions [1] . More recently they have also been applied to study the sorption behavior of actinides [2] .

From CTR measurements the complete adsorption structure, consisting of adsorbed water and the ions adsorbed as inner sphere, outer sphere or extended outer sphere complex can be derived. RAXR extends this approach by providing elemental specificity to the CTR measurements, thus characterizing the contribution of a particular element to the structure.

Using a purpose-built sample cell for radiological experiments, X-ray reflectivity data was collected *in situ* from muscovite ($KAl_2[(OH,F)_2|AlSi_3O_{10}]$) in contact with the actinide-bearing solutions varying in composition (ionic strength, actinide concentration and speciation, background electrolyte). The data is complemented by precise quantitative analysis by means of alpha-counting experiments. The results clearly show the strong influence of the actinides' aqueous chemistry on their sorption behavior. It will be shown that a full description of the sorption behavior requires parameters such as the hydration enthalpy, complexation constants, hydrolysis constants, and polymer formation constants. At low actinide concentrations the formation of hydrated surface complexes is observed in good agreement with the large hydration enthalpies of the highly charged ions. At large excess of background electrolyte sorption occurs under preservation of the complexation by the anion. When a threshold metal ion concentration is exceeded sorption of polymers is observed which grow up to 150Å in size, while covering only small fractions of the surface.

1. Fenter, P., Reviews in Mineralogy and Geochemistry 2002, 49, 149-220.

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2:40pm **AC+TF-ThA3 Crystal Chemistry of Thorium Oxy Compounds Containing Tetrahedral Oxyanions**, ***A.J. Albrecht***, *P.C. Burns*, University of Notre Dame

Here we examine the crystal chemistry and structural topologies of Th compounds containing various cations that are coordinated by oxygen atoms in tetrahedral arrangements. We define the structural unit to be the part of the structure that consists of those polyhedra that contain higher valence cations, with an emphasis on their connectivity. In most cases, structures also contain interstitial units that balance the charge of the structural unit. In the compounds under study, which include both new structures and those from the literature, we find structural units ranging from clusters and chains, through sheets, to extended frameworks. The structural units in thorium compounds are of particular interest because they provide insights into the possible structures of compounds consisting of tetravalent transuranium cations, especially Np and Pu.

3:00pm **AC+TF-ThA4 Solution Route to High Quality Epitaxial Actinide Films Form Oxides to Carbides**, ***T.M. McCleskey***, *E. Bauer, A.K. Burrell, B.L. Scott, Q.X. Jia, T. Durakiewicz, J.J. Joyce, S.A. Kozimor, S.D. Conradson, R.L. Martin*, Los Alamos National Laboratory

We report on the solution based synthesis of epitaxial thin films of neptunium oxide and plutonium oxide. Actinides represent a tremendous challenge to first principle calculations of orbital energies due to the complicating features that arise from f orbital interactions. Theoretical development from first principle calculations relies on predictions of continuous materials with no boundaries. To test these theories requires experimental results using high quality single crystals. For many materials this can be a straight forward process. For actinide oxides the experimental work is complicated by the radioactivity that makes CVD processes challenging from a safety perspective and by the recalcitrant nature of the oxides. The challenge of modeling actinide oxides is best represented in Mott insulators such as UO_2. Theoretical calculations that worked with transition metals predict UO_2 to be a metal as opposed to an insulator with a 2.3 eV band gap. Recent reports predict the same metallic behavior for NpO_2. Many theoretical reports have highlighted the need for experimental work on single crystals. In the absence of single crystals they rely on work done on powders as in the case of PuO_2. We report here on epitaxial films of PuO_2 that are thin enough to measure the optical band gap directly. XRD has been used to determine the alignment of the PuO_2 relative to the substrate and EXAFS confirm the stoichiometry.

3:40pm **AC+TF-ThA6 U(VI) Uranyl Cation-Cation Interactions in Framework Germanates**, ***J.M. Morrison***, *P.C. Burns*, University of Notre Dame

The crystal structure determinations of four highly complex U(VI) germanate framework compounds reveal three distinct U(VI) sites—two that are coordinated by five equatorial oxygen atoms each to form pentagonal bipyramids and one that is coordinated by six oxygen atoms to form a distorted octahedron without the uranyl ion [1]. This is uncommon as most inorganic U(VI) compounds contain the uranyl ion, $(UO_2)^{2+}$. Also present are cation-cation interactions which occur when an oxygen atom of the uranyl ion also acts as an equatorial oxygen atom in a neighboring U(VI) polyhedron. CCIs are present in fewer than 2% of U(VI) compounds. Finally, a disordered system with the possibility of a one-dimensional GeO_5 chain has led us to suggest three structural models with regard to Ge coordination. The interesting structural and chemical complexities of these CCI-bearing compounds will be presented along with a discussion of the densities of CCI-bearing U(VI) compounds.

[1] Morrison, J.M.; Moore-Shay, L. J.; Burns, P.C. *Inorg. Chem.* **2011**, 50, 2272-2277.

4:20pm **AC+TF-ThA8 The Crystal Chemistry of Uranyl Selenates and their Relations with Uranyl Sulfates**, ***E.M. Wylie***, *P.C. Burns*, University of Notre Dame

Uranyl sulfate minerals have been studied for several decades owing to their importance in understanding ore genesis, as well as the interaction of uranium mine and mill workings with the environment. In contrast, no uranyl selenate minerals have been described, although several uranyl selenites are known. We are exploring the crystal chemistry of synthetic uranyl selenates produced under mild hydrothermal techniques. We have obtained crystals of several compounds and characterized them with single-crystal X-ray diffraction. They contain a sheet of edge-sharing uranyl pentagonal bipyramids and selenate tetrahedra that is topologically identical to those found in the zippeite group of uranyl sulfate minerals. These synthetic materials provide further insights into layered uranyl phases, including the relationships between the configurations of the structural sheets and their corresponding interlayer complexes. These structures will be placed in the context of known synthetic and natural uranyl sulfate and selenate compounds.

4:40pm **AC+TF-ThA9 Radiation-Induced Degradation of Photoluminescence in YAG:Ce**, ***S.G. Gollub***, *D.G. Walker, S.L. Weeden-Wright*, Vanderbilt University

Thermographic phosphors are ceramic based materials whose photoluminescence is temperature dependent. We fabricated the phosphor YAG:Ce to determine its sensitivity and selectivity to various radiation environments. In particular we investigated the effects of non-ionizing radiation on the photluminescent spectra. No change to the spectrum was observed after exposure to 1 MRad of x-ray radiation. Because x-rays are typically ionizing, we did not expect to see any significant degradation. When the material was bombarded with protons, which are know to cause displacement damage in many materials, a degradation was observed. Results of damage cross section and stopping power were commensurate with predicted values using SRIM. Results are shown as a function of proton energy and dose.

5:00pm **AC+TF-ThA10 The Behavior of Uranyl Peroxide Pyrophosphate Nanoscale Cage Clusters in Aqueous Solution**, ***K.L. Pellegrini**, P.C. Burns, J. Szymanowski, J. Ling, J. Qiu*, University of Notre Dame

Twenty-six nanoscale cage clusters built from uranyl polyhedra have been reported to self-assemble in aqueous solutions over a range of pH conditions [1]. All contain peroxide groups that bridge between uranyl polyhedra, and some contain additional linkages such as pyrophosphate and oxalate. The focus of the current study is the U24P12 cluster that consists of 24 uranyl hexagonal bipyramids and 12 pyrophosphate groups. We have optimized the synthesis of this cluster to obtain pure yields. Subsequently, we have examined the behavior of the cluster in solution using electrospray ionization mass spectroscopy and small angle X-ray scattering. These studies are emphasizing the persistence of this cluster under a variety of conditions, as well as their aggregation in solution. Such materials are of considerable interest because of potential applications in an advanced nuclear energy system, including in fuel recycling. Results to date show that the U24P12 cluster persists in aqueous solution for several days under a range of conditions, and can be induced to aggregate via addition of various counterions.

1. Burns, P.C. *Mineralogical Magazine*. **2011**, 75, 1-25 Open Access on petercburns.com

Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-ThA

Spectroscopic Ellipsometry for Photovoltaics, Metals and Oxide Thin Films
Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands

2:00pm **EL+AS+EM+MS+PS+TF-ThA1 Applications of Ellipsometry in Photovoltaics**, ***D. Levi***, National Renewable Energy Laboratory **INVITED**

With the growing possibility of anthropomorphic-induced climate change there has come increasing concern over energy-related emissions of carbon dioxide into the atmosphere. The search for low or no-carbon energy sources has intensified. This has lead to a twenty first century gold rush into photovoltaics research and technology startups. Although the PV industry has maintained its exponential growth rate through the global economic downturn, electricity from photovoltaics is still a long ways from economic competitiveness with fossil fuel-based electricity sources. The U.S. Department of Energy recently announced the Sunshot program, with the expressed goal of $1/Watt installed cost for utility scale PV plants by 2017. This aggressive goal will require radical advances in new and existing PV technologies.

This presentation will begin with an overview of the major PV technologies and the state of the rapidly evolving global photovoltaics industry. Photovoltaics is a natural arena for application of spectroscopic ellipsometry. Nearly all PV devices are made of multiple thin films of semiconductors and transparent conducting oxides. New materials are constantly being introduced. Film thickness, optical properties, interfaces, electronic properties, and film growth dynamics are all critical aspects of these devices and lend themselves to investigation through the use of spectroscopic ellipsometry. I will present several case studies of how we have applied spectroscopic ellipsometry in our research in photovoltaics at the National Renewable Energy Laboratory.

2:40pm **EL+AS+EM+MS+PS+TF-ThA3 Comparison between Ex Situ and Real Time Spectroscopic Ellipsometry Measurements of Structurally Graded Si:H Thin Films**, ***N.J. Podraza***, University of Toledo

Analysis of spectroscopic ellipsometry measurements of graded thin films remains challenging, although analysis procedures and software have improved over the past several decades. Practical use of these processes remains somewhat time consuming and is often not fully utilized by the casual user. In this work, ex situ ellipsometric spectra collected for static samples and real time spectroscopic ellipsometry (RTSE) measurements collected during film growth will be compared to illustrate differences in results arising from the measurement procedures and analysis. As an application, consider hydrogenated silicon (Si:H) thin films used for solar cells. Devices typically incorporate either amorphous silicon (a-Si:H) or “nanocrystalline” silicon (nc-Si:H) absorber layers, although the best “nanocrystalline” absorber layers actually consist of mixed-phase amorphous+nanocrystalline (a+nc) material. Si:H thin films may initially (i) nucleate as amorphous and remain amorphous throughout growth; (ii) immediately nucleate as nanocrystallites; or (iii) initially evolve in the amorphous regime but nucleate crystallites which subsequently grow preferentially over the surrounding amorphous material until nanocrystallite coalescence. Analysis of ellipsometric spectra collected for (i) or (ii) simply involve using a substrate / bulk film / surface roughness model and complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) for the bulk material. For (iii), RTSE is ideally used to monitor the growth of Si:H that evolves through the amorphous, nanocrystalline, and mixed-phase regimes and a virtual interface analysis (VIA) procedure is used to extract ε for the amorphous and nanocrystalline components, the bulk and surface roughness thicknesses versus time, and the nanocrystalline fraction depth profile in the (a+nc) growth regime. For (a+nc)-Si:H films only measured with a single static ex situ measurement at the end of the deposition, obtaining ε and structural parameters of the film become less precise. Specifically, sensitivity to the variation in the nanocrystallite fraction with thickness may be lost and inaccurate ε for the component materials may be obtained. This works seeks to compare the structural and optical properties of (a+nc)-Si:H obtained by RTSE and VIA with those from analysis of static ex situ spectra with models using different structures, parameterizations in ε, and spectral range restrictions. These comparisons will be used to identify appropriate structural and dielectric function models to more accurately analyze structurally graded thin films under different material and measurement circumstances.

3:00pm **EL+AS+EM+MS+PS+TF-ThA4 Real-Time Spectroscopic Ellipsometry of Cu(In,Ga)Se_2 Thin Film Deposition: Copper Transition in 3-Stage Co-Evaporation Process**, ***D. Attygalle***, University of Toledo, *V. Ranjan*, Old Dominion University, *P. Aryal*, University of Toledo, *S. Marsillac*, Old Dominion University, *R.W. Collins*, University of Toledo

With record efficiencies above 20%, Cu(In,Ga)Se_2 (CIGS) based solar cells have shown the greatest potential for success among the thin film photovoltaics technologies. Thermal co-evaporation of individual elements has proven to produce extremely high quality CIGS materials, provides a high level of flexibility, but also generates greater challenges in process optimization. The limitations of existing process monitoring capabilities, hence the challenge of correcting process fluctuations in real time, has led the industrial community toward more controllable CIGS deposition processes. Real time spectroscopic ellipsometry (RTSE) can be used successfully in the monitoring of complicated processes -- including CIGS film preparation by co-evaporation using precursor films of $(In_x,Ga_{1-x})_2Se_3$. Information extracted from RTSE includes the evolution of bulk layer and surface roughness layer thicknesses, the composition and phase, as well as the layer dielectric functions, all of which can assist in understanding the fabrication process and in optimizing solar cells. In this study, the focus is on the transitions of Cu-poor to Cu-rich CIGS and vice versa by observing the changes in (ψ, Δ) spectra obtained by RTSE. The commonly used monitoring method, which involves observing the changes in emissivity of the film, largely depends on the apparatus design, the substrate, and the bulk layer thickness. When a CIGS film is prepared by exposing a precursor film of $(In_x,Ga_{1-x})_2Se_3$ to Cu and Se fluxes, thereby becoming Cu-rich, a semi-liquid $Cu_{2-x}Se$ phase is believed to form on top of a bulk layer consisting of mixed phases of Cu(In,Ga)Se_2 and $Cu_{2-x}Se$ [1]. A multilayer optical model, with appropriate effective medium approximation layers to represent this scenario, has shown good agreement with the observed (ψ, Δ) spectra. Since RTSE is highly sensitive to monolayer-level changes in the top-most layer, RTSE gives superior sensitivity in Cu-rich to Cu-poor end point detection, which occurs when the top $Cu_{2-x}Se$ phase drops below detectable limits. Furthermore this method is less affected by the substrate and bulk layer thickness. Although careful analysis of RTSE can give a wealth of information about CIGS material properties and their evolution, this type of end point detection can be successful simply by monitoring the real time changes in the (ψ, Δ) spectra.

[1] J. AbuShama, R. Noufi, Y. Yan, K. Jones, B. Keyes, P. Dippo, M. Romero, M. Al-Jassim, J. Alleman, and D.L. Williamson, "Cu(In,Ga)Se_2 Thin-film evolution during growth from $(In,Ga)_2Se_3$ precursors", *Mat. Res. Soc. Symp. Proc.* paper H7.2.1, (2001).

3:40pm **EL+AS+EM+MS+PS+TF-ThA6 Bulk Hetrojunction Solar Cell Characterization by Phase Modulated Spectroscopic Ellipsometry**, ***K. Uppireddi**, L. Yan*, HORIBA Scientific

The blend morphology, phase separation as well as crystallinity of organic photovoltaic solar cell are important properties to increase the efficiency. The performance of such cells is strongly influenced by blend composition and thermal annealing conditions. In this work we demonstrate the use of ellipsometry as a powerful and sensitive metrology means of monitoring organic solar cell based on the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-buytric acid methyl ester (PCBM). Ellipsometric measurements were performed on P3HT/c-Si, PCBM/c-Si and P3HT:PCBM/c-Si at an angle of incidence of 70 degree, across the spectral

range 190 – 2100 nm (0.6-6.5 eV). Two different analysis protocols were used to model the P3HT:PCBM blend structure. In the first protocol effective medium theory was used to represent the optical constant of layer, where as in the second one the blend was treated as one single homogenous material. The approach renders investigation of final morphology and composition.

4:00pm **EL+AS+EM+MS+PS+TF-ThA7** ***In Situ* Spectroscopic Ellipsometry during Atomic Layer Deposition of Pt, Pd and Ru**, ***N. Leick**, J.W. Weber, M.J. Weber, A.J.M. Mackus, H.C.M. Knoops, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The precise thickness control of atomic layer deposition (ALD) and its conformal growth make ALD the method of choice for nanometer thin film deposition. Platinum-group metals such as Pt, Pd and Ru have many applications in the areas of nanoelectronics and catalysis and recently there has been considerable interest to deposit films of these materials by ALD. Spectroscopic ellipsometry (SE) is a powerful, noninvasive optical technique that can be used *in situ* during ALD to precisely monitor the thickness of the films. SE also provides information on the optical and electrical properties of the films which is very relevant for their applications. Choi et al. [1] previously investigated the dielectric functions of Pt-group metal films with a thickness of ~400 nm as prepared by physical vapor deposition. For the aforementioned applications, however, the films are required to be much thinner, which leads to differences in film morphology as well as to dielectric functions that can be different from those of bulk films. In the spectroscopic ellipsometry work to be presented in this contribution we have therefore focused on films with thicknesses from 5 nm to 35 nm. *In situ* data was obtained during ALD in the photon energy range of 0.7 – 6.5 eV. Using a Kramers-Kronig consistent B-spline model to account for the thickness-dependent dielectric functions, we were able to obtain accurate ALD growth-per-cycle values for Ru, Pt and Pd (1.00 ± 0.06 Å, 0.47 ± 0.04 Å, 0.14 ± 0.02 Å). Furthermore, the contributions from free-carriers (Drude term) and interband absorptions (Lorentz-oscillator contributions) were investigated by combining the SE data with FT-IR reflectance data such that the photon energy range of 0.04 eV – 6.5 eV was covered. In this range, it was possible to represent each film with a unique Drude-Lorentz model although some ambiguities about the Lorentz oscillator contributions remained in the case of Ru. It will be shown that the extracted thicknesses and electrical resistivities from this model are in line with data obtained from X-ray reflectometry and four-point probe measurements (for example Ru: ρ_{SE} ~23 μΩ.cm and ρ_{FPP} ~16 μΩ.cm). Furthermore, in the case of Ru also the influence of the film roughness will be addressed.

[1] Choi *et al.*, Phys. Rev. B **74**, 205117 (2006)

4:20pm **EL+AS+EM+MS+PS+TF-ThA8 Manipulating the Optical Properties of Metals: Sculptured Thin Films Coated by Atomic Layer Deposition**, *D. Schmidt, N. Ianno, E. Schubert,* ***M. Schubert***, University of Nebraska - Lincoln

The fabrication of three-dimensional metal nanostructures with tailored geometry is one of the central challenges of nanotechnology because geometrical and material parameters are responsible for the optical, electrical, mechanical, chemical, or magnetic properties of such nanostructured thin films. Engineered artificial sculptured thin films (STFs) with designed anisotropies are potential candidates for applications in various fields such as optics, magneto-optics, as well as chemical and biological sensing and detection. However, in order to utilize metallic nanostructures for novel applications their size-, structure-, and material-driven physical properties have to be understood and quantified.

We utilize glancing angle electron-beam deposition, which exploits physical atomic-scale shadowing and dynamically varying particle flux azimuth for fabrication of three-dimensional highly spatially coherent STFs with different morphologies. Subsequently, nanostructures are individually covered with a thin conformal coating (cladding) by means of atomic layer deposition (ALD).

We will present the anisotropic optical properties of highly anisotropic ALD coated metal STFs determined by generalized spectroscopic ellipsometry in the visible and near-infrared spectral region. The analysis of our multilayer slanted columnar thin films deposited at glancing angle (θ_i = 85°) revealed that such STFs possess monoclinic optical properties, and the optical response may be described by an effective medium dielectric homogenization approach. It will be discussed how the anisotropic Bruggeman effective medium approximation (AB-EMA) allows for determination of structural parameters as well as fractions of individual film constituents. Furthermore, the AB-EMA analysis reveals that the anisotropic dielectric properties of the metal core changes upon deposition of a dielectric cladding.

4:40pm **EL+AS+EM+MS+PS+TF-ThA9 Ellipsometric Characterisation of Porous Aluminium Oxide Supports**, *W. Ogieglo, N.E. Benes,* ***H. Wormeester***, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Porous aluminium oxide is widely used as a support material for thin film inorganic micro- and mesoporous membranes. Such membranes are used in energy-efficient gas separation, pervaporation and nanofiltration processes. Ellipsometry can be used to determine material properties of the thin membrane films, as well as the penetrant loading [1]. Interpretation of the ellipsometry data requires a detailed knowledge of the porous aluminium oxide support. This support is made of aluminium oxide particles that are sintered together. In between the particles voids are present that amount to 38% porosity. We have studied the influence of the size of the voids on the optical response of the support material. For this study, voids with a diameter of around 60, 80 and 160 nm were used. We noted a strong decrease of the normal incidence specular reflection with void size and a subsequent increase in off specular reflection. In ellipsometry, only a limited depolarization of the specular reflected light was noted in the wavelength range between 300 and 1750 nm. The angle dependent ellipsometry measurements showed that the optical properties of these supports can not be obtained from a direct inversion. The reason for this is that at the interface the more or less spherical voids are cut, which leads to a distribution of openings at the surface, i.e., a substrate with a very rough surface. This roughness was modelled with a graded porosity changing from 38% in the bulk to 75% at the outer surface. This measured variation in porosity is very similar to the cumulative height distribution of the surface layer obtained from AFM. The validity of this graded porosity model was verified from the analysis of a sample with a thin polysulfone (PSU) layer deposited on the support. The PSU layer partly fills the open pores at the surface. This results in an interface with a graded variation in aluminium oxide, void and PSU.

The proper treatment of the surface layer also provides the optical properties of the porous aluminium oxide bulk material itself. These optical properties can in a limited wavelength range be modelled with Bruggeman's effective medium approximation. As a consequence of the size of the inclusions, their diameter is no longer negligible with respect to the wavelength of light in the UV part of the spectrum. For the material with the largest pore size, also a large part of the visible range has to be excluded. A more elaborate approach than the standard effective medium approach has to be used in this case.

[1] H. Wormeester, N.E. Benes, G.I. Spijksma, H. Verweij and B. Poelsema

Thin Solid Films **455-456**, 747-751 (2004)

5:00pm **EL+AS+EM+MS+PS+TF-ThA10 Optical Properties and Structure of Vanadium Oxide Thin Films**, ***M.A. Motyka**, M.W. Horn,* Pennsylvania State University*, N.J. Podraza*, University of Toledo

Vanadium oxide (VO_x) thin films are common materials used as imaging layers in uncooled microbolometer based thermal imaging devices. These films are used in this application largely due to the controllable resistivity of the film (ρ), the high temperature coefficient of resistance (TCR), and the low electrical noise. One of the main difficulties of this material system relates to the multiple valence states of vanadium, each of which results in materials with different electrical properties. Bolometer quality VO_x may consist of a composite of nanocrystalline face centered cubic (FCC) VO phase and amorphous materials. The thin film oxygen content via Rutherford back scattering (RBS) has suggested that the typical ratio V:O should be near 1:1.7-2.0, significantly higher than the stability window of the FCC phase. This off-stoichiometry ratio suggests that the amorphous material is a mixture of higher oxygen valence states similar to V_2O_5 and VO_2. The higher quality VO_x thin film material also has been observed via transmission electron microscopy (TEM) to contain VO/V_2O_3 nano-twin crystalline domains. The presence of each of these phases impacts the electrical and optical properties of the resulting VO_x film. Films with various oxygen contents and structures were studied with spectroscopic ellipsometry (SE) over a spectral range of 0.05 to 5.15 eV using a multichannel dual rotating compensator near-ultraviolet to near infrared instrument in conjunction with Fourier transform infrared spectroscopic ellipsometry (FTIR-SE). Thus, the complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) can be obtained for these materials over the full spectral range. Differences in ε due to variations in the film structure are observed as functions of processing, indicating that SE is a means of probing the material composition and structure. Specifically, ε are compared for various film composites fabricated by unbiased pulsed DC magnetron sputtering as well as composite films prepared by reactive ion beam sputtering and pulsed DC magnetron sputtering with a substrate bias. The microstructure and ε are correlated with films exhibiting the desirable device electrical properties. In situ real time spectroscopic ellipsometry (RTSE) has shown that environmental conditions alter the as-deposited VO_x thin films grown via pulsed DC-magnetron reactive sputtering of a metallic vanadium target. In order to prevent undesired atmospheric effects to the thin film, it is a

common practice to encapsulate the thin film with a more environmentally stable material. In this study, the material chosen was SiO_2 grown in the same deposition chamber, pre-atmospheric exposure, via rf sputtering.

5:20pm **EL+AS+EM+MS+PS+TF-ThA11 Sensitivity of Dielectric Properties of Vanadium Dioxide Thin Films to Growth Conditions**, *D.W. Ferrara, **R.E. Marvel**, J. Nag, R.F. Haglund*, Vanderbilt University

Vanadium dioxide (VO_2) is a strongly-correlated electron material with a well-known semiconductor-to-metal transition (SMT) that can be induced thermally (T_c = 68°C), optically, or electrically. Recently, VO_2 films have attracted attention as a component in active metamaterials, especially in conjunction with metal nanostructures. Since these structures are highly sensitive to the dielectric properties of the embedding material, the SMT of VO_2 can be used to tune the optical response of the structure. Accurately modeling the behavior of these structures requires detailed knowledge of the dielectric function of VO_2 as it undergoes the SMT; however, previous measurements of the optical constants of VO_2 reveal significant variations between experiments.

To understand systematic variations due to growth conditions, films of VO_2 were deposited on either silicon, glass, or sapphire substrates by pulsed laser ablation of vanadium metal targets in 10 mTorr oxygen (O_2) background gas, followed by annealing at 450°C in 250 mTorr of O_2. Anneal times were varied from 30 to 90 depending on film thickness; deposition thickness was varied from 20 nm to 200 nm. For each sample, temperature-dependent spectroscopic ellipsometry measurements at optical and near-infrared wavelengths were conducted to determine the dependence of the optical constants on film thickness, substrate and crystallinity, and temperature.

Bruggeman and Maxwell-Garnett effective-medium formulations were used to account for three constituent materials: semiconducting VO_2, metallic VO_2, and vanadium pentoxide (V_2O_5). The effective dielectric functions were modeled using Lorentz and Tauc-Lorentz oscillators. Our results show that the contribution of V_2O_5 to the effective dielectric function increases with annealing time, consistent with previous studies. The results are also substantiated using Rutherford backscattering, X-ray photoelectron spectroscopy and X-ray diffraction.

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+TF+NS-ThA

Graphene Nanoribbons and Related Structures
Moderator: Y.J. Chabal, University of Texas at Dallas

2:00pm **GR+TF+NS-ThA1 Rationally Patterned Large-Area Semiconducting Graphene Materials from the Top-Down and the Bottom-Up**, *N. Safron, M. Kim, P. Gopalan, **M. Arnold***, University of Wisconsin-Madison **INVITED**

We are experimentally investigating self-assembling lithography (e.g. block co-polymer and nanosphere lithography) to create nanostructured graphene materials with feature sizes below what is easily achieved using optical and electron-beam lithography (< 20 nm), with the motivation of opening up a technologically relevant band gap in graphene. We are particularly interested in a novel form of semiconducting graphene that we call nanoperforated graphene, which consists of graphene perforated by regular hexagonal arrays of nanoscale holes. Unlike nanoribbons, nanoperforated graphene advantageously retains a large-area two-dimensional form factor. In this talk, we will discuss the inter-relationship between the physical structure of nanoperforated graphene and its electronic properties, with specific emphasis on how its band gap experimentally varies with feature size and how charge transport is affected by structure (including the role of edge defects and the observation of single-electron charging effects). We will also report on efforts in our group to realize nanostructured graphene materials with well controlled edge structure and superior properties via scalable and rationally controlled bottom-up growth that avoids top-down etching without sacrificing arbitrary pattern forming ability.

2:40pm **GR+TF+NS-ThA3 Quantum Pumping in Graphene Nanoribbons**, ***T. Kaur***, Ohio University, *L. Arrachea,* Universidad de Buenos Aires, Argentina, *N. Sandler*, Ohio University

The interest in the development of devices at the nanoscale has intensified the search for mechanisms that provide tailored control of transport properties while reducing effects of heat dissipation and contact resistance. For instance, *charge pumping* is one of the current generating methods that allows for minimizing the effects of contact resistance. *Charge pumping* is the mechanism used to generate DC currents in open-quantum systems by applying local de-phased time-dependent potentials.

We analyze the properties of non-equilibrium zero-bias current through nano-ribbons using tight-binding Hamiltonians and the *Keldysh formalism*. This theoretical treatment, based on non-equilibrium Green's function techniques, is the most appropriate one to address questions for systems in non-linear, out of equilibrium conditions. We develop a numerical implementation for the models described below in a wide range of non-equilibrium regimes.

After reviewing results for quantum pumping in a one-dimensional chain attached to two reservoirs, with two local single-harmonic potentials oscillating in time, we study finite-width ribbons of square and graphene lattices. The transmission function reveals the value of the *resonant frequency* and explains how the quantum charge pumping works. We analyze the dependence of the *DC current* as a function of different parameters such as chemical potential, pumping amplitude, frequency, etc. In addition, the role of reservoirs is fully described. Pumped currents can also be generated by application of laser fields. We present the comparison between these two pumping methods. Possible extensions for disordered systems will be discussed.

3:00pm **GR+TF+NS-ThA4 First-principles Study of Field Emission from Graphene Nanoribbons**, ***J. Driscoll***, *K. Varga*, Vanderbilt University

A real-space, real-time implementation of time-dependent density functional theory [1,2,3] is used to study electron field emission from graphene nanoribbons. The structures are shown to be good field emitters with spatial variation of the emission current influenced by the presence of passivating hydrogen. The nanoribbons are seen to produce slightly lower currents than nanotubes formed from the ribbons. Spin-polarized field emission from carbon nanotubes has been calculated with and without Fe adsorbates (atoms and clusters). It was observed that various adsorbates cause the separation of density into spin-polarized regions. The calculations predict that carbon nanotubes with various adsorbates can be used as spin-polarized current sources. The spin-polarized results for nanotubes will be compared to similar

calculations for graphene nanoribbons.

References

[1] J.A. Driscoll and K.Varga, Phys. Rev. B 80, 245431 (2009).

[2] J.A. Driscoll, S. Bubin, W. French, and K. Varga (submitted).

[3] J.A. Driscoll, B. Cook, S. Bubin, and K. Varga (submitted).

Acknowledgments

This work is supported by NSF grant CMMI0927345.

3:40pm **GR+TF+NS-ThA6 Quantum Transport Properties of Modified Graphene Nanoribbons with Boron Nitride Domains at the Nanoscale**, ***A. Lopez-Bezanilla***, Oak Ridge National Laboratory

Carbon-based systems are being widely investigated as potential candidates for nanoelectronic interconnects and transistors. The control of electric current is, therefore, an important challenge in nanostructures engineering. The possibility of creating hybrid one-atom thick layers containing C, B and N atoms have attracted much attention as they can provide an efficient way to create new materials with properties complementary to those of graphene and h-BN.

Here we present a theoretical methodology and study of charge transport through GNRs with BN domains randomly distributed along the ribbon surface. We resort to both first principles calculations, to obtain a suitable parametrization of the electronic structure, and a transport approach based on the ab initio results to explore conduction regimes through large and disordered systems. The quantum transport modeling is based on the Green's function formalism, combining an iterative scheme for the calculation of transmission coefficients with the Landauer's formula for the coherent conductance.

Our results describe how the conductance of the hybrid systems is altered as a function of incident electron energy and BN domain density. We explore the transport regimes comparing different degrees of BN doping and BN domain size for ribbons of various widths and lengths on the order of the micrometer. A comparison with other types of defects such as atoms in epoxy configuration and functional groups covalently attached to the ribbon surface will be also discussed.

4:00pm **GR+TF+NS-ThA7 Simple and Scalable Route for the 'Bottom-Up' Synthesis of Few-Layer Graphene Platelets and Thin Films**, ***K. Coleman***, University of Durham, UK

Graphene has generated much interest owing to its exceptional electronic properties and high mechanical strength. This has enabled new types of electronic devices and composite materials to be envisaged. The main problem is the availability of the material and the difficulties associated

with its synthesis. Here we present a simple, convenient and scalable chemical vapour deposition method involving metal alkoxides in ethanol to produce few-layer graphene platelets. The graphene platelets have been fully characterised using TEM, SEM, AFM, XPS and XRD. The methodology used has the added flexibility in that it can be used to grow conducting transparent thin films on inert substrates such as silicon wafer and quartz glass. Importantly, no heavy metal catalysts were required to produce the few-layer graphene platelets or graphene films and all non-carbon by-products are soluble in water.

4:20pm **GR+TF+NS-ThA8 Approaching the Intrinsic Bandgap in Suspended High-Mobility Graphene Nanoribbons**, *M.-W. Lin, C. Ling,* Wayne State University, *L.A. Agapito, N. Kioussis,* California State University Northridge, *Y. Zhang, M.-C. Cheng,* Wayne State University, *W.L. Wang, E. Kaxiras,* Harvard University, ***Z.X. Zhou***, Wayne State University

We report the first variable-temperature electrical-transport study of suspended ultra-low-disorder GNRs with nearly atomically smooth edges. Suspension of the GNRs not only removes the substrate influence but also allows a thorough removal of impurities, including those trapped at the interface between the GNR and the substrate, leading to a substantial increase of the carrier mobility. We observe high mobility values over 3000 $cm^2 V^{-1} s^{-1}$ in GNRs that are ~ 20 nm wide, the highest reported to date on GNRs of similar dimensions. Furthermore, we demonstrate that the activation gap extracted from the simple activation behavior of the minimum conductance and residual carrier density at the charge neutrality point approaches the intrinsic bandgap in ultra-low-disorder GNRs. Comparison of the bandgap values of multiple samples shows that the bandgap in our ultra-low-disorder samples is approximately inversely proportional to the ribbon width, consistent with theoretical predictions. On the other hand, non-negligible disorder in GNRs obscures the observation of the intrinsic bandgap in transport measurements. In addition, the size of the bandgap derived from the transport measurements is in *quantitative* agreement with the results of our complementary tight-binding calculations for a wide range of chiral angles characterizing the GNR structure, suggesting that the underlying electronic origin of bandgap enhancement is the magnetism of the zigzag edges.

4:40pm **GR+TF+NS-ThA9 Fabrication of Polymer-Protected Graphene Nanoribbons by Thermal Dip-Pen Nanolithography (tDPN)**, ***W.K. Lee****, J.T. Robinson, R. Stine, A.R. Laracuente,* Naval Research Laboratory, *W.P. King,* University of Illinois at Urbana Champaign, *P.E. Sheehan*, Naval Research Laboratory

The lithographic patterning of graphene nanoribbons (GNRs) to engineer band gaps has gained much attention as one path to realizing graphene-based devices. We employed thermal dip-pen nanolithography (tDPN)[1] to pattern GNRs on CVD single-layer graphene (SLG) that had been transferred onto a SiO_2 substrate. In tDPN, a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. tDPN has been successful at depositing polymers ranging from semiconductors to insulators on a variety of surfaces. To create the nanoribbons, we deposited polystyrene (PS) ribbons via tDPN on a SLG film between the source and drain electrodes. The areas of the graphene not protected by the polymer were then modified to isolate thin graphene nanoribbons. We show that the PS protected ribbon was the only conductive pathway for active device. This method allows a wide range of nanoribbon widths to be created and avoids electron beams which can damage graphene. The impact of the polymer choice on conductivity as well as the choice of isolation will discussed. For instance, we find that the PS ribbon can serve not only as an etch mask to pattern GNRs but also a stable dopant layer. The detailed fabrication and characterization of these structures will be presented.

1. WK Lee, et al. (2010) "Maskless Nanoscale Writing of Nanoparticle-Polymer Composites and Nanoparticle Assemblies using Thermal Nanoprobes", *Nano Letters, 10, 129*

5:00pm **GR+TF+NS-ThA10 Edge Termination of Modified Graphene Oxide during Thermal Exfoliation**, ***M. Acik****, *Y.J. Chabal*, The University of Texas at Dallas

Nanopore formation in carbon materials (e.g. exfoliated nanostacks of graphite) has been widely studied through mechanical exfoliation, intercalation, electrochemical separation, chemical or thermal exfoliation of graphite oxide (GO) via expansion with partial oxygen removal. Amongst all these methods, exfoliation of modified graphene (GO), a solution-processable precursor compound where aromatic and heterocyclic rings with embedded oxygen functionalities exist, by thermal processing still remains elusive for the following reasons: (1) poor control of GO composition (initial oxygen content), (2) poor understanding of the chemical composition, (3) unknown role of oxygen, adjoining oxygen interactions, and edge termination with oxygen. Infrared absorption spectroscopy coupled with *in-situ* thermal annealing process [1] makes it possible to examine the chemical changes taking place during thermal reduction to identify and understand interacting molecular environment and the edge functionalization. To unravel the complex mechanisms leading the removal of oxygen in GO, we have performed *in-situ* transmission infrared absorption spectroscopy (IRAS) measurements of graphene/graphite oxide (GO) thin and bulk films upon thermal annealing (60-850°C) in vacuum (10^{-3}-10^{-4} Torr). Control of the edge geometry of finite-sized modified graphene flakes depends very much on the control of the processing methods. This edge reconstruction further determines electronic, electric, optical and mechanical properties of the exfoliated modified graphene flakes. Therefore, we not only perform studies deriving a thermal reduction mechanism, but also examine the edge reconfiguration with oxygen. We report here the observation of a surprisingly strong IR absorption band that occurs only upon thermal reduction of GO. After annealing at 850°C in vacuum, the strong enhancement of the new IR active absorbance band is observed at ~800 cm^{-1}[2]. The intensity of this band is 10-100 times larger than what is expected for the oxygen content of the reduced GO, namely between 5 and 8 at.%. This band is assigned to a specific oxidation state, involving oxygen located in the basal plane (forming C-O-C bonds) and at *atomically straight* edges of reduced graphene. The large enhancement in IR absorption is attributed to the direct participation of electrons, induced by the asymmetric C-O-C stretch mode displacement. These findings open new possibilities in the field of nanoelectronics for all sensor and energy storage applications. [1] M. Acik, *et al.* J. Am. Chem. Soc. (2011), *in preparation*. [2] M. Acik, *et al.* Nat. Mater. 9, 840-845 (2010).

5:20pm **GR+TF+NS-ThA11 Study of Ridges on Epitaxial Graphene on 6H-SiC(0001)**, ***Y.Y. Li****, Y. Liu, L. Li*, University of Wisconsin-Milwaukee

The graphitization of hexagonal SiC surfaces provides a viable alternative for the synthesis of wafer-sized graphene for mass device production. During the later stages of growth, ridges are often observed on the graphene layers as a result of bending and buckling to relieve the compressive strain between the graphene and SiC substrate, which also introduce ripples in the otherwise atomically flat graphene sheet. In this work, we show, by atomic resolution STM imaging, that ridges are in fact bulged regions of the graphene layer, forming one-dimentional (nanowire) and zero-dimentional (quantum dot) nanostructures. We further demonstrate that their structures can be manipulated and even new ones created by the pressure exerted by the STM tip during imaging. These results and their impact on the electronic properties of epitaxial graphene on SiC(0001) will be presented at the meeting.

Thin Film Division
Room: 110 - Session TF+EM+SS-ThA

Applications of Self Assembled Monolayers
Moderator: M.R. Linford, Brigham Young University

2:00pm **TF+EM+SS-ThA1 Organic Monolayers on Silicon-rich Substrates: Methods and Mechanisms**, ***H. Zuilhof***, Wageningen University, Netherlands **INVITED**

SAMs on silicon-containing substrates including silicon, silicon nitride and glass widely expand the applicability of such materials. The presentation will focus on 3 recent developments:

1) The surface modification of H-terminated Si has functioned as a stepping-stone for the construction of a wide-range of hybrid materials. Recent synthetic improvements and detailed mechanistic studies have shown how to optimally construct such modified substrates. These results will be presented in the light of further developments.

2) Silicon nitride can be modified by covalent SAM attachment to achieve chemically highly robust systems. Biofunctionalization thereof with oligosaccharides and antibodies provides novel diagnostic applications in terms of specific bacterial capture in combination with generally antifouling substrates when combined with lithographic structuring of the material. Proof-of-principle and remaining challenges will be demonstrated based on recent experimental progress.

3) A photochemical method we recently developed to modify glass (SiO2), and the application thereof within the field of modified glass microchannels will be shown, e.g. via the on-chip embedding of enzymatic cascade reactions using a combination of local SAM attachment and DNA-enzyme hybrids. Finally, generalizations to the modification of other oxidic surfaces will be provided.

* Morton S. Traum Award Finalist

Key references:

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2:40pm **TF+EM+SS-ThA3 Molecularly Modulated Electrical Transport at Chemically Passivated Silicon Surfaces**, ***G. Dubey***, NRC-SIMS, Canada, *F. Rosei*, INRS-EMT, Canada, *G.P. Lopinski*, NRC-SIMS, Canada

Adsorption of charged or polar species on semiconductor surfaces can modulate the electrical properties through long-range field effects. Hydrogen-terminated silicon-on-insulator (SOI-H) is an interesting model system for investigating this sensitivity to surface processes [1,2]. Accumulation mode SOI-H pseudo-MOSFETs [3] have been used to probe molecular adsorption and reaction events. Current-voltage characteristics of such *n*-channel devices are found to be sensitive to the environment, with the accumulation threshold voltage, or flat-band voltage (V_{FB}), exhibiting large reversible changes upon cycling between ambient atmosphere, high vacuum ($<10^{-5}$ Torr) and exposure to water and pyridine vapour at pressures in the torr range. Both these adsorbates act as effective electron donors, shifting the flat band potential to more negative values. The field-effect mobility is found to be comparatively less affected through these transitions. Adsorption of the well known electron acceptor tetracyanoethylene (TCNE), is shown to cause depletion, with ppm levels of TCNE vapour in ambient atmosphere found to rapidly decrease the saturation current by over two orders of magnitude. The effect is only partially reversible on the hydrogen terminated surface, due to the accumulation of strongly bound TCNE molecules on the surface. In addition, oxidation of the H-terminated surface is seen to result in irreversible shifts in both the flat-band voltage and field-effect mobility. In order to passivate the surface from these irreversible processes, a photochemical gas phase reaction [4] with decene was used to form a decyl monolayer on the SOI(100)-H surface. Formation of this monolayer is found to result in a relatively small shift of threshold voltage and only a slight degradation of the field effect mobility. Decyl passivation only slightly decreases the response of the FET to TCNE adsorption while significantly improving the reversibility of the response. These results suggest that alkyl monolayer dielectrics formed by the gas phase photochemical method can function as good passivating dielectrics in field effect sensing applications.

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3:00pm **TF+EM+SS-ThA4 Micrometer- and Nanometer-Scale Patterning of Azide-Functionalized Self-assembled Monolayers on Gold and Aluminum Oxide Surfaces**, ***O. El Zubir***, *I. Barlow, G. Leggett, N. Williams*, University of Sheffield, UK

Self-assembled monolayers (SAMs) have been prepared by the adsorption of [11-(4-azido-benzoylamino)-undecyl] phosphonic acid on aluminum oxide and by the adsorption of 11-(4-azido-benzoylamino)-undecylthiol. Exposure to near UV radiation causes elimination of nitrogen and the creation of a reactive nitrene species. Quantitative studies by X-ray photoelectron spectroscopy (XPS) and contact angle measurement show that the reaction is complete after an exposure of 20 J cm–2. The reaction enables selective introduction of primary amines to the surface. By exposure of the azide under a solution of the amine, derivatization may be carried out with high efficiency, providing a simple pathway for the creation of a variety of multiple-component surface chemical patterns. Micropatterned surfaces were fabricated by exposure the SAMs to UV-laser (λ=325 nm) through a mask in presence of amines. Photopatterning was carried out at the nanometer scale by using scanning near-field photolithography (SNP) in which a scanning near-field optical microscope (SNOM) coupled to a UV laser (λ=325 nm) is utilized as the light source. Selective modification of azide terminated monolayers on aluminum oxide by protein-resistant molecules enabled the fabrication of protein nanopatterns that could be imaged by fluorescence microscopy.

3:40pm **TF+EM+SS-ThA6 Free-standing, SAM-based, Hybrid Biocompatible Nanomembranes for Biological Applications**, ***N. Meyerbröker***, *W. Eck, M. Zharnikov*, Universität Heidelberg, Germany

Functional monomolecular films - so-called self-assembled monolayers (SAMs) - represent a broad platform for nanofabrication, sensor design, and molecular electronics, as well as a framework for Chemical Lithography, and a model system for organic interfaces and molecular, macromolecular and biological assemblies. These films can be prepared on different substrates which provide necessary support and guarantee the persistence of the 2D molecular assembly. Since the intermolecular interaction within the SAMs is relatively weak, such films cannot exist without support, dissipating into the individual constituents upon the separation from the substrate. However, as far as the individual molecules within a SAM can be cross-linked extensively by physical means such as electron irradiation, the resulting quasi-polymer film can be separated from the substrate and exist as a free-standing monomolecular membrane on its own. In this presentation we describe the formation of such free-standing membranes on the basis of aromatic SAMs. In contrast to the previous work, we used not only non-substituted but nitro- and nitrile-substituted SAM constituents which, due to either nitro-to-amine or nitrile-to-amine transformation, become chemically reactive after the irradiation treatment and can be subsequently coupled to further species. As such species we used oligo(ethylene glycol)-based molecules with a specific anchor group providing the coupling to the amine groups of the monomolecular template. After the attachment, these templates and respective hybrid membranes become protein-repelling and as such can be used as a non-disruptive and highly transparent support for proteins and cells in transmission electron microscopy (TEM) experiments. Whereas the ultimate thinness of this support guarantees a high imaging quality, protein-repelling ensures the lack of protein denaturing, which extents essentially the possibilities of TEM experiments in their specific application to sensitive biological targets.

4:00pm **TF+EM+SS-ThA7 Development of Nanoscale Heterostructures: From Single Component Nanostructures to Multicomponent Nanosystems**, ***N. Chopra***, The University of Alabama, Tuscaloosa **INVITED**

Chemical vapor deposition (CVD) and solution synthesis was coupled to realize a unique surfactant-free approach for the direct nucleation of nanoparticles on 1-D nanostructures. Towards this end, skeleton nanostructures such as carbon nanotubes and oxide nanowires were successfully utilized as a selective nucleation sites for nanoparticles. Carbon nanotubes (CNTs)–Ni/NiO nanoparticles and oxide nanowires -(Au or Co_3O_4) nanoparticles were synthesized. Morphological evolution of nanoparticles as a function of various growth parameters was studied using TEM, SEM, and XRD. New kinds of lattice relationships, interfaces, and morphologies were established. For example, CuO nanowire-Co_3O_4 nanoparticles showed unique optical characteristics leading to enhanced absorbance in visible light. Growth mechanisms of heterostructures revealed various competing phenomena at nanoscale including thermodynamic stability and chemical potential, and surface migration of nanoparticles on high curvature 1-D nanostructures as opposed to flat surface. These heterostructures also hold great promise as novel sensors and energy technologies.

4:40pm **TF+EM+SS-ThA9 Physical and Electrical Characterization of Metal Incorporated SAM-based Molecular Electronic Junctions**, ***S. Pookpanratana***, *M.A. Walsh, C.A. Richter, C.A. Hacker*, National Institute of Standards and Technology

Molecular electronics is attractive for next-generation applications because of the flexibility in tailoring the organic functionality and the facile formation of uniform monolayers by using thiol-Au chemistry for self-assembly. Added functionality can be achieved by using thiol self-assembled monolayers (SAMs) containing terminal carboxylic acid functional groups to chelate with metal ions [1], and thus can incorporate d-orbital transition metals with the SAMs. One challenge in molecular electronics has been the reliable formation of a top contact to the organic layer. Fabrication techniques involving metal evaporation of the top contact often result in penetration to the substrate [2] or into the SAM [3], either of which influences the measured electrical properties across the junction. Here, we utilize flip chip lamination (FCL), a soft metallization technique by nanotransfer printing, to form a top contact onto SAMs on Au [4].

Based on previous work by Ulman et al. [5] and Allara et al. [6], we have incorporated metal ions (Cu and Ni) with mercaptohexadecanoic acid (MHA) and formed a molecular junction by FCL. SAMs of MHA were prepared on Au on Si and Au on polyethylene terephthalate (PET) substrates. The MHA/Au/Si was exposed to metal ion (M) containing solution. The M-MHA/Au/Si samples were then laminated to MHA/Au/PET to create a 'molecular sandwich' which resulted in the

following structure: PET/Au/MHA-M-MHA/Au/Si where the PET substrate is removable.

The SAMs on Au were investigated by using X-ray photoelectron spectroscopy (XPS) and p-polarized reflection absorption infrared spectroscopy (p-RAIRS), and both methods confirm the initial presence of carboxylic acid on the (pre-FCL) surface. Successful incorporation of metal ions into the SAM were directly confirmed by XPS (occupying 30-50% of the –COOH sites), and indirectly by p-RAIRS with the appearance of C=O bands in an acid salt environment. Electrical and physical characterization (using backside p-RAIRS and near edge X-ray absorption fine structure (NEXAFS)) measurements to investigate the monolayer after FCL are currently ongoing. With these results, we are able to obtain a thorough picture linking electrical properties with physical characterization of the buried molecular junctions.

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5:00pm **TF+EM+SS-ThA10 Examining the Role of Laminin-Derived Peptides in Neuronal Attachment**, ***N.A. LaFranzo**, J.A. Maurer*, Washington University in St. Louis

Laminin-1 is a 900kD glycoprotein that is a major component of the extracellular matrix (ECM). Laminin is known to be involved in many cellular processes including cell adhesion, migration and differentiation *in vivo* and is often used in *in vitro* experiments to encourage neuronal attachment. While laminin contains some integrin-receptor binding sites, multiple domains on the protein including the peptide sequences IKVAV, YIGSR and RGD have also been shown to bind to non-integrin neuronal receptors, encourage cell adhesion, and encourage neurite outgrowth in the absence of the full protein structure. However, previous experiments performed using these peptides as substrates for neuronal culture fail to consider the effects of excretion of the cells own ECM proteins onto the surface, which we have shown can occur on surfaces with high peptide concentrations. By utilizing self-assembled monolayers (SAMs), we have created a substrate that prevents the non-specific adsorption of proteins excreted by neurons, while introducing a low-concentration of the peptide sequences to encourage neuronal attachment.

A pair of alkane-thiol monomers for assembly on a gold substrate have been designed which contain a tetra-ethylene glycol moiety at the tail to prevent the non-specific adsorption of proteins. One of the monomers is terminated with an azide moiety that can be used to specifically attach molecules with an alkyne group by a copper-mediated azide-alkyne cycloaddition (CuAAC) reaction, also known as the "click" reaction. By introducing 5-pentynoic acid at the N-terminus of each of the peptides during synthesis, we have introduced a bioorthogonal attachment point for reaction with the azide-terminated monomers on the surface. Once prepared, these surfaces have been confirmed to be resistant to adsorption of proteins by quartz-crystal microbalance (QCM) experiments. Primary culture neurons dissected from embryonic mice have been cultured on the surface and the effects of the peptides on neurite outgrowth have been quantified. To better understand the role of these peptides in cell adhesion, neurons transfected with a plasmid encoding EGFP-vinculin or EGFP-paxillin have been cultured on the surface and the focal adhesion morphologies have been observed in live-cell imaging experiments. These results are compared to those observed for a surface where the full laminin protein has been adsorbed. Together, these experiments help to design a surface resistant to non-specific protein adsorption that allows for neuronal adhesion, sheds light on laminin-mediated attachment, and aids in developing better small-molecule mimics of receptor-mediated cellular adhesion.

5:20pm **TF+EM+SS-ThA11 Contact-Free Electrical Characterization of Molecular Layers using CREM**, ***H. Cohen***, Weizmann Inst. of Science, Israel

While generally recognized as a powerful analytical tool, XPS is insensitive to hydrogen atoms and, in many cases, to fine variations in the environment of carbon atoms. As such, XPS characterization of organic molecular layers is rather limited, in particular under demands for high overlayer quality. On the other hand, a recent XPS-based technique for chemically resolved electrical measurements (CREM) proposes high sensitivity to even small amounts of defects or organization imperfections [1,2].

Here, CREM application to monolayers self-assembled on metallic or semiconducting substrates is overviewed, demonstrating some of the unique capabilities offered by this non-contact probe. Damage evolution under irradiation is specifically discussed; two of its extreme limits being modeled, yielding the effect of corresponding defect sites on the CREM-derived I-V curves. Potential applications to molecular electronics, approaching ***atomic*** resolution in the electrical data, will be discussed.

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Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-FrM

Spectroscopic Ellipsometry: Future Directions and New Techniques
Moderator: H. Wormeester, MESA, The Netherlands

8:20am **EL+AS+EM+MS+PS+TF-FrM1 Current Trends and Future Outlook for Spectroscopic Ellipsometry**, ***J.N. Hilfiker****, B. Johs, C.M. Herzinger, T.E. Tiwald*, J.A. Woollam Co., Inc. **INVITED**

This talk reviews the significant developments in spectroscopic ellipsometry (SE) in areas including extending spectral range, improving accuracy, and enhancing speed. Current SE applications owe much to hardware and software developments of the past. Thus, today's research efforts may reach full potential for applications years or even decades from now. With this in mind, we point to the current state-of-the-art and what this may mean for future SE applications.

Three important areas will be explored. First, there has been a continual trend to expand SE wavelength range. This has included extensions to both shorter and longer wavelengths. For the latter, there is current development into the THz. More immediate benefit may come from smaller SE extensions from the ultraviolet to the near infrared. For example, further near-infrared extensions help to characterize modern transparent conductive oxides (TCOs), used in both inorganic and organic photovoltaic stacks.

Second, we look at the search for improved SE accuracy. Substantial improvements have come with the development of new ellipsometer technologies, progressing from rotating analyzer/polarizer to rotating compensator and now dual-rotating compensator ellipsometers. In addition to improved accuracy, this technology provides advanced measurements, including the complete Mueller-matrix. This will open SE characterization to new applications of anisotropic, nanostructured, and even patterned thin films. Accuracy enhancements must be compatible with the expanding SE spectral range. Infrared SE has overcome many non-ideal optical components to provide measurements competitive to standard FTIR measurements.

Third, we look at the quest for improved measurement speed. This development is constrained by the previous requirements. The benefits of a wide spectral range generally outweigh speed requirements; otherwise laser-based ellipsometry would still have a strong foot-hold. Thus, compromises are made depending on application. Current instrumentation typically utilizes detector arrays for multi-channel SE measurements.

To conclude, we will look at the SE outlook and how it may take advantage of wavelength range, accuracy, and speed. In-line and in-situ SE measurements show special promise. Significant improvements in instrumentation, computing speed, and software are now making these applications more feasible. In addition, there are novel ideas to provide sample access and overcome non-ideal measurement conditions for in-line and in-situ SE. Significant progress in many different areas promises to extend ellipsometry into new areas – many of which are being studied by researchers today.

9:00am **EL+AS+EM+MS+PS+TF-FrM3 THz Optical Hall-effect and MIR-VUV Ellipsometry Characterization of 2DEG Properties in a HfO_2 Passivated AlGaN/GaN HEMT Structure**, ***S. Schöche****,* U. of Nebraska - Lincoln*, J. Shi,* Cornell U.*, A. Boosalis, P. Kühne,* U. of Nebraska - Lincoln*, C.M. Herzinger, J.A. Woollam,* J.A. Woollam Co., Inc.*, W.J. Schaff, L.F. Eastman,* Cornell U.*, V. Darakchieva,* Linkoping U., Sweden*, M. Schubert, T. Hofmann*, U. of Nebraska - Lincoln

Nitride based high electron mobility transistors (HEMT) utilize the formation of a two-dimensional electron gas (2DEG) at the interface between GaN and AlGaN due to a difference in spontaneous polarization. It is known that surface traps significantly influence the electrical properties of this 2DEG. Accurate knowledge about the influence of surface passivation on the channel properties is crucial. The device performance is governed by the mobility, the sheet charge density, and the effective mass of electrons in the 2DEG. These parameters are typically determined by electrical Hall effect (EHE), Shubnikov-de Haas (SdH), or cyclotron resonance (CR) measurements. Commonly these experiments require very low temperatures and high magnetic fields. Complex contact configurations are required for SdH and EHE and the ability to locate the 2DEG and possible parallel current paths is limited.

We present non-contact, optical measurements of free-charge carrier mobility, sheet density, and effective mass parameters of the 2DEG for a HfO_2-passivated AlGaN/GaN HEMT structure at room temperature. Spectroscopic ellipsometry in the spectral range from THz and Mid-IR to VUV and THz optical Hall-effect (generalized ellipsometry in magnetic field) (OHE) are employed.

The MIR measurements are performed for analysis of the heterostructure constituents' layer thickness, phonon modes, and volume free charge carriers. The phonon mode parameters were found to be in excellent agreement with literature values and the existence of significant volume charge carrier concentrations could be excluded. NIR to VUV ellipsometry is used to determine the thickness of the thin top layers. From a line-shape analysis in the VUV spectral range the optical constants of the HfO_2 passivation layer could be extracted. An amorphous structure of the HfO2 passivation layer could be confirmed by comparison with existing studies in literature.

OHE in the THz spectral range is performed for characterization of the 2DEG channel parameters. A classical Drude model for free charge carrier contribution to the dielectric function was applied to determine the sheet density, the carrier mobility, and the effective mass of the 2DEG electrons. The electron effective mass of $(0.22 \pm 0.04)\ m_0$ extracted here using OHE corroborates the values found in previous SdH and CR studies. The values for the high-frequency sheet density and carrier mobility obtained by the optical investigations in the THz spectral range are in excellent agreement with results from dc EHE measurements indicative within linear Boltzmann transport theory for frequency-independent carrier scattering mechanisms of the 2D carrier distribution.

9:20am **EL+AS+EM+MS+PS+TF-FrM4 Vector-Magneto-Optical Generalized Ellipsometry on Sculptured Thin Films**, ***D. Schmidt****, C. Briley, E. Schubert, M. Schubert*, University of Nebraska - Lincoln

Sculptured thin films are self-organized and self-assembled three-dimensional nanostructures with tunable geometries. These artificial nanostructured thin films exhibit highly anisotropic physical properties, which mainly depend on their specific geometry.

Slanted, highly-spatially coherent, columnar nanostructure samples were prepared by glancing angle electron-beam deposition. Glancing angle deposition is a bottom-up fabrication technique that employs a physical vapor deposition process at oblique angles where the trajectory of the incoming particle flux is not parallel to the substrate normal. The technique allows to engineer the columnar film structure and is today amongst the most promising self-organized fabrication processes in micro- and nanotechnology.

We present and discuss the novel approach of vector-magneto-optical generalized ellipsometry on ferromagnetic permalloy nanostructured thin films carried out at room temperature. Investigations have shown that the metal alloy thin films are highly transparent, reveal strong form-induced birefringence, and exhibit intriguing magneto-optical anisotropy. Spatial magnetization orientation hysteresis and magnetization magnitude hysteresis properties are studied using a three-dimensional Helmholtz coil arrangement. This particular octupole setup allows for arbitrary magnetic field directions at the sample position with field strengths up to 200 mT while optical access is granted for reflection and transmission-type ellipsometry measurements. Analysis of data obtained within this unique vector-magneto-optic setup reveals magnetization anisotropy of the permalloy slanted nanocolumns and gives insight into switching behavior of confined magnetic domains.

9:40am **EL+AS+EM+MS+PS+TF-FrM5 THz Dielectric Anisotropy of Metal Slanted Columnar Thin Films**, ***T. Hofmann****, D. Schmidt, A. Boosalis, P. Kühne, R. Skomski*, University of Nebraska-Lincoln*, C.M. Herzinger, J.A. Woollam,* J.A. Woollam Co., Inc.*, M. Schubert, E. Schubert*, University of Nebraska-Lincoln

Sculptured thin films (STFs) present an interesting class of self-organized, artificially made materials with three-dimensional, highly spatially coherent arrangements of nanostructures. Contemporary interest in materials for terahertz (THz) electronic, optoelectronic, and optical applications is redrawing attention to STFs that may enable designed optical properties for the THz frequency region.

We report on the anisotropic optical dielectric functions of a metal (cobalt) slanted columnar thin film deposited by electron-beam glancing angle deposition for the THz frequency domain using generalized spectroscopic ellipsometry. A simple anisotropic Bruggeman effective medium dielectric function homogenization approach is successfully employed to describe the observed optical response. This approach describes isolated, electrically conductive columns which render the thin film biaxial (orthorhombic). The anisotropy induced by the columnar film structure is very large. The anisotropic Bruggeman effective medium approach predicts upon slight modifications of Drude, fraction and/or depolarization parameters that

targeted optical properties of STF in the THz range can be achieved by variation of slanting angle, lateral column density, and material.

10:00am **EL+AS+EM+MS+PS+TF-FrM6 A Compact High-speed Spectroscopic Ellipsometer**, ***G. Chin***, ULVAC Inc., Japan

Recently, we developed a compact, high-speed spectroscopic ellipsometer. It analyzes the spectrums obtained from the polarization interference occurring between two multiple-order retarders which snapshot the wavelength distribution of the sample's spectroscopic polarization parameters. This innovative spectroscopic ellipsometer can measure the thickness and optical constants of thin films at a dramatically fast speed. Its acquisition time is as short as 10 ms. It does not require the conventional complex mechanical or active components for polarization-control, such as a rotating compensator and an electro-optical modulator. It can open great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. For example, it was integrated into the deposition tool and successfully measured thin films in the vacuum chamber.

This paper describes the principle, system configuration and our innovative efforts on developing the compact high-speed spectroscopic ellipsometer. Some typical application data will be also introduced, such as in line and in situ measurements for photovoltaic, flat panel display and semiconductor industries.

10:20am **EL+AS+EM+MS+PS+TF-FrM7 Ellipsometry Porosimetry (EP): In Situ Spectroscopic Ellipsometry Measurements Coupled with Pressure Controlled Adsorption of Organic Vapors to Study Properties of Nano-Porous Thin Films**, *J.P. Piel, L. Kitzinger,* ***A. Bondaz****, C. Defranoux*, SEMILAB-SOPRALAB, France

Ellipsometric porosimetry (EP) is a non contact, non destructive technique that is cited as a reference technique for porous thin film analysis [1, 2]. As it is based on a spectroscopic ellipsometric measurement, the technique allows the precise determination of the refractive indices and thickness of the porous films. The advantage of these EP tools is that the combination of this well established spectroscopic ellipsometric (SE) technique with a suitably adapted adsorption chamber permits access to all the information obtained by classic adsorption experiments (e.g. BET) on thin films with an excellent sensitivity. Information such as open and closed porosity, pore size distribution etc... can be thus obtained.

In addition the EP allows access to a multitude of information that the classic equipment does not. For example, Spectroscopic Ellipsometry allows to follow the variation of the sample thickness during the adsorption experiment, leading to the determination of the Young's Modulus for the thin films. This will be presented. The technique is highly sensitive to the detection of interfaces; it is thus possible to detect a porosity gradient or to study a multilayer structure and thereafter simultaneously plot the two corresponding adsorption isotherms [3]. In the same manner, the instrument permits the use of a range of different gases adsorptive in order to tailor the probe molecule to the morphology and to the chemistry of the porous layer at ambient temperature [4]. We thus obtain information on the chemistry of the pores within the layer, before, during and after the adsorption experiment. Recent developments include the implementation of the FTIR interferometer SE extension to the EP system. It allows a precise characterization of the chemistry of the pores within the layer. We thus obtain information on the chemical bonds present in the layers before, during and after the adsorption experiment. Preliminary results will be presented.

Specifically, this fundamental technique permits the thorough characterization of porous thin film samples. We will demonstrate some of the different features of the EP technique with regards to the morphological and chemical properties of the porous thin films. Additionally, we will illustrate the technique for various thin film applications such as solgel thin films, nanofilms for catalysis, photovoltaic cells, fuel cells, optical sensors, and bio-compatible materials to name but a few.

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Thin Film Division
Room: 110 - Session TF-FrM

Thin Films: Growth and Characterization II
Moderator: S. Gupta, University of Alabama

8:20am **TF-FrM1 Low-temperature CVD with Growth Inhibitors to Afford Uniform, nm-thick Films in Structures with Aspect Ratio ~ 200**, ***S. Babar****, J. Abelson*, University of Illinois at Urbana Champaign

In order to grow uniform, smooth and pinhole-free films of nm thickness, the nucleation step must occur with high areal density on the substrate and the nuclei must have a narrow size distribution. If the film must be deposited inside of a deep structure of very high aspect ratio, then the growth process must be strictly governed by the surface reaction rate of the precursor species rather than by the rate at which precursor is transported to the growth surface. Here, we present a method of control in chemical vapor deposition that simultaneously meets both of the above criteria.

We previously reported that the steady-state film growth rate is reduced when a molecular species, called the *inhibitor*, is added to the CVD process. The inhibitor interacts transiently with the growth surface but does not decompose and incorporate its elements into the film, i.e., the inhibitor is not consumed. We also reported that the inhibitor greatly improves the film nucleation step, e.g. for the growth of HfB_2, a high performance diffusion barrier, on SiO_2 substrates. In the absence of the inhibitor the nucleation density is low and the size distribution is broad, such that some islands attain a height of > 10 nm before the film even coalesces. In the presence of the inhibitor, nuclei attain a height of ~ 1 nm, but then grow only very slowly. Additional nuclei continue to form and fill in the bare substrate, such that coalescence occurs at a thickness of ~ 2 nm with a rms surface roughness of ≤ 0.5 nm.

The use of a growth inhibitor allows the *nucleation regime of film growth* to afford excellent nm-thick coatings in extremely high aspect ratio features. Note that when the film growth rate is low, so also is the consumption of precursor, such that a partial pressure of precursor species persists to the bottom of the feature. The inhibitor further assures that the nucleation process will be uniform. In features of aspect ratio > 200, we show that a film is deposited on all surfaces with a rms roughness of 0.6 nm. We also discuss the mechanisms that can afford the observed results. We suggest that the ability to reduce (homogenize) the size distribution and increase the areal density of nuclei will greatly extend the useful range of CVD precursor-substrate combinations which can afford nm-thick coatings in very high aspect ratio features.

8:40am **TF-FrM2 Understanding the Role of Hydrogen Impurity Scattering in Manganese Thin Films on the Si(001) Surface**, ***A.J. Stollenwerk****, B.J. Friend*, University of Northern Iowa

Interest in energy production via hydrogen has been increasing due to the fact that it does not emit harmful greenhouse gases associated with fossil fuels. Unfortunately, hydrogen is an explosive gas that is both colorless and odorless. This will make hydrogen sensors an important piece of safety equipment in a hydrogen based economy. Diffusion of hydrogen to the Mn/Si interface is believed to have an amphoteric effect on the interface characteristics making it a possible hydrogen sensor. This motivates a need to better understand electron transport properties through Mn/Si Schottky diodes. We performed ballistic electron emission microscopy (BEEM) on Mn/Si(001) Schottky diodes to study hot electron transport properties through this system. Samples were fabricated using electron-beam deposition of Mn onto n-type Si(001) with thickness ranging from 10 to 40 Å. Scattering in the Mn films as function of energy has been measured and compared to results obtained on Au/Si(001) Schottky diodes. Schottky heights on these samples were determined from the corresponding BEEM spectra using the Bell-Kaiser model. Future plans include introducing an atmosphere consisting of varying amounts of hydrogen and measuring the resulting effects on hot electron transport in the Mn film as well as the Schottky height. Should electron scattering or the Schottky height be affected by the presence of hydrogen, this system may prove useful as an inexpensive hydrogen sensor.

9:00am **TF-FrM3 Elimination of Indium Surface Segregation in InGaN Grown Throughout the Miscibility Gap**, ***M.W. Moseley****, B. Gunning, J.E. Lowder,* Georgia Institute of Technology*, G. Namkoong,* Old Dominion University*, W.A. Doolittle*, Georgia Institute of Technology

InGaN alloys have great potential in optoelectronics due to the tunable bandgap which spans the visible spectrum. However, these alloys are difficult to obtain as a result of thermal decomposition, indium surface segregation, and spinodal decomposition. To solve these problems, low growth temperatures, fast growth rates, and in situ surface analysis must be

used. These limitations make Metal-Modulated Epitaxy (MME) a promising growth candidate. Using MME, smooth InGaN has been grown without phase separation throughout the miscibility gap.

MME is a growth technique applied to molecular beam epitaxy of III-nitrides in which metal and dopant cell shutters are periodically opened and closed while active nitrogen flux remains constant. This technique uses metal-rich fluxes that would accumulate droplets in traditional MBE, taking advantage of the enhanced adatom mobility provided by excess metal. The periodic shuttering of the effusion cells allows the excess metal to be consumed, providing smooth, dry surfaces required for devices that demand abrupt interfaces.

In this study, MME is applied to the growth of InGaN and transient RHEED intensities are monitored for differing metal shutter open times (Fig. 1). It is found that these RHEED transients are the result of a RHEED oscillation associated with the buildup and consumption of the metal adlayer. This allows for observation and control of fractions of adsorbed metal layers. However, there is a drastic difference between the RHEED transients of low and high metal shutter open times. This difference is attributed to indium surface segregation, resulting in leftover In on the surface that does not form InN at these elevated temperatures. A model for adlayer buildup and consumption is developed, and a key RHEED signature is identified as the onset of surface segregation. The thickness of the adsorbed metal at this onset is found to be between 1 and 2 ML for various compositions. Samples grown throughout the miscibility gap using this technique exhibited single phase XRD spectra and < 1 nm RMS roughnesses (Fig. 2). High hole concentrations in p-InGaN are also achieved by MME (Fig. 3).

At the low temperatures required for high indium-content InGaN, an intermediate growth regime in MBE does not exist. Thus, traditional MBE cannot produce metal-rich InGaN without droplets or surface segregation. Because the onset of surface segregation ($1<x<2$ ML) occurs below droplet accumulation (<2.3 ML), this study confirms that for metal-rich InGaN growth, some form of modulation must be employed.

This work was supported by the Air Force Office of Scientific Research under a basic science grant managed by Kitt Reinhardt.

9:20am **TF-FrM4 Aging Effect on the Hydrophilicity of Metal Nanorod Arrays**, *N. Albarakati,* ***D. Ye***, Virginia Commonwealth University

Time dependent wettability of nickel nanorod arrays were studied by measuring the water contact angles on the samples. Nickel nanorods arrays were deposited on silicon substrates by sputtering oblique angle deposition with an 85° incident angle. The substrates are rotated at a speed of 0.5 rps by a stepper motor. Samples with varying nanorod heights were prepared. Water contact angles were measured for each sample on a sequence of time up to three months. The water contact angles on the fresh nanorod arrays are less than 10°. However, the contact angle increases with time after the samples were exposed to air. We observed that the contact angles on the samples with short nanorods increase quickly to an angle close to hydrophobic and that on the samples with long nanorods increase slowly and remain in the hydrophilic region. X-ray photoelectron spectroscopy was employed to study the change of the surface composition due to oxidation and hydrocarbon contamination. We believe that the change of water contact angles is due to the accumulation of hydrocarbon on the nanorod surface.

9:40am **TF-FrM5 Cubic ZnMgO and NiMgO for UV-C Applications**, ***R.C. Boutwell****, J.W. Mares, M. Wei, W.V. Schoenfeld*, University of Central Florida

We will report on two new ternary cubic oxides offering close lattice matching to MgO, ZnMgO and NiMgO, and compare the properties of films grown by both RF Plasma-Assisted MBE and a much more economical sol-gel deposition process. Using both methods we have successfully demonstrated band gap tuning in the UV-C spectral region, with ZnMgO films producing band gaps ranging from ~5eV to 7.8eV and NiMgO films having band gaps ranging from 3.5eV to 7.8 eV. XRD revealed 2θ FWHM values as narrow as 0.19°, and atomic force microscopy of ZnMgO films demonstrated surface roughness of 3.4nm with NiMgO films having roughness below 1Å. Optical, compositional, and morphological results from films produced using both synthesis methods will be presented. We will also report on initial photodetectors with 5µm interdigitated fingers that produced peak responsivities of 12 mA/W at 250 nm.

10:00am **TF-FrM6 Growth of Fe-Pd Nanoparticles and Thin Films via Pulsed Laser Deposition and the Matrix Assisted Pulsed Laser Evaporation of Metal Based Acetates**, ***M.A. Steiner****, J.M. Fitz-Gerald*, University of Virginia

Nanoparticle and thin film magnetic alloys of 3d-4d/5d metals such as Fe-Pt, Co-Pt, and Fe-Pd are of technological interest due to their ordered $L1_0$ tetragonal phase which exhibits high magnetocrystalline anisotropy. Hard magnetic properties combined with ductility and corrosion resistance make these alloys ideal for applications including micro-electro-mechanical systems and ultra high-density magnetic storage. These materials have also been shown to possess a unique strain-induced chessboard eutectoid microstructure between their hard $L1_0$ and soft $L1_2$ magnetic phases that features exchange coupling effects. Within this class of materials Fe-Pd alloys possess a low order-disorder transition temperature making them a good candidate for ordered structure studies.

Nanoparticles and thin films of eutectoid (61.5 at% Pd) Fe-Pd were deposited by pulsed laser deposition. Additionally ordered nanoparticles were deposited utilizing a novel technique involving the matrix assisted decomposition of metal-organic precursors. Nanoparticles and films were subsequently characterized by x-ray diffraction, vibrating sample magnetometry, high resolution transmission electron microscopy, and scanning electron microscopy.

10:40am **TF-FrM8 Surface Plasmon Resonance Excited in RuO_2 Films Grown on Glass and on Crystalline (001) TiO_2**, ***L. Wang****, K. Yang, C. Clavero, E. Crisman, V. Dinavahi, I. Novikova, R.A. Lukaszew*, College of William and Mary

PLEASE NOTE YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY PRESENT ONE PAPER ONLY (ORAL OR POSTER) AT THE CONFERENCE. YOU ARE ALREADY LISTED AS PRESENTER OF ABSTRACT #554Surface Plasmon Resonance (SPR) excitation in metallic thin films and nanostructures has been widely applied to study biomolecules absorption, bio-imaging, bio-sensing, and sensitivity enhanced Raman spectroscopy [1,2,3]. However, although the theoretical principles underlying SPR excitation are applicable to any conductive material, only metals, and in particular Au and Ag, have been considered for practical applications. Here we investigate SPR excitation in a conducting metal oxide such as RuO_2. Due to the optical properties frequency dependence, SPR excitation is more intense in the infrared region for this material. The RuO_2 thin films investigated were grown using reactive magnetron sputtering on two different substrates resulting on amorphous RuO_2 films when deposited on glass and crystalline RuO_2 films when epitaxially deposited on TiO_2 (001) substrates. We have used Atomic Force Microscopy (AFM) and Reflection High-Energy Electron Diffraction (RHEED) to characterize the surface morphology and microstructure of these samples. Four-point probe was used to investigate the electrical conductivity properties and ellipsometry was used to characterize the optical properties of the films. We will show a comparison of the physical properties including the SPR excitation between these two kinds of thin film RuO_2 samples. The investigation of SPR in conducting metal oxide materials provides a significant advancement for thin film characterizations as well as opens new venues for photonic and plasmonic applications.

This work was financially supported by NSF (DMR-1006013).

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11:00am **TF-FrM9 Towards Achieving a High Degree of Carbon Ionization in Magnetron Sputtering Discharges**, ***A. Aijaz****, K. Sarakinos, D. Lundin, U. Helmersson*, Linköping University, Sweden

Physical vapour deposition (PVD) methods, which are characterized by highly ionized deposition fluxes of the film forming species, provide added means for the synthesis of tailor-made materials. They can, for instance, facilitate the growth of meta-stable phases, nanostructures as well as selective deposition on complex-shaped substrates. In such methods, the generation of highly ionized deposition fluxes stems from high electron (plasma) densities. Cathodic arc and pulsed laser deposition are examples of such discharges where electron densities in the order of 10^{21} m^{-3} can be obtained. These techniques, while providing as high as 100% degree of ionization of the deposition flux, exhibit several drawbacks, such as macroparticle ejection from the target, lack of lateral film uniformity, and in some cases are difficult to scale up. Magnetron sputtering based techniques

are technologically more relevant, owing to their inherent advantages of conceptual simplicity, upscalability, and film uniformity. However, electron densities in magnetron discharges are significantly smaller, in the range of 10^{14}-10^{16} m^{-3} and therefore generation of a highly ionized deposition flux is often difficult. This difficulty is overcome by high power impulse magnetron sputtering (HiPIMS), where plasma densities on the order of 10^{19} m^{-3} are achieved. HiPIMS has been successful in enhancing the ionization for most common metals (Cu, Al, Ta, Ti), but it is challenged when non-metals such as carbon is considered. Previous investigations have shown that C^+/C ratio in HiPIMS does not exceed 5%, which does not provide efficient control over the physical properties and synthesis of carbon in various technologically relevant forms, e.g. tetrahedral amorphous carbon. In the present study we address the low degree of ionization of carbon in magnetron discharges. We have developed a new HiPIMS based process, which provides a plasma characterized by high electron temperature and plasma density as determined by time-resolved Langmuir probe measurements. The C^+ ion energy distribution functions (IEDFs) determined by time-averaged energy resolved mass spectrometry demonstrate an energetic C^+ ion population and an overall five-fold increase of the C^+ ion fraction as compared to standard HiPIMS methods. The enhanced ionized fraction of carbon facilitates the growth of carbon films with mass densities as high as approx. 2.8 g/cm^3 as determined by high resolution x-ray reflectively measurements. Determination of the D-peak to G-peak ratio (I(D)/I(G)) and full width at half maximum of the G-peak in Raman spectra indicate that the films contain a large fraction of diamond-like bonded (sp^3) carbon.

11:20am **TF-FrM10 Kinetics of Sputtered Metal Film Growth on Vertically Aligned Carbon Nanotube Arrays**, *C. Muratore, **A. Reed**, A. Waite, J. Bultman, J. Hu, T. Smith, A.A. Voevodin*, Air Force Research Laboratory

Controlling the surface morphology of metallized arrays of vertically aligned nanotubes (VACNTs) is useful for diverse technological applications, such as interface materials for thermal management of high-heat flux electronics and electrical contacts for MEMS switches. We have observed variation of the morphology of metal films sputtered on carbon nanotubes, ranging from thin continuous films surrounding individual bundles of carbon nanotubes along their entire length for tubes up to 100 microns in length, to metal canopies covering the surface, with only minimal penetration (10-20 microns) into the nanotube forest. There is a strong link between flux of metal ions and their kinetic energy and the morphology of metal films of technological interest, including titanium, nickel, copper, gold and aluminum. To explore the mechanisms dictating metal film architectures on VACNT arrays, we systematically altered the flux and energy of incident metal and inert gas ions. These processing conditions were characterized using a mass spectrometer and energy analyzer adjacent to VACNT substrates. For conditions of interest, film growth was carried out for different times in an ultra high vacuum processing chamber, followed by electron microscopy of VACNT film cross sections, which were examined to observe different stages of growth and identify mechanisms of film nucleation and growth on nanotube sidewalls and tips. Comparison of growth kinetics of metal films on planar (002) graphite surfaces to that observe on VACNTs was used to identify effects of curvature on film growth. Switch performance was shown to be strongly dependent on morphology.

11:40am **TF-FrM11 Crystallographic Orientation of Vanadium Dioxide Nano-Grains on Various Single-Crystal Sapphire Substrates**, ***F. Rivera***, Brigham Young University, *J. Nag, R.F. Haglund Jr.*, Vanderbilt University, *R. Davis, R. Vanfleet*, Brigham Young University

Vanadium dioxide (VO_2) is a material of particular interest due to the reversible semiconductor to metal phase transition that VO_2 exhibits near room temperature (~ 68 °C) and the accompanied hysteresis. Recent studies suggest that external stresses applied to VO_2 crystals have an effect on the transition temperature and hysteresis. Thin films of VO_2 were deposited on three different cuts of sapphire by Pulsed Laser Deposition (PLD). Electron Back-Scattered Diffraction (EBSD) was used to study the orientation of the crystalline VO_2 grains obtained and showed epitaxial relationships between the different single-crystal substrates. A predominant family of crystallographic relationships is present in all cuts of sapphire wherein the rutile VO_2 {001} planes tend to lie parallel to the substrate's {10-10} and the rutile VO_2 {100} planes lie parallel to the substrate's {1-210} and {0001}. This family accounts for the majority of the VO_2 grains observed on all substrates with specific orientations (and stresses) depending upon the substrate's normal direction. Transmission Electron Diffraction patterns taken from cross-section of particles of the A and R cut sapphire substrates helped to lift the ambiguity present in the rutile {100} axes. EBSD showed additional families of relationships in the C and R cuts of sapphire, most related to the aforementioned predominant family. Variations in the transition temperatures of the deposited thin films mentioned in this study are attributed to the stresses generated by the epitaxial relationships.

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Hacker, C.A.: TF+EM+SS-ThA9, 46
Haensch, W.E.: NM+MN+MS+TF-TuM10, 11
Haglund Jr., R.F.: TF-FrM11, 51
Haglund, R.F.: EL+AS+EM+MS+PS+TF-ThA11, 44
Haight, R.: EN1+TF-WeA3, 24
Hall, R.A.: TF1+EM-WeM11, **23**
Hallberg, T.: EL+AS+EM+MS+PS+TF-ThM4, 31
Hamaguchi, S.: PS+MN+TF-TuM12, 13
Hämäläinen, J.: TF-MoA10, 8
Han, S.M.: TF2-ThM10, 40; TF-MoM8, 3
Harl, R.R.: TF1-ThM9, 37
Har-Lavan, R.: EM+TF-ThM11, 33
Harris, K.D.: TF+SE-TuM4, 15
Harteneck, B.D.: NM+MN+MS+TF-TuM12, 11
Hellstrom, S.L.: TF2+EM-WeA10, **29**
Helmersson, U.: TF-FrM9, 50
Hemminger, J.C.: EN1+TF-WeA8, 24
Henager, C.H.: TF-MoM1, 2
Hensley, D.K.: TF2+EM-WeA9, 29
Herman, G.S.: TF1+EM-WeA1, **27**
Herzinger, C.M.: EL+AS+EM+MS+PS+TF-FrM1, 48; EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, 48
Hilfiker, J.N.: EL+AS+EM+MS+PS+TF-FrM1, **48**
Hill, S.B.: EL+AS+EM+MS+PS+TF-ThM9, 32
Hinkle, C.L.: EM+TF-TuM4, 9
Hirano, T.: TF-TuP3, 20; TF-TuP7, 21
Hmelo, A.B.: TF1-ThM5, 37
Hodson, C.: PS+TF-ThM11, 36
Hofmann, T.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, **48**
Hong, M.: EM+TF-TuM9, **10**
Horn, M.W.: EL+AS+EM+MS+PS+TF-ThA10, 43
Hryn, J.N.: TF-TuA1, 18
Hu, J.: TF-FrM10, 51
Hu, X.: TF+EN-TuM10, 14; TF-TuP11, 21
Huang, J.: EM+TF-TuM4, 9
Huang, M.L.: EM+TF-TuM9, 10
Hughes, K.J.: EM+TF-ThM4, 33
Hultman, L.: TF1-ThM11, 38; TF2-ThM5, 39; TF2-ThM6, 39
Hung, T.-H.: EM+TF-TuM12, **10**
Hurley, P.K.: EM+TF-TuM4, 9
Hurst, K.E.: TF+EN-TuM2, 13

— I —

Ianno, N.: EL+AS+EM+MS+PS+TF-ThA8, 43
Illiberi, A.: TF-MoA7, 7
Im, S.I.: EM+TF-ThM9, **33**
Inoue, T.: TF-TuP1, **20**
Irving, D.L.: TF2-ThM11, **40**; TF-MoM2, 2
Is, H.: TF+SE-TuM5, **15**
Itagaki, N.: PS+TF-ThM5, 35
Ito, T.: PS+MN+TF-TuM12, 13
Itou, A.: PS+MN+TF-TuM4, 12
Iwai, H.: NM+MS+NS+TF-MoM5, 1

— J —

Jain, R.: EM+TF-ThM12, **34**
Jakubiak, R.: PS+TF-ThM2, 34
Jansson, U.: TF1-ThM11, 38
Järrendahl, K.: EL+AS+EM+MS+PS+TF-ThM4, 31
Jennings, G.K.: NM+MN+MS+TF-TuM3, **10**
Jeon, H.T.: TF-MoA6, 7
Jeon, H.Y.: TF-MoA6, 7
Jia, Q.X.: AC+TF-ThA4, 41
Jiang, H.: PS+TF-ThM2, 34
Jiang, W.: TF-TuP2, 20
Jiang, X.: TF-TuA10, 19
Jin, R.Z.: TF2+EM-WeA10, 29
Johnson, E.V.: EN+TF-TuA4, 17
Johs, B.: EL+AS+EM+MS+PS+TF-FrM1, 48
Jones, K.: TF+EN-TuM2, 13
Jordan-Sweet, J.L.: TF1+EM-WeA9, 28; TF-MoM9, 3
Joseph, E.A.: PS+MN+TF-TuM4, 12; TF1+EM-WeA9, **28**
Joshi, P.: EM+TF-ThM11, 33
Jourdan, N.: TF1-ThM12, 38
Jourde, D.: TF1+EM-WeA2, 27
Joyce, J.J.: AC+TF-ThA4, 41
Jur, J.S.: TF+EN-TuM9, 14; TF-MoA9, 7; TF-TuA9, 19

— K —

Kafrouni, W.: PS+MN+TF-TuM3, 12
Kakushima, K.: NM+MS+NS+TF-MoM5, 1
Kalanyan, B.: TF+EN-TuM9, 14
Kappe, E.: EM+TF-ThM6, 33
Karabacak, T.: TF+SE-TuM5, 15
Karahashi, K.: PS+MN+TF-TuM12, **13**
Karakawa, T.: PS+TF-ThM1, **34**
Kariis, H.: EL+AS+EM+MS+PS+TF-ThM4, 31
Karki, S.: TF1-ThM10, 38
Kasputis, T.: EL+AS+EM+MS+PS+TF-ThM5, 31
Kaul, A.: EN1+TF-WeA1, **24**
Kaur, T.: GR+TF+NS-ThA3, **44**
Kawakami, R.K.: GR+TF+ET-MoA10, 6
Kaxiras, E.: GR+TF+NS-ThA8, 45
Kaya, S.: GR+TF+ET-MoA3, 5
Kayani, A.: TF-TuP2, 20
Kazaz, R.: EM+TF-ThM11, 33
Kelkar, U.: TF2-ThM2, 38
Kessels, W.M.M.: EL+AS+EM+MS+PS+TF-ThA7, 43; EM+TF-TuM11, 10; PS+TF-ThM9, 35; TF-MoA4, 6
Khalil, M.: TF-MoA3, 6
Khare, A.: EN1+TF-WeA11, 25; EN1+TF-WeA7, **24**
Kiehlbauch, M.: PS+MN+TF-TuM9, **13**
Kilcoyne, A.L.D.: PS+TF-ThM12, 36
Kim, D.: TF+EN-TuM9, **14**; TF1+EM-WeM4, 22
Kim, J.: EM+TF-TuM2, 9; EM+TF-TuM3, 9
Kim, M.: GR+TF+NS-ThA1, 44
Kindermann, M.E.: GR+TF+ET-MoA6, 5
King, W.P.: GR+TF+NS-ThA9, 45
Kioussis, N.: GR+TF+NS-ThA8, 45
Kirk, W.P.: EM+TF-TuM4, 9
Kitzinger, L.: EL+AS+EM+MS+PS+TF-FrM7, 49; EL+AS+EM+MS+PS+TF-ThM10, **32**
Knaapen, R.: TF-MoA7, 7
Knez, M.: TF1+EM-WeM9, **23**
Knoops, H.C.M.: EL+AS+EM+MS+PS+TF-ThA7, 43
Ko, Y.B.: TF-MoA6, 7
Kocha, S.: TF+EN-TuM2, 13
Koga, K.: PS+TF-ThM5, 35
Kohler, R.: TF-TuP4, 20
Koleske, D.: EN+TF-TuA11, 18
Kondic, L.: TF2+EM-WeA4, 29
Kongkanand, A.: TF+EN-TuM3, 13
Konstantinidis, S.: TF1-ThM6, 37
Koo, H.J.: TF+EN-TuM9, 14
Kostamo, J.: NM+MS+NS+TF-MoM6, 1
Kouda, M.: NM+MS+NS+TF-MoM5, 1
Kozen, A.C.: TF-MoA3, **6**
Kozimor, S.A.: AC+TF-ThA4, 41
Krause, K.M.: TF+SE-TuM4, 15
Krishnamoorthy, S.: EM+TF-TuM12, 10
Kuchibhatla, S.V.N.T.: TF-MoM1, 2; TF-TuP2, 20
Kühne, P.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, 48
Kulshreshtra, P.: NM+MN+MS+TF-TuM12, 11
Kummel, A.C.: EM+TF-ThM6, 33
Kuo, Y.: TF1-ThM3, **37**
Kurihara, M.: NM+MN+MS+TF-TuM4, **11**
Kuznetsov, V.I.: TF-MoA1, **6**
Kwo, J.: EM+TF-TuM9, 10

— L —

Ladroue, J.: PS+MN+TF-TuM3, 12
LaFranzo, N.A.: TF+EM+SS-ThA10, **47**
Lagally, M.G.: TF2+EM-WeA11, 29
Lai, R.Y.: EL+AS+EM+MS+PS+TF-ThM6, 32
Lai, S.-C.: TF1+EM-WeA9, 28
Lakhtakia, A.: TF+SE-TuM11, 16
Lalany, A.: TF+SE-TuM4, 15
Lam, C.H.: TF1+EM-WeA9, 28
Lambert-Milot, S.: TF-MoM9, 3
Landin, J.: EL+AS+EM+MS+PS+TF-ThM4, 31
Laracuente, A.R.: GR+TF+NS-ThA9, 45
LaRose, J.D.: EM+TF-TuM6, 9
Larsen, G.K.: TF+SE-TuM10, **15**
Lavoie, C.: TF-MoM9, 3
Law, M.: EN1+TF-WeA8, 24
Lecordier, L.: NM+MS+NS+TF-MoM3, 1
Lee, B.H.: TF1+EM-WeM3, **22**
Lee, J.S.: TF-MoA6, **7**
Lee, K.: TF+EN-TuM9, 14
Lee, S.: EN+TF-TuA11, 18
Lee, S.S.: AC+TF-ThA1, 41
Lee, W.C.: EM+TF-TuM9, 10
Lee, W.K.: GR+TF+NS-ThA9, **45**
Lefaucheux, P.: PS+MN+TF-TuM3, 12
Leggett, G.: TF+EM+SS-ThA4, 46
Lehto, T.: NM+MS+NS+TF-MoM6, 1
Lei, Z.: EN+TF-TuA9, 17
Leick, N.: EL+AS+EM+MS+PS+TF-ThA7, **43**; TF+EN-TuM2, 13
Leighton, C.: EN1+TF-WeA11, 25
Lekkala, J.: TF-MoA10, 8
Leonhardt, D.: TF2-ThM10, 40; TF-MoM8, **3**
Leroy, F.: TF2+EM-WeA3, 28
Leskelä, M.: TF-MoA10, 8
Leusink, G.J.: EM+TF-TuM6, 9
Levi, D.: EL+AS+EM+MS+PS+TF-ThA1, **42**
Levy, J.: TF2+EM-WeA7, 29
Li, H.: EN+TF-TuA9, 17
Li, L.: EN+TF-TuA9, **17**; GR+TF+NS-ThA11, 45
Li, Q.: EN+TF-TuA11, 18
Li, W.: EN+TF-TuA9, 17; TF1-ThM10, 38
Li, Y.: EN1+TF-WeA7, 24; TF-TuP11, **21**
Li, Y.Y.: GR+TF+NS-ThA11, **45**
Libera, J.A.: TF-TuA1, 18
Lie, F.L.: TF-TuA12, 19
Lin, C.-H.: NM+MN+MS+TF-TuM10, 11
Lin, M.-W.: GR+TF+NS-ThA8, 45
Lin, T.D.: EM+TF-TuM9, 10
Ling, C.: GR+TF+NS-ThA8, 45
Ling, J.: AC+TF-ThA10, 42
Liu, G.: NM+MS+NS+TF-MoM3, 1

Liu, Y.: EN1+TF-WeA8, 24; GR+TF+NS-ThA11, 45
Liu, Z.: EN1+TF-WeA8, 24; TF-TuP11, 21
Lobb, C.: TF-MoA3, 6
Lopez-Bezanilla, A.: GR+TF+NS-ThA6, **44**
Lopinski, G.P.: TF+EM+SS-ThA3, 46
Losego, M.D.: TF2-ThM11, 40
Lowder, J.E.: EN+TF-TuA11, 18; TF1-ThM2, **36**; TF-FrM3, 49
Lozzi, L.: EN2+TF-WeA11, **26**
Lu, P.: EM+TF-ThM5, 33
Lucatorto, T.B.: EL+AS+EM+MS+PS+TF-ThM9, 32
Lukaszew, R.A.: TF-FrM8, 50
Lundin, D.: TF-FrM9, 50
Lung, H.-L.: TF1+EM-WeA9, 28
Luttrell, T.: EN2+TF-WeA7, **25**
Lyding, J.W.: EN1+TF-WeA10, 25

— M —

MacElroy, J.M.D.: EN2+TF-WeA8, 26
Mackus, A.J.M.: EL+AS+EM+MS+PS+TF-ThA7, 43; TF-MoA4, 6
Maitrejean, S.: TF1+EM-WeA2, 27
Malgorzata, M.: TF1+EM-WeA3, 27
Malinen, T.: NM+MS+NS+TF-MoM6, 1
Mandoc, M.M.: EM+TF-TuM11, 10
Manno, M.: EN1+TF-WeA11, **25**
Mansour, A.: PS+TF-ThM12, 36
Mares, J.W.: TF-FrM5, 50
Margarella, A.: EN1+TF-WeA8, 24
Maria, J.-P.: TF2-ThM11, 40; TF-MoM2, **2**
Marsillac, S.: EL+AS+EM+MS+PS+TF-ThA4, 42
Martin, R.L.: AC+TF-ThA4, 41
Martin, R.M.: TF1+EM-WeA9, 28
Martín-Palma, R.J.: TF+SE-TuM11, 16
Marvel, R.E.: EL+AS+EM+MS+PS+TF-ThA11, **44**
Masters, A.E.: TF+EN-TuM10, 14
Matsumoto, H.: PS+MN+TF-TuM4, 12
Matsuura, G.: PS+MN+TF-TuM4, 12
Maurer, J.A.: TF+EM+SS-ThA10, 47
McCleskey, T.M.: AC+TF-ThA4, **41**
McCreary, K.M.: GR+TF+ET-MoA10, **6**
McGimpsey, W.G.: EM+TF-ThM1, **32**
McKnight, T.E.: TF2+EM-WeA9, 29
Melechko, A.V.: TF2+EM-WeA9, 29
Melendez-Lira, M.A.: EN1+TF-WeA9, **25**
Membreno, D.: TF+EN-TuM4, 13
Meng, Y.: EN+TF-TuA9, 17
Meyerbröker, N.: TF+EM+SS-ThA6, **46**
Michallon, P.: TF1+EM-WeA2, 27
Miller, D.: TF1+EM-WeA9, 28
Minami, T.: TF-TuP3, 20; TF-TuP7, 21
Mitzi, D.B.: EN1+TF-WeA3, **24**
Miyata, T.: TF-TuP3, **20**; TF-TuP7, 21
Morikawa, Y.: PS+MN+TF-TuM1, **12**
Morrish, R.: EN2+TF-WeA8, **26**
Morrison, J.M.: AC+TF-ThA6, **41**
Moseley, M.W.: EN+TF-TuA11, 18; TF1-ThM2, 36; TF-FrM3, **49**
Motyka, M.A.: EL+AS+EM+MS+PS+TF-ThA10, **43**
Moutinho, H.R.: EN1+TF-WeA1, 24
Mryasov, O.N.: TF2-ThM3, **39**
Muhlberger, S.A.: TF+SE-TuM11, 16
Müller, P.: TF2+EM-WeA3, 28
Murali, S.: TF1+EM-WeA1, 27
Muratore, C.: TF-FrM10, 51
Murayama, T.: PS+MN+TF-TuM1, 12
Muscat, A.J.: EM+TF-ThM12, 34; TF-TuA12, 19
Musgrave, C.: TF-MoA3, 6

— N —

Nachimuthu, P.: TF1+EM-WeA1, 27; TF-MoM1, 2; TF-TuP2, 20
Nag, J.: EL+AS+EM+MS+PS+TF-ThA11, 44; TF-FrM11, 51
Nakamura, I.: TF-TuP9, 21
Nakamura, M.: PS+MN+TF-TuM4, 12
Namkoong, G.: TF-FrM3, 49
Nandasiri, M.I.: TF-TuP2, 20
Narkilahti, S.: TF-MoA10, 8
Nascente, P.A.P.: TF-MoM10, **4**
Natarajarathinam, A.: TF1+EM-WeA8, **27**
Nath, D.N.: EM+TF-TuM12, 10
Nealey, P.F.: NM+MN+MS+TF-TuM5, **11**
Nedfors, N.: TF1-ThM11, **38**
Negishi, N.: NM+MN+MS+TF-TuM4, 11
Neria-Gonzalez, M.I.: EN1+TF-WeA9, 25
Neumayer, D.: TF1+EM-WeA9, 28
Ng, A.: EM+TF-ThM12, 34
Nilsson, A.: GR+TF+ET-MoA3, 5
Nishida, T.: NM+MN+MS+TF-TuM4, 11
Nizamidin, N.: NM+MN+MS+TF-TuM3, 10
Noguchi, Y.: TF-TuP3, 20
Nomoto, J.: TF-TuP3, 20; TF-TuP7, **21**
Norris, D.J.: EN1+TF-WeA7, 24
Novikova, I.: TF-FrM8, 50
Nozawa, T.: PS+TF-ThM1, 34

— O —

Ocola, L.E.: NM+MN+MS+TF-TuM9, 11
Odom, T.W.: NM+MN+MS+TF-TuM1, **10**
Ogasawara, H.: GR+TF+ET-MoA3, 5
Ogieglo, W.: EL+AS+EM+MS+PS+TF-ThA9, 43
Oka, M.: PS+TF-ThM1, 34
Oldham, C.J.: TF-TuA9, 19
Oleynik, I.I.: GR+TF+ET-MoA4, 5
Oliva, A.I.: TF1-ThM1, 36
Olynick, D.L.: NM+MN+MS+TF-TuM12, 11
Ortiz, C.: EN2+TF-WeA12, 26
Osborn, K.D.: TF-MoA3, 6
Oshima, A.: TF1+EM-WeM6, 22
Otaño, W.: EN2+TF-WeA12, **26**
Oyler, N.A.: TF1-ThM10, 38

— P —

P. Ryan Fitzpatrick, P.R.: NM+MS+NS+TF-MoM8, 1
Paisley, E.A.: TF2-ThM11, 40; TF-MoM2, 2
Palmans, J.: TF-MoM4, 2
Pannier, A.K.: EL+AS+EM+MS+PS+TF-ThM5, 31
Pantojas, V.: EN2+TF-WeA12, 26
Paquette, M.M.: TF1-ThM10, **38**
Park, J.G.: TF-MoA6, 7
Park, T.Y.: TF-MoA6, 7
Parsons, G.N.: TF+EN-TuM9, 14; TF1+EM-WeM4, 22; TF-MoA9, 7; TF-TuA9, 19
Paskiewicz, D.M.: TF2+EM-WeA11, **29**
Patel, R.: TF-MoM11, **4**
Paulin-Filho, P.I.: TF-MoM10, 4
Pearce, R.C.: TF2+EM-WeA9, **29**
Peixoto, T.: EM+TF-ThM3, 32
Pellegrini, K.L.: AC+TF-ThA10, **42**
Pelucchi, E.: EM+TF-TuM4, 9
Peña Martin, P.: EN1+TF-WeA10, **25**
Perera, P.: NM+MN+MS+TF-TuM12, 11
Perng, Y.-C.: TF+EN-TuM4, 13; TF-TuA2, **18**
Petrov, I.: TF2-ThM5, 39
Petz, C.: TF2+EM-WeA7, **29**
Pfleging, W.: TF-TuP4, 20
Pham, C.D.: TF1+EM-WeA7, **27**
Pi, T.W.: EM+TF-TuM9, 10
Piel, J.P.: EL+AS+EM+MS+PS+TF-FrM7, 49; EL+AS+EM+MS+PS+TF-ThM10, 32
Pilvi, T.: NM+MS+NS+TF-MoM6, 1
Pireaux, J.-J.: PS+TF-ThM12, **36**
Podraza, N.J.: EL+AS+EM+MS+PS+TF-ThA10, 43; EL+AS+EM+MS+PS+TF-ThA3, **42**
Polop, C.: TF1-ThM1, 36
Poodt, P.: TF-MoA7, **7**
Pookpanratana, S.: TF+EM+SS-ThA9, **46**
Pouliquen, S.: EN+TF-TuA4, **17**
Proell, J.: TF-TuP4, 20
Profijt, H.B.: PS+TF-ThM9, **35**
Pulsifer, D.P.: TF+SE-TuM11, **16**
Putkonen, M.: TF-MoA8, **7**

— Q —

Qiu, J.: AC+TF-ThA10, 42

— R —

Rack, P.D.: TF2+EM-WeA4, 29
Rahman, M.: EN2+TF-WeA8, 26
Rajachidambaram, J.S.: TF1+EM-WeA1, 27
Rajan, S.: EM+TF-TuM12, 10
Rajasekaran, S.: GR+TF+ET-MoA3, **5**
Ramana, C.V.: TF-MoM1, 2
Rangel-Chavez, L.G.: EN1+TF-WeA9, 25
Ranjan, V.: EL+AS+EM+MS+PS+TF-ThA4, 42
Ranson, P.: PS+MN+TF-TuM3, 12
Raoux, S.: TF1+EM-WeA9, 28
Rauch, S.: EL+AS+EM+MS+PS+TF-ThM3, **31**
Reed, A.: PS+TF-ThM2, 34; TF-FrM10, **51**
Reed, R.A.: TF1-ThM9, 37
Ren, J.: TF-TuP11, 21
Reniers, F.: PS+TF-ThM12, 36
Rice, A.R.: TF-MoM2, 2
Richter, C.A.: TF+EM+SS-ThA9, 46
Richter, L.J.: EL+AS+EM+MS+PS+TF-ThM9, **32**
Rider, D.A.: TF+SE-TuM4, 15
Rivera, F.: TF-FrM11, **51**
Roberts, N.A.: TF2+EM-WeA4, 29
Robinson, J.T.: GR+TF+NS-ThA9, 45
Rockett, A.: EN1+TF-WeA10, 25
Rodenhausen, K.B.: EL+AS+EM+MS+PS+TF-ThM5, **31**; EL+AS+EM+MS+PS+TF-ThM6, 32
Rodríguez Cañas, E.: TF1-ThM1, 36
Rodríguez-Vindas, D.: EN2+TF-WeA12, 26
Rogers, B.R.: TF1-ThM9, 37
Roozeboom, F.: TF-MoA7, 7
Rosei, F.: TF+EM+SS-ThA3, 46
Royer, J.: EM+TF-ThM6, **33**
Rubloff, G.W.: TF+EN-TuM5, **14**; TF-MoA3, 6
Ruggieri, F.: EN2+TF-WeA11, 26
Ryu, J.H.: TF-MoA6, 7
Ryynänen, T.: TF-MoA10, **8**

— S —

Sacedón, J.L.: TF1-ThM1, 36
Safron, N.: GR+TF+NS-ThA1, 44
Sakuishi, T.: PS+MN+TF-TuM1, 12
Sandler, N.: GR+TF+NS-ThA3, 44
Sanghavi, S.P.: TF1+EM-WeA1, 27
Sangiovanni, D.G.: TF2-ThM5, 39; TF2-ThM6, **39**
Santucci, S.: EN2+TF-WeA11, 26
Sarabi, B.: TF-MoA3, 6
Sarakinos, K.: TF-FrM9, 50
Satake, M.: NM+MN+MS+TF-TuM4, 11
Sato, M.: PS+TF-ThM5, 35; TF-TuP9, 21
Savage, D.E.: TF2+EM-WeA11, 29
Sawant, R.: TF1+EM-WeA9, 28
Sazegar, M.: TF-MoM5, 3
Scarel, G.: TF+EN-TuM10, **14**
Schaff, W.J.: EL+AS+EM+MS+PS+TF-FrM3, 48
Schamberger, F.: TF2-ThM12, **40**
Schmidt, D.: EL+AS+EM+MS+PS+TF-FrM4, **48**; EL+AS+EM+MS+PS+TF-FrM5, 48; EL+AS+EM+MS+PS+TF-ThA8, 43; EL+AS+EM+MS+PS+TF-ThM5, 31
Schmidt, M.: AC+TF-ThA1, **41**; NM+MN+MS+TF-TuM12, 11
Schneller, E.: EN1+TF-WeA1, 24
Schöche, S.: EL+AS+EM+MS+PS+TF-FrM3, **48**
Schoenfeld, W.V.: TF-FrM5, 50
Schubert, E.: EL+AS+EM+MS+PS+TF-FrM4, 48; EL+AS+EM+MS+PS+TF-FrM5, 48; EL+AS+EM+MS+PS+TF-ThA8, 43
Schubert, M.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM4, 48; EL+AS+EM+MS+PS+TF-FrM5, 48; EL+AS+EM+MS+PS+TF-ThA8, **43**; EL+AS+EM+MS+PS+TF-ThM5, 31; EL+AS+EM+MS+PS+TF-ThM6, 32
Schuck, P.J.: NM+MN+MS+TF-TuM12, 11
Schwartzberg, A.: NM+MN+MS+TF-TuM12, 11
Scott, B.L.: AC+TF-ThA4, 41

Seal, S.: TF-TuP2, 20
Sershen, M.: NM+MS+NS+TF-MoM3, 1
Shaler, R.C.: TF+SE-TuM11, 16
Sharma, K.: EN+TF-TuA3, 17
Shearer, J.C.: TF2+EM-WeA8, **29**
Sheehan, P.E.: GR+TF+NS-ThA9, 45
Shelby, R.M.: TF1+EM-WeA9, 28
Shi, J.: EL+AS+EM+MS+PS+TF-FrM3, 48
Shi, Z.: EM+TF-ThM5, 33
Shida, S.: TF-TuP1, 20
Shiratani, M.: PS+TF-ThM5, **35**
Shukur, H.: TF-TuP9, **21**
Shutthanadan, S.V.: TF-MoM1, 2
Shutthanandan, V.: TF1+EM-WeA1, 27; TF-TuP2, 20
Siew, Y.K.: TF1-ThM12, 38
Sikorski, E.M.: PS+MN+TF-TuM4, 12
Simpson, M.L.: TF2+EM-WeA9, 29
Sitar, Z.: TF2-ThM11, 40; TF-MoM2, 2
Sivula, K.: EN2+TF-WeA9, **26**
Skomski, R.: EL+AS+EM+MS+PS+TF-FrM5, 48
Smets, M.: TF-MoA7, 7
Smith, T.: TF-FrM10, 51
Snyders, R.: TF1-ThM6, **37**
Soderholm, L.: AC+TF-ThA1, 41
Sonnet, A.M.: EM+TF-TuM4, 9
Sowa, M.: NM+MS+NS+TF-MoM3, 1
Sowa, M.J.: TF1+EM-WeM5, **22**
Stacchiola, D.: GR+TF+ET-MoA3, 5
Steigerwald, A.D.: TF1-ThM5, **37**
Steiner, M.A.: TF-FrM6, **50**
Stemme, F.: TF-MoM5, **3**
Stine, R.: GR+TF+NS-ThA9, 45
Stollenwerk, A.J.: TF-FrM2, **49**
Stoltenberg, R.M.: TF2+EM-WeA10, 29
Sun, L.: PS+TF-ThM2, **34**
Sundaram, G.M.: NM+MS+NS+TF-MoM3, 1
Sung, M.M.: TF1+EM-WeM1, **22**
Suu, K.: PS+MN+TF-TuM1, 12
Suzuki, M.: TF+SE-TuM2, **14**
Suzuki, T.: NM+MS+NS+TF-MoM5, **1**
Sweet, W.: TF-MoA9, **7**
Szymanowski, J.: AC+TF-ThA10, 42

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Tada, Y.: NM+MN+MS+TF-TuM4, 11
Takano, I.: TF-TuP9, 21
Tallarico, D.A.: TF-MoM10, 4
Tang, B.: EN+TF-TuA9, 17
Tanto, B.: TF2+EM-WeA11, 29
Tapily, K.N.: EM+TF-TuM6, 9
Tarrio, C.: EL+AS+EM+MS+PS+TF-ThM9, 32
Taschuk, M.T.: TF+SE-TuM4, 15
Taylor, P.C.: EN+TF-TuA1, **17**
Tchoua Ngamou, P.H.: PS+TF-ThM6, **35**
Tengstrand, O.: TF1-ThM11, 38
Terlinden, N.M.: EM+TF-TuM11, **10**
Thevuthasan, S.: TF1+EM-WeA1, 27; TF-MoM1, 2; TF-TuP2, **20**
Thiruvengadam, S.: EN1+TF-WeA3, 24
Thissen, P.: EM+TF-ThM3, **32**
Thomas, K.: EM+TF-TuM4, 9
Thomas, M.: TF+SE-TuM4, 15
Thompson, C.V.: TF2+EM-WeA1, **28**
Tillocher, T.: PS+MN+TF-TuM3, **12**
Tiwald, T.E.: EL+AS+EM+MS+PS+TF-FrM1, 48
To, B.N.: PS+MN+TF-TuM4, 12
Todorov, T.K.: EN1+TF-WeA3, 24
Toivola, M.: NM+MS+NS+TF-MoM6, 1
Tőkei, Zs.: TF1-ThM12, 38
Tolk, N.H.: TF1-ThM5, 37
Tosun, B.S.: EN1+TF-WeA2, **24**; EN1+TF-WeA7, 24
Toyoda, S.: PS+MN+TF-TuM1, 12
Trogler, W.: EM+TF-ThM6, 33
Tsuchiya, Y.: NM+MN+MS+TF-TuM4, 11
Tuberquia, J.C.: NM+MN+MS+TF-TuM3, 10
Tucker, R.T.: TF+SE-TuM4, **15**
Tweedie, J.S.: TF2-ThM11, 40

— U —

Uchida, G.: PS+TF-ThM5, 35
Ueda, H.: PS+TF-ThM1, 34
Uppireddi, K.: EL+AS+EM+MS+PS+TF-ThA6, **42**

— V —

Vallée, C.: TF1+EM-WeA2, 27
van Asten, A.: TF-MoA7, 7
Van Besien, E.: TF1-ThM12, **38**
van de Sanden, M.C.M.: EM+TF-TuM11, 10; EN+TF-TuA3, 17; PS+TF-ThM6, 35; PS+TF-ThM9, 35; TF-MoM4, 2
van der Marel, C.: TF-MoA4, 6
Van Dijken, J.G.: TF+SE-TuM4, 15
Van Elshocht, S.: TF1-ThM12, 38
Vanfleet, R.: TF-FrM11, 51
Vanhart, D.: EN1+TF-WeA12, 25
Varga, K.: GR+TF+ET-MoA11, **6**; GR+TF+NS-ThA4, 44; TF1-ThM5, 37
Varga, T.: TF1+EM-WeA1, 27; TF-MoM1, 2; TF-TuP2, 20
Vasco, E.: TF1-ThM1, 36
Vasekar, P.: EN1+TF-WeA12, **25**
Vasenkov, A.W.: TF2+EM-WeA9, 29
Vasquez, K.A.: TF+EN-TuM10, 14
Vega, A.: EM+TF-ThM3, 32
Vemuri, R.S.: TF-MoM1, **2**
Venkattraman, A.: TF2-ThM1, 38
Verheijen, M.A.: TF-MoA4, 6
Vermont, P.: TF-MoA1, 6
Vilan, A.: EM+TF-ThM11, **33**
Vincent-Johnson, A.J.: TF+EN-TuM10, 14
Vitale, S.A.: PS+TF-ThM11, **36**
Voevodin, A.A.: TF-FrM10, 51
Vogel, E.M.: EM+TF-TuM2, 9; EM+TF-TuM4, **9**

— W —

Wagner, F.T.: TF+EN-TuM3, 13
Waite, A.: TF-FrM10, 51
Walczyk, Ch.: TF1+EM-WeA3, 27
Walczyk, D.: TF1+EM-WeA3, 27
Walker, A.V.: EM+TF-ThM5, **33**
Walker, D.G.: AC+TF-ThA9, 41
Wallace, R.M.: EM+TF-TuM2, 9; EM+TF-TuM3, 9
Walsh, M.A.: TF+EM+SS-ThA9, 46
Wang, C.M.: TF-MoM1, 2
Wang, H.: EL+AS+EM+MS+PS+TF-ThM5, 31; EL+AS+EM+MS+PS+TF-ThM6, 32; TF-TuA10, 19
Wang, L.: TF-FrM8, **50**
Wang, W.L.: GR+TF+NS-ThA8, 45
Wang, Y.: PS+TF-ThM5, 35
Washington, J.S.: TF1+EM-WeA9, 28
Weber, J.W.: EL+AS+EM+MS+PS+TF-ThA7, 43
Weber, M.J.: EL+AS+EM+MS+PS+TF-ThA7, 43; TF-MoA4, **6**
Weeden-Wright, S.L.: AC+TF-ThA9, 41
Wei, M.: TF-FrM5, 50
Weiss, S.M.: TF1-ThM9, 37
Weller, R.A.: TF1-ThM9, 37
Wells, I.B.: EM+TF-TuM6, 9
Wenger, Ch.: TF1+EM-WeA3, **27**
Westgate, C.R.: EN1+TF-WeA12, 25
Wierer, J.: EN+TF-TuA11, 18
Williams, N.: TF+EM+SS-ThA4, 46
Willis, B.G.: TF-TuA10, **19**
Wills, A.W.: EN1+TF-WeA7, 24
Wilson, R.E.: AC+TF-ThA1, 41
Wolden, C.A.: EN2+TF-WeA8, 26; PS+TF-ThM3, **34**; TF-MoM11, 4
Woodroof, M.: TF+EN-TuM9, 14
Woollam, J.A.: EL+AS+EM+MS+PS+TF-FrM3, 48; EL+AS+EM+MS+PS+TF-FrM5, 48
Worfolk, B.J.: TF+SE-TuM4, 15
Wormeester, H.: EL+AS+EM+MS+PS+TF-ThA9, **43**
Wu, Y.: TF2+EM-WeA4, **29**
Wylie, E.M.: AC+TF-ThA8, **41**

— X —

Xu, Z.: EN+TF-TuA9, 17

— Y —

Yaffe, O.: EM+TF-ThM11, 33
Yan, B.: EN+TF-TuA7, **17**
Yan, L.: EL+AS+EM+MS+PS+TF-ThA6, 42
Yang, D.: TF2+EM-WeA7, 29
Yang, F.: GR+TF+ET-MoA3, 5
Yang, J.: EM+TF-ThM5, 33; EN+TF-TuA7, 17
Yang, K.: TF-FrM8, 50
Yasuda, T.: NM+MS+NS+TF-MoM5, 1
Ye, D.: TF-FrM4, **50**
Ye, J.: TF2+EM-WeA1, 28
Ye, L.: TF-TuP5, **21**
Ylä-Outinen, L.: TF-MoA10, 8
Yoshida, H.: NM+MN+MS+TF-TuM4, 11
Yoshimura, T.: TF1+EM-WeM6, **22**

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Zhang, C.: TF-TuA10, 19
Zhang, E.X.: TF1-ThM9, 37
Zhang, F.: EN+TF-TuA9, 17
Zhang, J.Z.: TF+SE-TuM10, 15
Zhang, Y.: GR+TF+NS-ThA8, 45
Zhao, L.: TF1-ThM12, 38
Zhao, Y.P.: TF+SE-TuM10, 15; TF+SE-TuM9, 15
Zharnikov, M.: TF+EM+SS-ThA6, 46
Zhernokletov, D.M.: EM+TF-TuM2, 9; EM+TF-TuM3, **9**
Zhou, D.: EN+TF-TuA9, 17
Zhou, Z.X.: GR+TF+NS-ThA8, **45**
Zhu, W.: GR+TF+ET-MoA7, **5**
Zhu, Y.: TF1+EM-WeA9, 28
Ziebert, C.: TF-TuP4, 20
Zuilhof, H.: TF+EM+SS-ThA1, **45**
Zvanut, M.E.: TF1-ThM2, 36