Graphene Topical Conference
Room: 306 - Session GR+TF+NC-MoM

Graphene and 2-D Carbon Nanostructures

Moderator: B.C. Holloway, Luna Innovations Incorporated, M.Y. Zhu, College of William and Mary

8:20am **GR+TF+NC-MoM1 Electrical Transport Properties of Two-Dimensional Carbon Nanostructures**, ***Y. Wu***, National University of Singapore, *H. Wang*, National University of Singapore and Data Storage Institute, Singapore, *S.S. Kushvaha*, National University of Singapore, *S.Y.H. Lua*, National University of Singapore and Data Storage Institute, Singapore **INVITED**

Recently 2D carbon nanostructures have attracted great interest due to their peculiar structural and electronic properties, especially after the successful mechanical exfoliation of single and few layer graphene from bulk graphite and epitaxial growth of graphene on SiC. We have reported previously the growth of well-aligned 2D carbon nanostructures – carbon nanowalls(CNWs), using MPECVD. Although the CNWs are structurally not as perfect as graphene sheets obtained by other techniques, its free-standing structure makes it an excellent candidate for studying electrical transport properties of 2D carbon nanostructures using end-point contacts of various types of materials including normal metal, semiconductor and superconductors. In this talk, we will present our results on (1) lateral electrical transport measurements using end-point Ti and Nb electrodes with a gap length in the range of 200 nm – 3000 nm (2) vertical transport measurements using nanoprobes in a UHV system. In (1) we focus on conductance fluctuation and proximity effect and in (2) we investigate the contact resistance between 2D carbon and different types of materials. In lateral transport measurements using Ti electrodes, excess conductance fluctuations with peculiar temperature-dependence from 1.4 to 250 K were observed with an electrode gap length of 300 and 450 nm, whereas the conductance fluctuation is greatly suppressed above 4.2 K when the electrode gap length increases to 800 and 1000 nm. The former is discussed in the context of the presence of both a small energy bandgap, while the latter is attributed to the crossover from mesoscopic to diffusive transport regime. On the other hand, in the case of Nb electrodes, we have observed proximity effect in samples with an electrode gap length of 200 – 500 nm and a reentrant behavior for samples with smaller gap length. Strong conductance oscillation was observed in samples using four-point probes which is attributed to the formation of SNS structures in CNW. In the vertical transport measurement using nanoprobes, it was found that the end-point contact resistance of carbon nanowalls on stainless steel is the lowest, followed by graphite, Si, Cu, Au (100 nm) / Ta (1 nm) / Si and Au wire. Both the contact resistance and I-V characteristics are in good agreement with the results of first principles calculations reported in the literature. The results may serve as the guides for selecting metal contacts in graphene-based devices.

9:00am **GR+TF+NC-MoM3 Characterization of Functionalized Carbon Nanosheets as a Step Towards the Development of Advanced Graphene Devices**, ***R.A. Quinlan***, College of William and Mary, *E. Widenkvist*, Uppsala U., Sweden, *J. Groff*, College of William and Mary, *M. Rooth*, Uppsala U., Sweden, *M. Kelly*, Stanford U., *R.A. Outlaw*, College of William and Mary, *V. Coleman, O. Karis, B. Sanyal, O. Eriksson, H. Grennberg*, Uppsala U., Sweden, *B.C. Holloway*, Luna Innovations, Inc., *U. Jansson*, Uppsala U., Sweden

Carbon nanosheets (CNSs) are novel free-standing carbon nanostructures, composed of horizontal basal planes and vertical sheets which are made up of 1-7 graphene layers.[1] Previous work described the successful creation of defects in the graphene lattice via an acid-treatment and the characterization of these defects with x-ray absorption near-edge spectroscopy (XANES). The presence of a peak in the carbon K-edge spectra at 287eV was assigned to a C-O σ* resonance. Theoretical modeling of a di-vacancy in a graphene bilayer system reproduced the spectra and predicts metallic conductivity of the states surrounding the defect.[2] Here we report the further characterization of functionalized carbon nanosheets (f-CNSs) via high resolution x-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). Measurements were made at room temperature up to 700K with as-deposited, water- and acid-treated CNSs. XPS measurements indicate an increase in the oxygen content of the nanostructures from 1-2% in as-deposited up to 3-4% in the acid-treated samples. The decrease of sub-peak areas in the C1s and O1s spectra with heating correlates well with the decrease in atomic oxygen content. The partial pressures of H_2, O_2, CO_2, CO and H_2O measured desorbing from the f-CNSs support the model of oxygen and hydrogen decorated defects in the graphene system. The XPS and TDS results support XANES measurements of similar samples. These results support the use of a non-oxidizing acid-treatment for controlled defect formation in a graphene system, a first step towards the development of graphene based devices.

[1] Wang et al., Free-standing subnanometer graphite sheets. Applied Physics Letters, 2004. 85(7): p. 1265-1267

[2] Coleman et al., Defect formation in graphene nanosheets by acid treatment: an x-ray absorption spectroscopy and density functional theory study. Journal of Physics D: Applied Physics, 2008(6): p. 062001.

9:20am **GR+TF+NC-MoM4 Application of Carbon Nanowalls to Negative Electrode in Lithium-Ion Battery for High-Rate Use**, ***N. Kitada***, *H. Yoshimura*, Yokohama City University, Japan, *O. Tanaike*, Advanced Industrial Science and Technology, Japan, *K. Kojima, M. Tachibana*, Yokohama City University, Japan

Recent design and fabrication of electrode in Lithium-ion battery have been focused for the high rate use since rapid charge and discharge of the battery with high power density are usually required for quick start and stop of electric vehicle or hybrid electric vehicle in next generation. One of the ways to develop the electrode for high rate use is to use nano-sized active materials since the diffusion distance of lithium ions in the solid during charge and discharge is decreased by using them. Here, we reports a new nano-sized and graphitized carbon material, two-dimensional carbon nanostructures called carbon nanowalls (CNWs) [1-5], as a promising one for negative electrode material of lithium ion battery in high rate use. CNWs were synthesized at very low temperature of 973K by a dc plasma-enhanced chemical vapor deposition. They were mixed with binder Polyvinylidenefluoride in N-methylpyrrolidone, pressed and then dried to produce carbon sample electrodes. Conventional three electrodes test cells were constructed for electrochemical measurements by carbon sample as a working electrode and two lithium foils as counter and reference ones. Lithium insertion properties were studied using these test cells by cyclicvoltammetry (CV) and charge/discharge measurements. CNWs is found to be an interesting graphitic active material for negative electrode of lithium ion battery having reversible capacity of more than 200 mAh/g with relatively stable charge/discharge potential which is very similar to the properties of graphite, even though CNWs are synthesized at very low temperature of 973K without any graphitization process at high temperature. These CNWs are well layered particles in nano scale having large exposure surface of graphene edge, which is expected to be suitable for lithium insertion at high rate charge/discharge, and present results of CVs and charge/discharge tests support it. [1] Y. Wu et al., Adv. Matter. 14, 64(2002). [2] M. Zhu et al,. Carbon. 42, 2867(2004). [1] S. Kurita et al., J. Appl. Phys. 97, 104320 (2005). [2] K. Kobayashi et al., J. Appl. Phys. 101, 094306 (2007). [3] I. Kinoshita et al., Chemi. Phys. Lett. 450, 360 (2008).

9:40am **GR+TF+NC-MoM5 Carbon Nanosheets: Novel Two-Dimensional Materials**, *A. Beyer, C.T. Nottbohm, X. Zhang, A. Turchanin*, Universität Bielefeld, Germany, *A. Sologubenko, J. Mayer*, RWTH Aachen, Germany, ***A. Gölzhäuser***, Universität Bielefeld, Germany

1 nm thick, mechanically and thermally stable carbon nanosheets are fabricated by combining molecular self-assembly with lithography. Self-assembled monolayers of aromatic molecules are cross-linked via electron or EUV irradiation. The cross-linked monolayers are released from the substrate, resulting in "free-standing carbon nanosheets" with the thickness of a single molecule.[1] We show that the nanosheets can be transferred onto arbitrary surfaces and we determine their elastic constants by AFM. We have found that nanosheets posses an extraordinarily high mechanical and thermal stability.[2] Carbon nanosheets can be used as ultrathin sample supports for transmission electron microscopy (TEM). Free-standing nanosheets were transferred onto TEM grids and nanoparticles were deposited onto them. When imaged by high-resolution TEM, the nanoparticles show a much higher contrast than those made with a conventional carbon film.[3]

[1] W. Eck, A. Küller, M. Grunze, B. Völkel, A. Gölzhäuser: Free-standing nanosheets from cross-linked biphenyl self-assembled monolayers, Adv. Mat., 17, 2583-2587, (2005)

[2] A. Turchanin, M. El-Desawy, A. Gölzhäuser: High thermal stability of cross-linked aromatic self-assembled monolayers: Nanopatterning via selective thermal desorption. Appl. Phys. Lett., 90, 053102 (2007)

[3] C. T. Nottbohm, A. Beyer, A. S. Sologubenko, I. Ennen, A. Hütten, H. Rösner, W. Eck, J. Mayer, A. Gölzhäuser: Novel carbon nanosheets as support for ultrahigh resolution structural analysis of nanoparticles. Ultramicroscopy, in press.

10:20am **GR+TF+NC-MoM7 Enhanced Field Emission of Vertical Aligned Carbon Nanosheets**, ***M.Y. Zhu***, *R.A. Outlaw, H. Chen, M. Bagge-Hansen, D.M. Manos*, College of William and Mary

Field emissions from two-dimensional free-standing carbon nanosheets with ultra-thin edges synthesized in radio frequency (RF) plasma enhanced chemical vapor deposition from CH_4/H_2 gas mixture have been previously reported. When C_2H_2/H_2 gas mixture was used, the growth temperature was lowered by 100-150 °C and well aligned vertical sheets with uniform height distribution were obtained. Typical C_2H_2 nanosheets were deposited on Si substrates using 80% C_2H_2 diluted in H_2 gas (5 sccm total gas flow rate) at 600 ºC substrate temperature and 35 mTorr total pressure with 1000 W RF power for 10 min. The growth rate of the nanosheets measured from cross-sectional scanning electron microscopic images was 10.8 µm/hr. In this report, field emission measurements were taken from nanosheet samples 1.8 µm in height. Custom LabView software controlled automatic diode I-V measurements of C_2H_2 nanosheets yielded a threshold field, for an emission current density of 10 µA/cm^2, of ~3 V/µm, which was ~2 V/µm lower than CH_4 nanosheets. At an applied field of 5.3 V/µm, the current density was 1.1 mA/cm^2 compared to the CH_4 nanosheets of ~0.007 mA/cm^2. Calculations from the Fowler-Nordheim plots and their linear fits indicated that the effective emission area of C_2H_2 nanosheets was ~15 times that of CH_4 nanosheets and the β factor of C_2H_2 nanosheets was ~26% higher than CH_4 nanosheets. The results are consistent with the morphology differences between the two kinds of nanosheets. The lifetime tests of C_2H_2 nanosheets conducted in a DC mode with a base pressure lower than 5×10^{-9} Torr showed a conditioning from an emission current of ~1.1 mA to a current level of 0.65 mA after 200 hour operation without any drop-outs or arcing failure. These tests were conducted with minimal anode cooling, which may account for the decay of the current on this timescale. The vacuum pressure of the testing system was recorded along with the emission current, and found to be closely correlated to the emission current.

10:40am **GR+TF+NC-MoM8 Control of Structures and Electrical Properties of Carbon Nanowalls Using Plasma Enhanced CVD Employing N_2/O_2 Addition to C_2F_6/H_2 Gases**, ***W. Takeuchi***, Nagoya University, Japan, *M. Hiramatsu*, Meji University, Japan, *Y. Tokuda*, Aichi Institute of Technology, Japan, *H. Kano*, NU Eco-Engineering Co., Ltd., Japan, *M. Hori*, Nagoya University, Japan

Carbon nanowalls (CNWs), that is two-dimensional carbon nanostructure of freestanding vertically oriented graphitic sheets, attract great attentions because of several applications such as electrical devices. Recently, it was reported that the 2-D multilayer graphene sheet devices offer the high mobility and the huge sustainable currents. Therefore, CNW films would have high performances of electric devices, since the CNWs basically consist of graphene sheets. In order to realize the CNW devices, it is necessary to control structures and properties. In this study, we have successfully controlled structures and electric properties of CNWs. CNWs were fabricated on the quartz substrate by plasma enhanced CVD (PECVD) employing C_2F_6 gas with H radical injection. The influences of N_2 and N_2/O_2 addition to C_2F_6/H_2 gas mixtures on structures and electric properties of CNWs were investigated. The cross-sectional scanning electron microscopy (SEM), Hall measurement and secondary ion mass spectrometry (SIMS) were used to evaluate structures, electric properties and atomic compositions of CNWs, respectively. The SEM image of the CNWs film synthesizes by N_2/O_2 mixture gas addition indicated that the size of the individual graphene of CNWs increased with less branching. The Hall coefficient indicated the positive value for the CNW film synthesized without N_2 addition. In the case of N_2 addition, it displayed the negative one. The positive or negative value means p- or n-type conduction, respectively. CNW films doped with N atoms were characterized by SIMS to investigate the effect of the N_2 addition on the atomic composition of CNWs. The carrier and N concentration in the CNW films formed by N_2/O_2 mixture gas addition were almost the same as those in the CNW film by N_2 addition. It is considered that the N atom in the CNWs act as a donor and the electrical property of N-doped CNWs can be controlled by N atom concentration. These results will be crucial to fabricate the electrical devices of CNWs without deteriorating crystallinity.

11:00am **GR+TF+NC-MoM9 Wafer-Scale Synthesis and Electrochemical Property of Graphene Formed by Microwave Plasma Enhanced Chemical Vapor Deposition**, ***L.C. Chen***, National Taiwan University **INVITED**

The recent experimental breakthroughs on graphene-based nanoelectronics have triggered enormous academic activities. Among the production methods of graphene, mechanical exfoliation of graphite and surface evaporation of SiC are widely used. Despite the successful fabrication in surface evaporation of SiC, process integration of graphene into the well-established Si-based technology remains a challenging task. In view of this, it is also desirable to develop a reliable and large-scale (or wafer-based) production of graphene for practical applications. In this presentation, we will demonstrate a novel synthetic route for graphene growth on silicon substrate by microwave plasma enhanced chemical vapor deposition (MPECVD). The resultant nanoarchitecture exhibits a wall-like morphology with a high density of sharp edges. Structure wise, each nanowall is composed of SiC decorated by a few layer of graphene (i.e. concrete paint on concrete wall). Moreover, direct deposition of Pt nanostructures onto these graphene samples is also performed to explore their potentials for electrochemical energy applications. Preliminary cyclic voltammetry studies for electro-oxidation of methanol show a high ratio of forward anodic peak current to reverse peak current, suggesting an efficient oxidation of methanol to CO2 on the Pt/graphene electrode. The effective suppression in the reverse cathodic peak current probably suggests a selective growth of Pt on graphene. Other electrochemical properties (such as electron-transfer kinetics and chemical reactivity) of MPECVD-grown graphene will also be addressed in this presentation. Our synthetic approach offers an alternative route toward wafer-scale fabrication of graphene for fundamental research and opens up various potential applications in nanoelectronics, sensing, catalysis, and energy production.

11:40am **GR+TF+NC-MoM11 Growth and Structures of Carbon Nanowalls during Plasma-Enhanced Chemical Vapor Deposition**, ***H. Yoshimura***, *N. Kitada, K. Kojima, M. Tachibana*, Yokohama City University, Japan

Recently two-dimensional carbon nanostructures called carbon nanowalls (CNWs) have been fabricated by plasma-enhanced chemical vapor deposition.[1] The CNWs are vertically grown on the substrate. According to our previous studies of Raman spectroscopy[2] and transmission electric microscopy (TEM),[3] and Ultraviolet photoelectron spectroscopy,[4] CNWs are composed of small crystallites with a high degree of graphitization. And these small crystallites so-called “nano-graphite domains” were slightly rotated each other. Such shapes and structures of CNWs may provide us with various applications, such as gas storage, membranes for electrochemical energy storage, and field emitters. The understanding of growth process and structures in CNWs is required for the practical applications. In this paper, we report the detail of growth process and structures of CNWs. CNWs were grown by using a dc plasma-enhanced chemical vapor deposition method with a gas mixture of CH_4, H_2, Ar. Typical flow rate of CH_4, H_2 and Ar were 10, 10, and 80 sccm (standard cubic centimeters per minutes at standard temperature and pressure). To investigate the growth process, specimens were prepared for plasma reaction times of 1, 2, 3, 4, 5, 7 and 15 minutes. The shapes and structures of the specimens were investigated by means of atomic force microscopy (AFM), grazing incidence X-ray diffraction (GIXD), and Raman spectroscopy. In addition, the change in the size and quality of crystallites was observed. As reported previously,[5] it was observed that CNWs changes from parallel to perpendicular to the substrate with deposition time. In addition, the transition structure from parallel to perpendicular was clearly observed. From these results, the growth process of CNWs will be discussed.

[1] Y. Wu, et al., Adv. Matter. 14, 64 (2002)
[2] S. Kurita, et al., J. Appl. Phys. 97, 104320 (2005)
[3] K. Kobayashi, et al., J. Appl. Phys. 101, 094306 (2007)
[4] I. Kinoshita, et al., Chem. Phys. Lett. 450, 360 (2007)
[5] B. L. French, et al., Thin Solid. Film, 494, 105, (2006).

Thin Film
Room: 302 - Session TF+NC-MoM

ALD of Hybrid Materials and ALD on 3D Nanostructures
Moderator: S.M. Rossnagel, IBM T. J. Watson Research Center

8:20am **TF+NC-MoM1 Interfacial Organic Layers: Tailored Nucleation and Growth of Inorganic Thin Films for Applications in Molecular Electronics and Barrier Layers**, ***J.R. Engstrom***, Cornell University **INVITED**

Interfacial organic layers, including self-assembled monolayers, have long been recognized for their potential to modify the chemical and physical properties of surfaces. One particularly exciting concept is to use interfacial organic layers to promote thin film deposition of inorganic materials, particularly in situations where nucleation is problematic. Another interesting concept involves making use of the organic layer itself as an active component in molecular-based electronics. Here, a challenge is to make electrical (top) contact with the organic layer, whilst not degrading its properties, nor forming electrical shorts due to penetration of the organic layer. Key to the realization of both of these concepts is developing an understanding of the interactions between thin film precursors, and interfacial organic layers possessing a variety of terminal organic functional groups and also microstructures. In this talk we will summarize our work in this area concerning: (i) the formation of the interfacial organic layers and their characterization; (ii) the reactions of these layers with Ti- and Taamido coordination complexes; and (iii) the formation of inorganic thin films on these layers using atomic layer deposition. Here we make use of supersonic molecular beam scattering techniques, atomic force microscopy, scanning transmission electron microscopy, and x-ray photoelectron spectroscopy. We will find that (undesired) penetration of the organic layers by the coordination complexes can be avoided and/or minimized by proper design of the organic layer. Concerning growth on the layers using atomic layer deposition, we find that the chemical termination and microstucture of the organic layers play an important role in terms of the kinetics of nucleation and growth, and the evolution of thin film morphology.

9:00am **TF+NC-MoM3 New Approaches to Molecular Layer Deposition Using Ring-Opening and Heterobifunctional Reactants**, ***D. Seghete****, B. Yoon, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Molecular layer deposition (MLD) can produce organic or hybrid organic-inorganic films. Current MLD schemes usually employ two homobifunctional monomers as reactants. This approach presents practical difficulties because the homobifunctional monomer can react with two chemical functional groups on the surface. These "double" reactions can remove the active surface species and reduce the MLD growth rate. Homobifunctional reactants can be avoided by using ring-opening and heterobifunctional reactants. The ring-opening reactants prevent double reactions by containing a concealed functionality that only expresses itself upon reaction. The heterobifunctional reactants have two chemical functional groups that are different. These precursors react only monofunctionally with the surface to avert double reactions and growth termination. In this study, we report a three-step MLD process that involves trimethylaluminum (an inorganic trifunctional reactant), ethanolamine (a heterobifunctional reactant), and maleic anhydride (a ring-opening reactant). The extension to three-step ABC MLD processes expands the variety of reactants and compositional diversity that can be achieved for MLD. In this three-step process, trimethylaluminum (TMA) reacts with carboxylic acid species (-COOH) to deposit -AlCH$_3$ species. The -AlCH$_3$ species then react preferentially with the hydroxyl end of ethanolamine (EA) to form a surface terminated with -NH$_2$ species. Maleic anhydride (MA) then reacts with these amine species and undergoes a ring-opening reaction to produce carboxylic acid (-COOH) species. The TMA can then react again with the carboxylic acid species to repeat the ABC cycle. In situ Fourier transform infrared spectroscopy and quartz crystal microbalance measurements were employed to monitor the surface reactions and measure the mass changes at temperatures from 80-150 ºC. Ex situ x-ray reflectivity (XRR) confirmed the linear growth of the MLD films versus number of ABC cycles. The growth rates decreased with increasing temperature from 23 Å per ABC cycle at 90 ºC to 8 Å per ABC cycle at 150 ºC. The XRR scans also established the low surface roughness, uniform composition and low density of the MLD films.

9:20am **TF+NC-MoM4 Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers Based on Metal Alkyl and Diol Reactants**, ***B. Yoon****, J.L. O'Patchen, S.D. Davidson, D. Seghete, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Hybrid organic-inorganic polymers can be deposited by molecular layer deposition (MLD) using metal alkyl and diol reactants. Our earlier work studied the deposition of alucone MLD films using trimethyl aluminum (TMA) and ethylene glycol (EG). In this work, we extend the possible metal alkyl reactants to diethyl zinc (DEZ) and the diols to 1,4-butanediol (BD), and 1,4-hydroquinone (HQ). Our studies were performed using in situ Fourier transform infrared (FTIR) spectroscopy to identify the surface species, in situ quartz crystal microbalance (QCM) measurements to quantify the mass gains with each surface reaction, x-ray reflectivity (XRR) studies to measure the film thicknesses and densities and transmission electron microscopy (TEM) to image the MLD films on nanoparticles. The reaction of TMA and EG results in a poly(aluminum ethylene glycol) film that can be described approximately as (Al-O-CH$_2$CH$_2$-O)$_n$. These (Al-O-R-O)$_n$ polymer films are known as alucones. The reaction of DEZ with organic diols produces zinc-containing (Zn-O-R-O)$_n$ polymer films that can be called "zincones". FTIR spectroscopy studies revealed that the surface chemistry for zincone MLD was similar to alucone MLD. QCM measurements showed linear growth for zincone MLD versus number of reaction cycles. Corresponding XRR and TEM studies revealed zincone MLD growth rates of 2.0 Å per AB reaction cycle. Different organic constituents can be incorporated into alucone MLD films using other organic diols. Alucone MLD was studied using TMA + BD and TMA + HQ. QCM measurements showed linear growth with total mass gains of 30 ng/cm^2 for TMA + BD and 89 ng/cm^2 Using film densities obtained from XRR studies, these total mass gains represent growth rates of 2.3 Å and 5.4 Å per AB reaction cycle for TMA + BD and TMA + HQ, respectively. The larger growth rates for TMA + HQ may be explained by the greater rigidity of HQ that could prevent "double" reactions from reducing the number of active surface sites and lowering the growth rate per AB reaction cycle.

9:40am **TF+NC-MoM5 Infrared Analysis of Conformality of Al$_2$O$_3$ and ZnO Atomic Layer Deposition on 3D Fibrous Structures**, ***G. Scarel****, G.K. Hyde, J.C. Spagnola, J.-S. Na, B. Gong, Q. Peng, G.N. Parsons*, North Carolina State University

Conformally coated 3D natural fibers are becoming important in various areas of catalysis, bio-scaffolds, drug delivery, energy storage and conversion applications. In this work we report on growth and characterization of inorganic coatings (Al$_2$O$_3$ and ZnO) on fibers including cotton and polypropylene. The coatings were prepared using low temperature (about 100 degree centigrade) ALD. We used tri-methyl aluminum and H$_2$O for Al$_2$O$_3$ and di-ethyl zinc and H$_2$O for ZnO. ALD is well known to produce conformal coatings on planar surfaces and deep trenches. However it is more difficult to establish and to characterize linear growth and conformality in complex 3D fibrous systems. We have developed a new method to evaluate linear growth and conformality on complex nano- and micro 3D structures. The method uses infrared spectroscopy to detect longitudinal optical (LO) modes in off-normal configurations (Berreman effect). These features pertain to ionic oxides and are sensitive to film thickness because they are generated by vibrations normal to the ionic oxide layer surface. We show that the height of a peak related to an LO mode grows linearly with the number of ALD cycles and that this linear behavior is related to the linearity of the growth on a planar Si(100) substrate. In addition, the angular behavior of the height of peaks related to LO modes in transmission infrared spectra can be related to the degree of coating conformality. In addition the data show that on 3D structures, especially on fibers, the number of incubation cycles needed before linear growth starts is even higher than on planar substrates. We investigate this phenomenon considering the structural, compositional, and the surface energy properties of the coated structures. The method we propose offers an easy non-local method to ascertain linear growth and conformality on complex 3D samples coated using ALD.

10:20am **TF+NC-MoM7 Ferromagnetic Nanostructures by Atomic Layer Deposition: From Thin Films to Ferrofluids and Core-Shell Nanotubes**, ***K. Nielsch***, Hamburg University, Germany, *J. Bachmann*, Hamburg University and Max Planck Institute of Microstructure Physics, Germany **INVITED**

Magnetic nanostructures have a broad range of applications, most prominently in the areas of data storage, microelectronics, biosensing, and cell separation. For the preparation of such structures, we use atomic layer deposition (ALD), a thin film technique with the unique ability to coat pore structures of high aspect ratio conformally and uniformly while accurately tuning the layer thickness. We approach the preparation of the magnetic materials Fe$_3$O$_4$, Co, and Ni in two steps. ALD is first used to deposit Fe$_2$O$_3$,[1] CoO or NiO,[2] either from the reaction of the corresponding metallocene with ozone or from that between the metal alkoxide and water. The oxide is subsequently reduced to the desired ferromagnetic phase by hydrogen gas. By conformal coating of self-ordered porous anodic alumina membranes, arrays of magnetic nanotubes with diameters down to 20 nm and wall thicknesses of less than 5 nm have been achieved. The magnetic properties of the nanotube arrays, studied by SQUID magnetometry, strongly depend on the geometric parameters. The effects of tube wall thickness and tube diameter have been studied systematically,[1] and the experimental data match the results of our theoretical simulations.[3] Dissolution of the alumina matrix yields ferrofluidic suspensions, made out of widely tunable magnetic particles. Finally, ALD also enables us to create core-shell nanoobjects combining different magnetic materials in various, accurately controlled geometries.

[1] J. Bachmann, J. Jing, M. Knez, S. Barth, H. Shen, S. Mathur, U. Gösele, K. Nielsch, J. Am. Chem. Soc. 2007, 129, 9554-9555.

[2] M. Daub, M. Knez, U. Gösele, K. Nielsch, J. Appl. Phys. 2007, 101, 09J111.

[3] J. Escrig, J. Bachmann, J. Jing, M. Daub, K. Nielsch, D. Altbir, Phys. Rev. B 2008, accepted.

11:00am **TF+NC-MoM9 Tube-in-Tube Nanostructures Formed from the Kirkendall Effect using Atomic Layer Deposition on Three Dimensional Electrospun Fiber Templates**, ***Q. Peng****, X.Y. Sun, J.C. Spagnola, R.J. Spontak, C. Saquing, S.A. Khan, G.N. Parsons*, North Carolina State University

Three-dimensional (3D) macrostructures consisting of well-defined nanoscale elements with controlled properties have attracted significant interest for a range of fields. To date, large-scale fabrication of these 3D macrostructures remains an important outstanding challenge. We are currently exploring atomic layer deposition on a variety of nano- and micro-scale fiber systems for fabrication of macro size 3D structures with molecular-scale control. Recently, we have applied low temperature (< 80 degree C) Al2O3 and ZnO ALD processes onto 3D polyvinyl alcohol electrospun fiber matrix templates to form Al2O3, ZnO and

Al2O3/ZnO/Al2O3 multilayer nanotubes with controlled tube wall thickness. SEM, TEM and XRD have been used to probe the structure and crystal structure of the materials as a function of deposition parameters and post-deposition calcination and annealing. We find that upon annealing at 700 degree C, the ZnO and Al2O3 layers in the Al2O3/ZnO/Al2O3 coaxial structures can react with each other, due to the solid-state reaction and diffusion process between ZnO/Al2O3 (Kirkendall effect), to form pairs of coaxial ZnAl2O4 hollow nanotubes separated by a nanoscale gap. Moreover, by controlling the thickness of the individual Al2O3 and ZnO layers and the ZnO/Al2O3 thickness ratio, the final thickness of the nanotubes and the separation nanogap can be tuned to form a variety of well-defined tube-in-tube nanosystems. Under some conditions, unreacted ZnO layers can remain after annealing, resulting in multi-compositional structures with segregated voids. These results show the feasibility of extending reactivity of ALD thin films and Kirkendall effect to form a range of quasi-one-dimensional nanostructures for a variety of potential applications.

11:20am **TF+NC-MoM10 Structured Photoanodes for Enhanced Electron Transport in Dye Sensitized Solar Cells (DSSC) with Atomic Layer Deposition (ALD)Functionalization***, **M.J. Pellin**, A.B.F. Martinson, J.W. Elam,* Argonne National Laboratory*, J.T. Hupp*, Northwestern University **INVITED**

Inexpensive, efficient solar energy conversion requires synthetic methodology capable of creating structures that resolve the conflict between the long lengths required for efficient photon absorption with the short photoelectron diffusion lengths found for all but the most perfect crystalline materials. DSSC's photoanodes utilize titania nanocrystals sensitized with monolayers of dye to achieve efficient photon absorption. However, DSSC conversion efficiencies have been limited to ~10% by a charge collection time of milliseconds at the maximum power point. Thus efficient charge extraction is only possible with an iodide/triiodide (I-/I$_3^-$) redox shuttle with both the high driving force needed to regenerate dyes at acceptable rates (and the consequent >500 mV energy cost/photon)and a remarkably inefficient I$_3^-$ electron interception rate. We have been addressing this problem using the ability of ALD to conformally grow nm thick, pin-hole free layers on nanoporous, high surface area supports. The charge collection times can be improved either by reducing the dimensionality of the photoanode or by reducing the electron collection distances. We address the former with precision films grown on nanoporous substrates such as anodic aluminum oxide (AAO) or silica aerogel supports. The AAO, for instance, has a regular array of 200 nm straight channels that traverse its 60 @smicron@ thick membrane. ALD is used to conformally coat with either ZnO or TiO$_2$ (achieving peak efficiencies at ~ 4-5 nm thickness) the membrane channels. One side of the membrane is coated with a thick transparent conducting oxide such as ITO. The pore walls are then sensitized with a dye and the resulting photoanode is assembled into a photocell. The linear tubes thus created form a one-dimensional network of 60 μm long tubes with excellent charge collection times. Dramatically reduced electron collection distances can be tested with a more complex structure grown by first coating the AAO substrate with a transparent conducting oxide such as ITO, then adding a wide band gap oxide (TiO$_2$), before completing the cell with dye attachment and assembly. In these cells, electron diffusion occurs radially through the thin (~5 nm) TiO$_2$ layer into the TCO, rather than along the pore. Again the electron diffusion times are dramatically reduced. The wide palate, precision composition, and conformal nature of ALD synthesized films enable the exploration of these complex structures improving our understanding of the factors limiting solar energy conversion. *The work at Northwestern is supported by the U.S. Department of Energy, Basic Energy Sciences Program, under Grant DE-FG02-87ER13808. Work at Argonne is supported by the U.S. Department of Energy, BES-Materials Sciences under Contract W-31-109-ENG-38.

Thin Film
Room: 302 - Session TF-MoA

ALD: Functionalization and Surface Chemistry
Moderator: R.G. Gordon, Harvard University

2:00pm **TF-MoA1 Atomic Layer Deposition of Platinum on Strontium Titanate Surfaces**, ***J.W. Elam***, Argonne National Lab., *S.T. Christensen, F.A. Rabufetti*, Northwestern U., *W. Setthapun, B. Lee,* Argonne National Lab., *Z. Feng,* Northwestern U., *P.C. Stair,* Argonne National Lab. & Northwestern U., *C.L. Marshall,* Argonne National Lab., *K.R. Poeppelmeier,* Northwestern U., *M.J. Bedzyk,* Argonne National Lab. & Northwestern U., *M.C. Hersam*, Northwestern U.

Platinum supported on metal oxide surfaces has important technological applications in oxidative dehydrogenation catalysis, photocatalysis, and in catalytic converters. The atomic layer deposition (ALD) of Pt on oxide surfaces is unusual because it proceeds via nucleation, growth and coalescence of islands in contrast to the layer-by-layer behavior typically observed during the ALD of metal oxides. This natural tendency towards agglomeration combined with the ability to infiltrate porous materials makes ALD Pt an attractive method for preparing catalysts on high surface area supports. In this presentation, I will describe our recent work exploring Pt ALD on strontium titanate (STO) surfaces including both single crystal STO(001) substrates as well as novel STO nanocubes prepared by hydrothermal methods. We use a broad variety of methods to characterize these samples including atomic force microscopy, scanning- and transmission-electron microscopy, grazing incidence small angle X-ray scattering, X-ray reflectivity, X-ray fluorescence, and extended X-ray absorption fine structure measurements. These ex situ measurements are complemented by in situ quartz crystal microbalance and quadrupole mass spectrometer studies examining the mechanism of Pt ALD. These measurements clearly reveal the nucleation and growth of nm-sized Pt clusters on the STO surfaces where the Pt cluster size is controlled by the number of Pt ALD cycles. These Pt clusters are remarkably active for catalyzing the oxidation of hydrocarbons as demonstrated by propane light-off studies. The Pt clusters are very stable on the STO surfaces at temperatures up to 400-500°C, but sinter when heated to 800°C in vacuum.

2:20pm **TF-MoA2 Remote Plasma and Thermal ALD of Platinum and Platinum Oxide Films**, ***W.M.M. Kessels***, *H.C.M. Knoops, A.J.M. Mackus, S.A.F. Dielissen, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

Due to its chemical stability and excellent electrical properties platinum has wide application prospects in catalysis and microelectronics. Recently the deposition of Pt films in complex 3D structures by ALD has gained interest for catalyst applications in fuel cells and as a current collector layer in Si-integrated solid-state thin film Li-ion batteries. In this contribution we report on thermal and remote plasma ALD of Pt films using $MeCpPtMe_3$ precursor combined with O_2 gas and O_2 plasma, respectively. For the thermal process the results obtained by Aaltonen et al.[1] were reproduced (growth per cycle is 0.045±0.005 nm) and special attention was given in characterizing the growth incubation period on Si with thermal and native oxide by using in situ spectroscopic ellipsometry. With the new remote plasma ALD process (growth per cycle is 0.047±0.005 nm) the growth incubation could be reduced to a few cycles yielding the possibility to initialize Pt growth by depositing a remote plasma ALD "seed layer" and thickening the film by thermal ALD. A short plasma exposure (0.5 s) was necessary to deposit Pt films with no detectable amount of oxygen while a long O_2 plasma exposure (5 s) resulted in platinum dioxide ($PtO_{2.2}$, growth per cycle is 0.048±0.004 nm). Pt films were deposited with a mass density of 20.8 g/cm^3 and an electrical resistivity of 14 $\mu\Omega$ cm, both close to the bulk values of 21.4 g/cm^3 and 10.8 $\mu\Omega$ cm. The platinum oxide films had a mass density of 8.9 g/cm^3 and they showed a semi-conductive behavior (resistivity of >100 Ω cm, bandgap 0.85 eV). In addition to ex situ film analysis, several in situ diagnostics have been employed. With spectroscopic ellipsometry the film thickness and (optical) film properties were monitored as a function of the number of cycles. From the Drude parameters in the Drude-Lorentz optical parameterization of the platinum, information about mass density and electrical resistivity was extracted. With infrared transmission spectroscopy the consumption of $MeCpPtMe_3$ precursor was measured while currently also the reaction products generated during the surface reactions are being investigated.

[1] T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskela, Chem. Mater. 15, 1924 (2003).

2:40pm **TF-MoA3 Growth Kinetics and Mechanism of Rapid SiO_2 ALD Using Tris(tert-Pentoxy)Silanol**, ***S.M. George***, *B.B. Burton*, University of Colorado

Rapid SiO_2 ALD can deposit very thick, ~100 Å, conformal SiO_2 films by exposure of various silanol precursors to surfaces covered with Al-catalysts. Rapid SiO_2 ALD with tris(tert-butoxy)silanol (TBS) was reported at temperatures from 200─300°C and deposited SiO_2 film thicknesses as large as 120 Å [R.G. Gordon and coworkers (Science 298, 402 (2002)]. In this study, we have explored the growth of rapid SiO_2 ALD films using liquid tris(tert-pentoxy)silanol (TPS). TPS can deposit even thicker SiO_2 films at lower temperatures. The rapid SiO_2 ALD growth is believed to result from the growth of siloxane polymer chains at Al-catalytic sites and the cross-linking of these polymer chains to form a dense SiO_2 film. The SiO_2 film thicknesses deposited during one silanol exposure are dependent on the temperature, silanol pressure, and silanol exposure time. SiO_2 film thicknesses were determined using quartz crystal microbalance and x-ray reflectivity measurements. For TPS exposures of 1 second, the SiO_2 ALD growth rate was larger at lower temperatures and larger TPS pressures. SiO_2 ALD thicknesses of 125─140 Å were observed at the highest TPS pressures of ~1 Torr at the lower temperatures. These results indicated that higher TPS fluxes increase the siloxane polymerization rates. Likewise, the lower temperatures reduce the cross-linking rates between the siloxane polymers that self-limits the SiO_2 deposition. To explore the rate of cross-linking between the siloxane polymers, experiments were conducted where small TPS micropulses were employed with different delay times between the micropulses. The final limiting SiO_2 ALD mass gains decreased with increasing delay times. This behavior suggested that the longer delay times produced more cross-linking that self-limits the SiO_2 deposition. Other experiments showed that higher temperatures produced faster nucleation of the rapid SiO_2 ALD. The nucleation was nearly immediate at the higher temperatures and could be as long as 10 seconds at the lower temperatures. The growth kinetics of rapid SiO_2 ALD can be understood in terms of the temperature dependence of nucleation and cross-linking and the pressure dependence of the siloxane polymerization rate.

3:00pm **TF-MoA4 Atomic Layer Deposition of Titanium Dioxide: Reaction Mechanism Studies using In Situ Attenuated Total Reflection Fourier Transform Infrared Spectroscopy**, ***V.R. Rai***, *S. Agarwal*, Colorado School of Mines

The authors have investigated the surface reaction mechanism during the atomic layer deposition (ALD) of TiO_2 using titanium tetraisopropoxide (TTIP) as the metal precursor and O_3, atomic O, and H_2O as the oxidizers. The surface species during each half-reaction cycle were detected using in situ, real-time attenuated total reflection Fourier-transform infrared spectroscopy. Sub-monolayer sensitivity was obtained by multiple internal reflections through the ZnSe internal reflection crystal, which has a refractive index that is closely matched to that of amorphous TiO_2. We find that the surface reaction mechanism is very different for O_3- and H_2O-based ALD. Surface hydroxyl groups are generally the reactive sites for the metal precursors in a H_2O-based ALD process. In contrast, we do not detect any hydroxyl groups on the surface after the O_3 cycle. Our data shows that the reactive sites for the adsorption of TTIP after O_3 exposure of the surface are carbonate groups with symmetric and anti-symmetric stretching absorptions in the 1400 – 1700 cm^{-1} region. These surface carbonates can be present as mono-, bi-, or poly-dentates. Due to their thermal stability at the growth temperature, all three types of carbonated are present simultaneously resulting in several overlapping absorption bands in the 1400 – 1700 cm^{-1} region, which could not be deconvoluted. We hypothesize that during O_3 exposure, CO_2 and H_2O are formed due to the combustion of isopropoxy ligands and a small fraction of these molecules react with the TiO_2 surface producing these surface carbonates. CO_2 was in fact detected as one of the reaction products in the gas-phase by the IR beam passing through the chamber. When the isopropoxy ligands react with the surface, CO_2 from the carbonates was released into the gas phase and was again detected by the IR beam. Using O_3 as the oxidizer, relatively contaminant-free TiO_2 films were deposited at 150 °C: this is nearly 100 °C lower than the widely-accepted minimum temperature for the TTIP-H_2O ALD window. Ex situ spectroscopic ellipsometry data shows a refractive index of ~2.2 and a nearly constant growth rate of ~0.52 Å/cycle over the temperature range of 150-250 °C.

3:20pm **TF-MoA5 Surface Preparation and Interface Cleaning during HfO_2 ALD on GaAs**, ***T. Gougousi***, *J.C. Hackley,* UMBC, *J.D. Demaree*, Army Research Laboratory

The atomic layer deposition of HfO_2 thin films is studied on GaAs(100) surfaces. The films are grown using tetrakis(dimethyl)amino hafnium

(TDMAH) and H_2O precursors at a deposition temperature of 275°C. Several GaAs starting surfaces are investigated, including native oxide and both HF and NH_4OH-treated substrates. Wet chemical etching in either HF or NH_4OH solutions are shown to remove most of the Ga and As native oxides. Spectroscopic ellipsometry (SE) confirms linear growth rates of ~1.0 Å/cycle for all surfaces. Rutherford backscattering spectrometry (RBS) shows that steady-state growth of 2.6×10^{14} Hf/cm^2/cycle is reached after 10 ALD cycles for the HF-etched GaAs surface while much smoother growth is observed for the native oxide surface (~2.9×10^{14} Hf/cm^2/cycle). The interface of HfO_2 films deposited on GaAs surfaces is probed by X-ray photoelectron spectroscopy. Both the HF and NH_4OH treatments passivate the surface and prevent the oxidation of the interface during the deposition of coalesced HfO_2 films (> 15 ALD cycles). Deposition of HfO_2 films on the native oxide GaAs surfaces show gradual consumption of the native oxides during the process, indicating the presence of an "interfacial cleaning" mechanism comparable to that observed for other metal oxide ALD processes on GaAs and InGaAs substrates.[1,2,3,4] The As-oxide and most of the Ga-oxide is removed after 20 ALD cycles. The presence of As oxides is not detected for films as thick as ~100Å (100 cycles) deposited on native oxide substrates.

[1] M.M. Frank, G.D. Wilk, D. Starodub, T. Gustafsson, E. Garfunkel, Y.J. Chabal, J. Grazul, D.A. Muller, Appl. Phys. Lett. 86, 152904 (2005)

[2] M.L. Huang, Y.C. Chang, C.H. Chang, Y.J. Lee, P. Chang, J. Kwo, T.B. Wu, M. Hong, Appl. Phys. Lett. 87, 252104 (2005)

[3] C.-H. Chang, Y.-K. Chiou, Y.-C. Chang, K.-Y. Lee, T.-D. Lin, T.-B. Wu, M. Hong, J. Kwo, Appl. Phys. Lett. 89, 242911 (2006)

[4] D. Shahrjerdi, E. Tutuc, S.K. Banerjee, Appl. Phys. Lett. 91, 063501 (2007).

4:00pm **TF-MoA7 New Barium, Strontium, and Titanium Precursors for the Deposition of Barium/Strontium-containing and Titanium Nitride Thin Films**, ***Q.M. Wang**, D.V. Shenai,* Rohm and Haas Electronic Materials LLC, *R.G. Gordon*, Harvard University

Atomic Layer Deposition (ALD) is a technology gaining recognition in the semiconductor industry because of its exceptional benefits: an extremely precise thickness control, a very good composition control, an excellent conformality over aggressive geometries, and a wide deposition temperature window. As a result, numerous ALD-based processes are currently being developed for depositing a wide variety of metals and dielectrics for high-k gate dielectrics, metal gate/capacitor electrodes, barrier metals, seed layers, and ferroelectric films. Identification of suitable precursors has often been one of the challenges and critical success factors in ALD process development. The thermal stability and vapor pressure of the sources play a significant role in the stringent selection criteria along with a high reactivity with the second reactant in a wide temperature window, an acceptable shelf-life, and an ultra-high purity. For the ALD of high-k dielectrics, metal halides were adopted early on as the precursors of choice, which were later replaced by metalorganic sources with metal-nitrogen bonds such as metal dialkylamides and more recently developed metal amidinates. The metal amidinate sources have produced excellent results in the deposition of many thin film materials. In this study, we report the synthesis of new dialkylamidinate precursors for barium, strontium and titanium. These amidinate complexes display high thermal stabilities, acceptable vapor pressures and promise to be superior sources for deposition of barium/strontium-containing titanate, niobate, or tantalate thin films, as well as titanium nitride films by ALD. Volatility and thermal stability data for the barium, strontium and titanium amidinate complexes will be discussed. The barium and strontium amidinates are dimeric crystalline materials. The new titanium(III) amidinate is a low-melting material that greatly facilitates its handling in bubblers, while the titanium(IV) amidinate is a dimeric crystalline material. Data showing the high purity of the amidinate sources will be demonstrated by ICP-MS and FT-NMR analysis, and data characterizing their thermal stabilities will be provided from TGA/DSC and FT-NMR analysis. Preliminary deposition results of barium titanate, strontium titanate, and barium-strontium titanate thin films with these amidinate precursors will be provided.

4:20pm **TF-MoA8 Ab Initio and FTIR Study of TDMAH and HTB Adsorption and Reaction on Hydrogen-terminated Si Surfaces**, ***K. Li**, N. Li, H.C. Turner, T.M. Klein*, University of Alabama

An ab initio study of the reaction pathway and energetics of HfO2 deposition from tetrakisdimethylamido hafnium (TDMAH) and hafnium tert-butoxide (HTB) onto hydrogen terminated Si(111) and Si(100) is compared with ATR-FTIR experimental data between 330K and 520K. Hf-OH streching modes are evident at low temperatures for the HTB reaction while Hf-H streching modes are predominant for TDMAH chemisorbed layers. A mechanism involving silyl radicals for the later is proposed. The results are important towards understanding the limitations of atomic layer deposition during the initial growth phase. Factors influencing the interface bonding and coverage limitation will be discussed.

4:40pm **TF-MoA9 In-situ Quadrupole Mass Spectroscopy Analysis of Low Temperature Cobalt Deposition Reactions using $Co_2(CO)_8$ and $Co(C_5H_5)(CO)_2$ in Atomic Layer Deposition Process Sequencing**, ***S.J. Oh**, G.N. Parsons*, North Carolina State University

Cobalt is of interest as a catalyst in Fisher-Tropsch synthesis, in the Pauson–Khand reaction and for carbon nanotube growth. Cobalt's high magnetic permittivity also makes it valuable for data storage applications. Cobalt thin films are widely deposited by thermal and plasma ALD and CVD at temperatures between 200 and 400 ºC. Lower temperature deposition processes are beginning to open new applications, including coating of temperature sensitive polymers and templating of biological materials. However, processes for conformal metal film deposition at less than 150 ºC are not widely available. Previous studies of CVD Co from $Co_2(CO)_8$ show a transition in reaction kinetics at temperatures near 100 - 150 ºC, consistent with a thermally activated increase in gas phase interactions between precursor molecules resulting in a decrease in deposition rate with increasing temperature. For this work, we undertook a study of low temperature cobalt thin film deposition using ALD process sequencing under the hypothesis that avoiding precursor interactions may produce a viable low temperature ALD process. Film growth was studied between 30 and 130 ºC using $Co_2(CO)_8$ and H_2 gases using on-line quadrupole mass spectrometry and Auger electron spectroscopy. Similar experiments using cobalt cyclopentadienyl dicarbonyl and H_2 reactants were also performed between 140 and 350 ºC. For the dicobalt octacarbonyl precursor, film deposition rate and in-situ quadrupole mass spectroscopy results demonstrate that for all gas pulse times studied, film growth proceeds continuously at temperature as low as 60 ºC, with no indication for self-limiting precursor adsorption. The observed continuous film growth with the $Co_2(CO)_8$ is related to the zero-valent metal center, where no reduction step is required to produce a reactive surface for adsorption. The cyclopentadienyl dicarbonyl precursor showed evidence for carbonyl cleavage and volatile Co(cyclopentadienyl), without film growth at less than 300 ºC. In addition, the mass spectroscopy results show evidence for CH_4 and C_2H_6 production during Co film nucleation, with no hydrocarbons present during subsequent processing. This is consistent with an interesting self-catalytic effect of the cobalt nuclei that decreased upon continuous film formation.

5:00pm **TF-MoA10 Reaction Mechanism Studies on ALD and CVD of Cobalt from Dicobalt Hexacarbonyl Tert-Butylacetylene**, ***T.Y. Park**, K.W. Lee, J.S. Lee, D.O. Kim, J.S. Lee, H.T. Jeon, Y.D. Won*, Hanyang University, Korea Republic

Atomic layer deposition (ALD) and chemical vapor deposition (CVD) have been widely used to deposit many different materials in many different applications in the fields of semiconductors, and displays, recently. Generally, in these deposition methods they use MO precursors because of its high reactivity, liquid source and easy to control. In this study we tried to deposit Co film with MO precursor with two different deposition methods. There is very few precursors are available as a Co source and we chose CCTBA (dicobalt hexacarbonyl tert-butylacetylene) as Co source and hydrogen as a reactant gas. Reaction mechanism in both ALD and CVD was studied in the deposition system equipped with quadrupole mass spectrometer(QMS) and Auger electron spectroscope (AES). And we compared results with CVD and ALD. In this particular precursor CVD method give low impurity concentration and high growth rate compared to ALD grown films. This difference of impurity contents of cobalt films is due to their different reaction mechanism during deposition. In case of ALD, we think some of the ligands in a precursor were not broken completely and then incorporated into cobalt film during deposition. But for CVD, there was under 3% of carbon that was detected by AES (with RBS calibration). Therefore we will present the reaction mechanism of CCTBA precursor for depositing cobalt film by ALD & CVD method and the results that we analyzed this with in-situ QMS and AES.

5:20pm **TF-MoA11 Excellent Si Surface Passivation Properties of ALD Al_2O_3 Films Studied by Optical Second-Harmonic Generation**, ***J.J.H. Gielis**, B. Hoex, N.M. Terlinden, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Thin films of Al_2O_3 synthesized by (plasma-assisted) atomic layer deposition (ALD) provide an excellent level of surface passivation of c-Si and III-IV compound semiconductors, which is vital for the performance of devices such as nanocrystal or wafer-based light emitting diodes, photodetectors, and high-efficiency solar cells. Recently, it was demonstrated that the surface passivation properties of Al_2O_3 thin films arise after a postdeposition anneal.[1] In general, surface passivation can be achieved by a reduction of surface defects or by electrostatic shielding of charge carriers by internal electric fields (i.e., field-effect passivation). In this contribution the nonlinear optical technique of second-harmonic generation (SHG) has been applied to study Al_2O_3 thin films on c-Si substrates with interfacial SiO_x layers, both before and after anneal. SHG is a surface and interface specific technique that is extremely sensitive to internal electric fields. Spectroscopic SHG, carried out with a femtosecond Ti:sapphire laser tunable in the 2.66-3.50 eV SHG photon energy range, has revealed the presence of negative fixed charge in the Al_2O_3. For as-deposited Al_2O_3 films the negative fixed charge density was found to be on the order of 10^{11} cm^{-2}, which increased to 10^{12}-10^{13} cm^{-2} after anneal. The corresponding internal electric field most likely accounts for the surface passivation properties of Al_2O_3 thin films after anneal. The important role of the negative fixed charge density in the passivation properties of Al_2O_3 was confirmed by carrier lifetime spectroscopy and capacitance-voltage measurements. In addition, real-time SHG experiments causing multiple-photon-induced charge trapping suggest a reduction of recombination channels after anneal, which could play an additional role in the surface passivation mechanism by Al_2O_3. It is straightforward to extend the approach discussed in this contribution to enable contactless characterization of charge and charging dynamics in c-Si/high-κ dielectric structures in situ and during processing, which provides not only relevant information on field-effect passivation but also for nonvolatile memory and CMOS transistor applications.

[1] B. Hoex et al. Appl. Phys. Lett. 89, 042112 (2006); Appl. Phys. Lett. 91, 112107 (2007).

Thin Film
Room: 302 - Session TF-TuM

Applications of Atomic Layer Deposition
Moderator: G.N. Parsons, North Carolina State University

8:00am **TF-TuM1 Atomic Layer Deposition Templating Techniques and Materials for Photonic Crystals**, ***C.J. Summers,*** Georgia Institute of Technology, *E. Graugnard,* Rollins College, *D. Gaillot,* IEMN Laboratoire Central - CNRS, France, *J. Blair*, Georgia Institute of Technology **INVITED**

Atomic layer deposition is shown to be a powerful tool for the fabrication of novel 3D and 2D periodic dielectric structures. It is a unique complement to a variety of template technologies by providing a mechanism to invert, replicate and convert materials while precisely retaining the form of the original template. The ability to change material type not only enables additional functionalities to be added to the structure, but also significantly enhances the processing range when high melting point materials are substituted for low melting point materials. The ability to refine lattice geometries by the sacrificial layer and backfilling technique are shown to be powerful methods to enhance and tune structural and optical properties. This is demonstrated for both synthetic silica opal and polymer (holographically) derived templates, where dielectric lattice inversion, and the development of large pore structures offer significant enhancement to the photonic band gap by backfilling with different high-index materials. Additionally, the incorporation of luminescent, electro-optic and liquid-crystals can be used to significantly increase the functionality of the original structures. Theoretical and experimental investigations of these structures are presented and provide clear evidence of the precise control enabled by atomic layer deposition. Also we report further extensions of the ALD technique for surface preparation and functionalization for multilayer growth, and developments for the deposition of high index and optically transparent materials such as GaP and Zr3N4. The recent extension of these deposition techniques to the development of novel 2D slab waveguide structures is presented.

8:40am **TF-TuM3 Effect of Yb^{3+} co-Doping on the Luminescent Properties of Er^{3+}:Y_2O_3 Thin Films**, *J. Hoang,* ***J.P. Chang***, University of California, Los Angeles

Radical enhanced atomic layer deposition (ALD) has been previously shown to enable the control of the Er^{3+} spatial distribution in Y_2O_3 thin films, thereby achieving an enhanced direct absorption cross section at 1540 nm and much improved photoluminescence with well-resolved Stark features.[1] Given the larger index of refraction of Y_2O_3 compared to that of SiO_2, this suggests that Er:Y_2O_3 thin films has the potential to achieve compact optical amplification. In this work, we report the utilization of radical enhanced atomic layer deposition to synthesize controlled concentrations and spatial distances of Yb and Er in Yb^{3+} co-doped Er:Y_2O_3 thin films and the corresponding improvement in their optical characteristics. The electronic energy level and a large absorption cross section of Yb^{3+} make it an effective sensitizer for Er^{3+}. Thin films of approximately 10 nm are synthesized by sequential radical-enhanced ALD of Y_2O_3, Er_2O_3, and Yb_2O_3 at 350°C. The composition, microstructure, cation distribution, local chemical bonding and optical properties of the as-synthesized thin films were determined by x-ray spectroscopy, electron microscopy and photoluminescent measurements. To optimize the effect of the sensitizer and minimize the concentration quenching, the concentration of Yb^{3+} and Er^{3+} were controlled by changing the global deposition cycle sequence. Extended x-ray absorption fine structure analysis verified spatial control of Yb^{3+} and Er^{3+} in the Y_2O_3 host. Much improved effective absorption cross sections were estimated using the photoluminescence yield as a function of the pump power, as compared with measurements from thin films without Yb^{3+} sensitizers. From these measurements, an optimum concentration and spatial arrangement is chosen for the design of spiral ridge waveguide devices. These waveguides can achieve potential gains of two orders of magnitude over Er:SiO_2 and an order of magnitude over ion implanted Al_2O_3.

[1] Hoang, J., T. T. Van, et al. Journal of Applied Physics. 101(12).

9:00am **TF-TuM4 Atomic Layer Deposition of Gallium Nitride Using $GaCl_3$ and NH_3 Reactants**, ***O.H. Kim,*** *D.J. Kim, T.J. Anderson*, University of Florida

GaN films were grown on silicon substrates by atomic layer deposition (ALD) using $GaCl_3$ and NH_3. It is postulated that incomplete purging of $GaCl_3$ for long $GaCl_3$ exposure times allows gas phase formation of $(Cl_2GaNH_2)_n$ species with n=1-3,[1] which results in higher chlorine content. X-ray photoelectron spectroscopy was used to determine N/Ga ratio in the film over exposure time, and showed a maximum N/Ga ratio in the saturation limit. Ab-initio calculations were implemented to understand the surface reactions in the saturation limit growth condition. Potential Energy Surface (PES) diagrams for the two adsorption reactions were used to explain the high N/Ga ratio in the ALD limit.

[1] A. Kovács, Inorg. Chem. 2002, 41, 3067-3075.

9:20am **TF-TuM5 Ruthenium and Ruthenium Oxide Thin Films prepared by Atomic Vapor Deposition for MIM Applications**, ***P.K. Baumann***, *C. Manke,* AIXTRON AG, Germany, *G. Ruhl,* Infineon Technologies AG, Germany, *A. Schroeder-Heber, L. Pfitzner, M. Schellenberger*, Fraunhofer IISB, Germany

As outlined in the International Technology Roadmap for Semiconductors (ITRS), new electrode and high-k materials have to be introduced to replace polysilicon and silicon dioxide, to allow continued scaling of further device technologies. In this study ruthenium and its metallic oxide RuO2 have been examined as possible candidates for MIM (metal-insulator-metal) capacitors. Ruthenium has a low bulk electrical resistivity of 7 microOhmcm. Ruthenium and ruthenium oxide also have very good diffusion barrier properties. We have deposited ruthenium and ruthenium oxide films by AVD (atomic vapor deposition), a pulsed MOCVD (metal organic vapor deposition) method. This method allows to combine features of ALD (atomic layer deposition), such as atomic layer control with the high deposition rate of MOCVD. The electrode films with a typical thickness of 10 nm were deposited on hafnium oxide dielectrics and silicon dioxide as reference. Physical characterization was done by Transmission Electron Microscopy (TEM), Ellipsometry, Atomic Force Microscopy (AFM), and X-Ray Reflectometry (XRR). Near bulk densities of Ru and RuO2 of 12 and 7 g/cm3 have been obtained. For Ru on hafnium oxide a sheet resistance of 10 Ohm/square was achieved. Advanced MIM capacitors were fabricated and characterizes by I vs. U and C vs. U measurements. Even after 5 months storage in ambient conditions the structures showed almost no change in breakdown characteristics. Results from physical and electrical measurements will be presented and correlated. This work was performed within the SEA-NET project funded within the 6th Framework Program of the European Commission, SEA-NET Contract no.: 027982. See www.sea-net.info.

9:40am **TF-TuM6 In-Situ FTIR Study of Atomic Layer Deposition of Ruthenium**, *Y.J. Chabal,* ***S.K. Park,*** *J. Kwon, M. Dai,* University of Texas at Dallas, *R. Kanjoliab,* SAFC Hitech, *R. Odedrac,* SAFC Hitech Ltd., UK, *N. Boagd*, University of Salford, UK

Ruthenium is a potential capacitor electrode material for DRAMs and FRAMs, and potential gate metal MOSFETs due to is relatively high work function (4.7eV).[1] There is also recent interest in Ru as a combined barrier and seed layer for copper. Since atomic layer deposition (ALD) is technique of choice for deposition of thin and conformal film growth even on structured surfaces such as trenches and via holes, there is an active search for Ru ALD precursors possessing appropriate physical and chemical properties, which are important for the development of a proper deposition process. There is also the need to understand the chemical interaction of these new precursors with various surfaces and the mechanism of ALD growth to advance the field. So far, surface nucleation, overall interface formation and growth mechanisms are not well understood since most of film characterization has been performed with ex-situ measurements. In this study, we present in-situ FTIR studies of ALD growth of Ru thin films on Si substrates using newly synthesized cyclopentadienyl methylruthenium dicarbonyl ($CpRuMe(CO)_2$) and D_2O. Film growth rates were determined from ex-situ RBS measurements. SiO_2/Si(100) and atomically flat hydrogen-terminated Si(111) surfaces were used as substrates for Ru film growth. For the H/Si(111) substrate maintained at 300°C during growth, the first half-cycle Ru precursor pulse almost completely consumes the surface hydrogen as evidenced by the loss of monohydride Si-H stretching mode at 2084 cm^{-1}, which suggests a very high reactivity of the precursor toward the H/Si(111) surfaces at 300°C. The initial Ru deposition on H/Si(111) is initially good at 300°C, then becomes harder (lower growth rate). The precursor reactivity strongly decreases at lower substrate temperatures, involving only 30% of the surface hydrogen at 250°C substrate temperature. More importantly, there is no measurable Ru deposition, presumably because of competitive surface reactions. The reactivity and Ru growth on oxides, specifically SiO_2/Si(100) substrate, are surprisingly lower than on H/Si(111) substrates at 300°C. Despite this low growth rate, the IR spectra give clear evidence for ligand exchange and adsorption of surface species, making it possible to identify and quantify surface chemical reactions during the ALD process.

[1] Titta Aaltonen et al., Chem. Vap. Deposition 9, 45 (2003).

10:40am **TF-TuM9 Mechanistic Study of Atomic Layer Deposition of Copper**

***M. Dai**, J. Kwon,* Rutgers University*, S.Y. Park,* University of Texas at Dallas*, L.S. Wielunski,* Rutgers University*, Y.J. Chabal,* University of Texas at Dallas*, Z. Li, R.G. Gordon*, Harvard University

In microelectronics, Cu is replacing Al for IC interconnects because of its lower resistance and higher melting point. For such microelectronics applications, a controlled metallization method to deposit very thin, uniform and conformal copper films is required. Atomic Layer Deposition (ALD) is the best method but is dependent on the synthesis of appropriate precursors. As recently reported,[1] a novel precursor-Copper(I)di-sec-butylacetamidinate ([Cu(^{s}Bu-amd)]$_2$)-has shown good performance for ALD of Cu films with high conductivity. Given its novelty and the stringent microelectronics application, it is important to probe the chemistry of both interface formation and thin film growth. We have used in-situ FTIR spectroscopy to monitor the reaction of [Cu(^{s}Bu-amd)]$_2$ with two types of surfaces, the hydrogen-terminated Si(111) surface and silicon oxide surface, and to probe the next step of the ALD growth (H_2 reduction of the adsorbed Cu precursor). The Cu film growth rates were determined using ex-situ RBS measurements. We find that the reactivity of [Cu(^{s}Bu-amd)]$_2$ on these two surfaces is quite different. H/Si(111) surfaces are less reactive than oxidized surfaces. The IR vibrational spectra show that only ~20% of surface H react at 185°C. RBS measurements indicate that only 0.09 nm of Cu grows on H/Si(111) after 10 cycles. In contrast, there is a substantial loss of the SiO_x TO and LO phonon mode intensity at 1075cm^{-1} and 1247cm^{-1} after the 1st Cu precursor pulse at 185°C on SiO_2 surface, indicating that the surface SiO_2 matrix chemically interacts with the precursor. Meanwhile, a broad absorption band centered at 1010cm^{-1} is observed, corresponding to the formation of Si-O-Cu bonds. Upon H_2 exposure, the intensity of the SiO_x phonon modes is partial recovered, suggesting that Cu atoms diffuse and agglomerate as the Cu precursor is reduced to pure Cu at 185°C. As agglomeration takes place (i.e. Si-O-Cu bonds are broken), the initial hydroxylated oxide surface is restored (in a hydrogen environment) and is characterized by the original SiO_x phonon absorption. The ALD process is investigated by following the ligand exchange and ligand rearrangement on the surface. RBS measurements show 1.18nm of Cu is deposited on SiO_2 after 10 cycles.

[1] Z. Li, S. T. Barry, R. G. Gordon, Inorganic Chemistry, (2005)44, 1728.

11:00am **TF-TuM10 Modification of Nonwoven Polymer Fiber Structures by Atomic Layer Deposition**

***J.C. Spagnola**, G.N. Parsons*, North Carolina State University

Nonwoven polymer fiber structures are receiving much recent attention due to their potential industrial, medical, and military applications. We report the modification of nonwoven fiber structures by the deposition of thin metal oxide films via ALD. Fiber substrates coated to date include melt blown polypropylene micro and nanofibers, electrospun PVC nanofibers and nylon hydroentangled microfibers. Our specific focus is to characterize the effect of film thickness and/or coating material the resulting mechanical properties of coated fiber structures Initial experiments involved the deposition of Al2O3 by trimethylaluminum and water at temperatures from 50 to 100C. The gas pulse and purge times used resulted in film growth rates of 1.2A/cycle on planar silicon independent of temperature. Substrates for ALD coating consisted of fiber mats approximately 1cm x 3cm x 0.05cm. After ALD, some samples were calcined in air at ~850°C for 30 min to remove the polymer substrate to allow SEM analysis of the deposited oxide layer. SEM images show good macroscopic uniformity of the ALD coating over the substrate surface area. Other samples that were not heat treated were analyzed under tensile testing to observe the stress-strain behavior as a function of ALD process conditions and film thickness. Specifically, melt-blown polypropylene nonwoven fiber mats were tested using a microstrain analyzer to determine elastic modulus, yield stress and material toughness. Coating the polypropylene with Al2O3 ALD at 50°C or 100°C lead to an increase in the elastic modulus that scaled linearly with the number of ALD cycles, resulting in an increase of ~50% after 200 ALD cycles (~25nm). In addition, when the ALD was performed at 50C, the samples showed an increase in yield stresses with some improvement in material toughness. However, when processed at 100C, the coated polypropylene structures showed a decrease in yield stress and toughness as compared to untreated substrates, consistent with some degradation of the starting material properties at elevated temperature. Strengthening of the fiber structure by the deposition of a thin metal-oxide film may allow coated nonwovens to be used in applications where the traditional low-strength of nonwoven structures prevents the required level of performance.

11:20am **TF-TuM11 Mechanical and Tribological Property Comparison of Melt-Compounded Nanocomposites of Atomic-Layer-Deposition-Coated Polyamide Particles and Commercial Nanofillers**

K.M. Nevalainen, R.J. Suihkonen, Tampere University of Technology, Finland*, **N.A. Isomäki**,* Beneq Oy, Finland*, C. Hintze,* Technical University of Chemnitz, Germany*, P.S. Eteläaho, J.E. Vuorinen, P.K. Järvelä*, Tampere University of Technology, Finland

A recently developed process to form homogenously dispersed nano-sized titanium dioxide (TiO_2) particles within a polymer matrix was introduced and compared to traditionally melt-compounded nanofillers. Micron-sized polyamide particles were pre-coated with thin TiO_2 films by atomic-layer-deposition (ALD). ALD coating was performed at 40 °C by alternately exposing polyamide powder to titanium tetrachloride and water, separated by nitrogen purge steps. TiO_2 coatings on polyamide particles possessed nominal thicknesses of 10 nm or 40 nm. The ALD-coated polyamide particles and the composites manufactured from the two different commercial TiO_2 nanofillers were melt-compounded using a 5 cm^3 micro-compounder. The dispersion of the crushed TiO_2 shells in the polyamide matrix were studied after extrusion using a transmission electron microscopy and the results suggested very different morphology from the traditional TiO_2 nanocomposites. The ALD-created TiO_2 appeared as ribbons in the polyamide matrix whereas the commercial TiO_2 fillers formed spherical clusters. The effect of these TiO_2 morphology changes on the mechanical response of the specimens subjected to tensile and impact loading was investigated. The results demonstrated that the nanocomposites based on ALD-coated polyamide particles possess 50-150% higher Young's modulus than pure and commercially filled polyamide matrix whereas yield strength is only slightly increased for 10 nm ALD-coated composite and in fact somewhat decreased for 40 nm ALD-coated composite. Furthermore, the ductility upon tensile loading is significantly affected. A transition from ductile to brittle deformation occurs for both ALD-coated nanocomposites. Notched impact strength experiments supported this phenomenon showing that the impact strength of ALD-coated composites decreased 50% compared to pure and traditionally filled polyamide matrix whereas the traditional TiO_2 nanocomposites showed no significant changes. The fracture surfaces of the nanocomposites examined with scanning electron microscope suggested that the nanoparticle dispersion was good but some impurities in the matrix were found and their origin is discussed. The tribological properties of the selected specimens were also determined using pin-on-disc type apparatuses and the effect of the titanium dioxide fillers on the friction and wear properties of polyamide matrix is examined.

11:40am **TF-TuM12 Atomic Layer Deposition of Zinc Hybrid Films from Diethyl Zinc and Ethylene Glycol**

*Q. Peng, R.M. VanGundy, G.K. Hyde, **G.N. Parsons***, North Carolina State University

Atomic/molecular layer deposition of organic-inorganic hybrid materials could significantly expand the range of materials available in thin film applications. However, the detailed mechanisms associated with the integration of organic materials into the ALD process scheme need to be more fully understood. In this study, zinc hybrid films were formed by atomic layer deposition using alternative dosing of diethyl zinc (DEZ) and ethylene glycol (EG). The process was characterized using in-situ quartz crystal microbalance (QCM), as well as a range of external characterization tools and results were compared directly to the ZnO ALD process (DEZ/H2O) performed under similar reaction conditions. Consistent with literature results, during the ZnO ALD process at 120degree C, the mass uptake during the DEZ exposure is ~130 ng/cm2 per cycle, with a small mass loss during H2O exposure. The QCM results confirmed the self-limiting surface adsorption during both reaction steps of ZnO ALD. When H2O is replaced with ethylene glycol in the process sequence at 120 degree C, the mass uptake during the DEZ pulse is reduced significantly to ~19 ng/cm2 , and the positive mass uptake of ~ 4 ng/cm2 is observed during the EG pulse in the steady-state deposition of Zn hybrid. The reduced mass uptake during DEZ exposure is likely due to the lower density of reaction sites resulting from: (i) the twice reaction of EG with surface bonded –O-Zn-C2H5 ligands; (ii) steric hindrance of bulky EG molecules and its related surface bonded ligands; (iii) the possible dehydration reaction between the surface bonded EG ligands. Self-limiting adsorption of DEZ and EG, which is consistent with a typical ALD process, was confirmed by QCM. The process steps of Zn hybrid can continue for several hundred cycles with consistent and repeatable mass uptake. The growth rate per cycle of the hybrid material decreases as the deposition temperature increases. Infrared analysis of as-formed Zn hybrid films shows modes consistent with EG and Zn-O bonds. Upon exposure to laboratory air, the resulting hybrid films readily undergo hydrolysis, resulting in films consisting of ZnO and hydroxide with significant carbon content, as evidenced by FTIR and XPS analysis. AFM shows the films are uniform, and TEM analysis indicates that hydrolysis process results in conformal and porous layers. Further results of in-situ characterization and post-deposition analysis of the zinc hybrid materials will be presented.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+EM+NS+PS-TuA

Photovoltaics
Moderator: B.J. Stanbery, Helio Volt Corporation, J. Xue, University of Florida

1:40pm **EN+EM+NS+PS-TuA1 Thin films, Plasmas and Solar Cells**, ***M.C.M. van de Sanden***, Eindhoven University of Technology, The Netherlands **INVITED**

Solar cells, devices which can convert sunlight directly into electricity by the photovoltaic (PV) effect, is now recognized as one of the options to provide a significant fraction of the energy mix in 2050 to power the world. Presently the PV industry is booming and two important challenges lie ahead: increasing the efficiency of conversion of sunlight into electricity and obtaining the required scale in terms of the surface area produced. The latter requires high throughput processing of solar cells in all its aspects. Increasing the efficiency is scientifically attaining the most attention, but history has shown that more cost reduction can be obtained by improving processes and increasing the scale of the industry. This talk will address both challenges by discussing the role of thin film and plasma technology. Presently the solar cell market is dominated by solar cells based on crystalline silicon. In this solar cell technology, where the photo-active material is wafer based silicon, thin films still play an important role to increase efficiency by effectively passivating bulk and surface defects and enhancing light trapping in the solar cell. The high rate deposition of a-SiNx:H as passivation and anti-reflection coating, by means of the expanding thermal plasma technique, will be shortly reviewed. Possible combinations with novel concepts to convert the solar spectrum will be addressed. Recently, we also introduced plasma assisted atomic layer deposition of Al_2O_3, a high k dielectric containing a large amount of negative charge, to passivate future p-type emitters on n-type silicon based solar cells. Demonstration of improved performance of n-type solar cells using this type of passivation layer with an efficiency as high 23.2 % will be discussed. To obtain the required large scale by 2050 further improvement of thin film solar cell technology will be essential, both in terms of materials as well as in terms of processes. Apart from the need for high throughput deposition of the photo-active materials, additional thin film technologies will be needed for barrier layers on substrates to limit impurity transport, for efficient light trapping (textured surfaces and anti-reflection layers) and last but not least encapsulation layers to guarantee the lifetime of the thin film solar cell. Apart from the further development of improved materials and device concepts, process monitoring and control to improve quality and throughput becomes more and more important. I will discuss here the monitoring of high rate deposition of microcrystalline silicon by means of optical emission spectroscopy. This optical probing method also enables the in situ detection of the crystallinity of the material deposited as well as fundamental insights in the growth mechanism.

2:20pm **EN+EM+NS+PS-TuA3 Effects of Nanostructures formed by Plasma Etching on Reflectance of Solar Cells**, ***S.H. Ryu***, *C. Yang, W.J. Yoo,* Sungkyunkwan University, Korea, *D.-H. Kim, T. Kim*, Samsung Advanced Institute of Technology, Korea

We investigated the lithography-free plasma etching methods to modify surface of single crystalline Si which was widely used for manufacturing of solar cells. Experiments were performed using SF6/O2 gases dry etching for the purpose of reducing the reflectivity at the Si surface. Upon inductively coupled plasma etching in SF6/O2 pillar-shaped nanostructures were formed on the surface which changed to black in color. The absorption factor was estimated by measuring reflection and transmission on the surface across near UV to near IR. Before etching, reflectance of Si wafer was ~ 35% in the wavelength range of 600-1000 nm and > 50% in the wavelength range of 200-400nm, whereas it decreased to < 5% after performing SF6/O2 plasma etching. The absorption factor of Si wafer after etching was increased up to ~ 90% from 65% compared to that without etching, in the wavelength range of 600-1000 nm. Furthermore, various etching methods and conditions to suppress reflectivity in a broad spectral range were investigated for optimization of the surface property of the solar cells, ie, enhancement of solar cell efficiency. We investigated the effects of various processing parameters on surface property by changing gas ratio, bias power and etching time. The current-voltage characteristics on the surface textured solar cells showed that short circuit current (Isc) and open circuit voltage (Voc) changed sensitively depending on the surface treatment. The relation between the surface morphology and the absorption factor was analyzed.

2:40pm **EN+EM+NS+PS-TuA4 Nanoscale Heterojunction Engineering to Grow High-Quality Ge on Si for Multijunction Solar Cells**, ***D. Leonhardt***, *J. Sheng, T.E. Vandervelde,* University of New Mexico, *J.G. Cederberg, M.S. Carroll,* Sandia National Laboratories, *S.M. Han*, University of New Mexico

In an effort to reduce the manufacturing cost of multijunction solar cells, we have scaled up a process to grow low-defect-density Ge films on 2-inch-diameter Si substrates. This growth technique makes use of nanoscale heterojunction engineering to minimize the interfacial strain density. The engineered substrates may potentially replace the Ge wafers that are currently used in multijunction solar cell fabrication, if the Ge film's bulk and surface quality can match that of the epi-ready Ge wafers. We will present results for the scaled-up process of Ge film production, including key aspects of the nucleation process and film characterization, using transmission electron microscopy and etch pit counting. Next, we present our efforts to produce a high-quality surface finish, using chemical-mechanical planarization, and method for cleaning and passivating the Ge surface. Additionally, results of GaAs film growth on our engineered substrates will be presented and compared to growth on Ge and GaAs wafers, both offcut and nominal. We find that the offcut wafers effectively eliminate anti-phase domains in the GaAs. We also observe room-temperature photoluminescence from GaAs epilayers grown on our engineered Ge/Si substrates. Lastly, future work and directions will be discussed in light of our findings.

3:00pm **EN+EM+NS+PS-TuA5 On a New Concept of Tandem Photovoltaic Cells Based on III-V Semiconductor Materials**, ***M. Emziane***, Masdar Institute of Science and Technology, UAE, *R.J. Nicholas*, University of Oxford, UK

We have investigated single-junction and double-junction photovoltaic devices using ternary and quaternary InGaAs(P) semiconductor materials. These were designed and optimized for potential applications in conventional photovoltaics, thermophotovoltaics and concentrator photovoltaics.Different bandgaps were considered for single-junctions, and various bandgap combinations were simulated for the top and bottom cells of the tandem devices where the structure comprises two single-junction cells connected back to back and separated by a middle common contact. For both single and double-junctions, the device structures were modeled and optimized as a function of the doping concentration and thickness of the active layers, and the simulations show that optimum device performance can be achieved by using relatively thin structures and low doping concentrations in the emitter and base layers. The variation of the device performance with the black-body source temperature, incident intensity and operating temperature was also simulated and discussed. Due to the split of the incident spectrum, the bottom cell response is found to be different from that expected for a single-junction cell having the same bandgap. The optimal bandgap combination that delivers the best total efficiency for the tandem device was also determined and the data discussed.

4:00pm **EN+EM+NS+PS-TuA8 Thin Film Preparation of Chalcopyrites for Solar Cells and Fundamental Material Physics**, ***S. Siebentritt***, University of Luxembourg **INVITED**

Thin film solar modules are expected to be the next generation of photovoltaics technologies. Their cost reduction potential has been estimated much higher than that of Si wafer technologies. Among the various thin film technologies solar cells based on chalcopyrite ($CuInGaSe_2$, CIGS) absorbers show the highest efficiencies, reaching 19.9% in the lab. These record solar cells are prepared by a high vacuum co-evaporation process that proceeds in three stages with different composition. A simplified two stage co-evaporation process is used in the first mass production of chalcopyrite solar modules. Further industrial processes are the sputter deposition of metallic precursors which are reacted in an annealing process to the semiconductor compound. Recently electrochemical deposition has appeared as a low cost approach to the precursor deposition. In all cases the knowledge on fundamental growth processes, nucleation behaviour and detailed reaction is limited. The details of the processes and their advantages and disadvantages for solar module production will be discussed. The afore mentioned deposition processes result in polycrystalline films with grain sizes of approximately 1 micrometer. For the investigation of the fundamental material physics it is necessary to obtain grain boundary free material. The lattice mismatch between $CuInSe_2$ and $CuGaSe_2$ on one side and GaAs on the other side is between 2.2 and -0.7% and allows epitaxy of chalcopyrite films on GaAs. Several methods for the epitaxy have been developed: metal organic vapour phase epitaxy (MOVPE), molecular beam epitaxy (MBE) and a hybrid sputter/evaporation process. The specifics of these processes will be briefly discussed and some results of epitaxial films will be presented.

4:40pm **EN+EM+NS+PS-TuA10 Influence of a Single Grain Boundary on Epitaxial CuInSe$_2$ Film Growth**, ***A.J. Hall***, *D. Hebert, A. Rockett*, University of Illinois at Urbana-Champaign

Very large multigrain copper indium diselenide (CuInSe2) films were grown on gallium arsenide (GaAs) multigrain wafers using a hybrid sputtering/effusion growth process. Scanning electrom microscopy (SEM) morphology shows excellent epitaxial grain growth on the substrate with intimate grain boundary contact. Electron backscatter diffraction analysis shows a crystal misorientation common axis and misorientation angle for a high-angle, non-twin, boundary. Atomic force microscope and transmission electron microscope images are presented which confirm the surface morphology and the atomic intimacy of the grain interface. Kelvin probe force microscopy shows that the grain-boundary has little electrical influence on the film in comparison to other features present in the crystallites. Growth of large multicrystalline or bicrystalline CuInSe2 films allows more careful study of both physical and electrical influence of grain-boundaries on film properties. Current work on the physical influence of a single boundary on film growth is discussed.

Graphene Topical Conference
Room: 306 - Session GR+TF+NC-TuA

Graphene: Characterization, Properties, and Application
Moderator: Y.J. Chabal, University of Texas at Dallas

1:40pm **GR+TF+NC-TuA1 Computational Modeling of Graphene**, ***K.J. Cho***, *G. Lee*, University of Texas at Dallas **INVITED**

Using the ab initio density functional theory (DFT), tight-binding (TB), and non-equilibrium Green's function (NEGF) methods, we have studied the electronic properties of graphene oxides (GOs) and graphene nanoribbons (GNRs). Dry oxidation of graphene induces epoxide groups on the basal plane, and the corresponding electronic structures of GOs show directional band gap opening. We found that GOs have small energy gaps due to the lattice distortion at low oxygen coverage θ_O, and that they become semiconductors for $\theta_O \geq 1/2$ with the larger gap at the higher θ_O (Eg=3.3 eV at θ_O=1). However, for intermediate coverage, GOs become metallic along one zigzag direction while opening directional energy gaps along other zigzag directions depending on O adsorption patterns. We apply the percolation theory and NEGF method to explain the electron transport behavior of GOs. The insulating property of GOs is used to explain the inactive edge width of GNRs which are observed in GNR experimental studies. Electronic properties of GNRs are shown to have strong dependence on the edge chemistry indicating a practical challenge in graphene nanoelectronics using GNRs as channel materials.

2:20pm **GR+TF+NC-TuA3 Control of Conductivity in Graphene by Formation of Defects**, *S.H.M. Jafri, T. Blom, E. Widenqvist, K. Carva, B. Sanyal, O. Eriksson, H. Grennberg, U. Jansson*, Uppsala University, Sweden, *R.A. Quinlan*, College of William and Mary, *B.C. Holloway*, Luna Innovations Incorporated, *A. Surpi*, ***K. Leifer***, Uppsala University, Sweden

Due to their large surface areas, the conductivity of graphene and carbon nano-sheets depends strongly on their chemical environment. This is the base for future environmental sensors containing graphene sheets. Here, ab-initio calculations propose a possibility of conductivity increase. In the experiment, a 1-2 orders of magnitude increase of the conductivity is observed experimentally on sub-nanometre carbon nano-sheets by using an in-situ nano-manipulation set-up. The conductivity of the graphene sheets was assessed from first-principle simulations. Insertion of defects in the graphene sheets can lead to a strong increase of the conductivity of single graphene sheets. To study this result experimentally, we carried out conductivity measurements on sub-nanometre graphene nano-sheets that are deposited on W-substrates by radio-frequency plasma-enhanced chemical vapour deposition. This deposition process creates free-standing micrometer-sized carbon nano-sheets with sub-nanometre thickness. These nano-sheets were exposed to an acid treatment. It has been shown recently that such acid treatment creates defects in these sheets. Using a nano-manipulator inside a scanning electron microscope, we individually contacted the nano-sheets and measured their resistance as a function of their functionalization. From more than 1000 measurements we obtain a 1-2 order of magnitude increase of conductivity in the functionalised carbon nano-sheets as compared to just water treated or untreated carbon nano-sheets. This result corresponds well to the conductivity change obtained from theory. This study makes it possible to create environmental sensors based on graphene like carbon nano-sheets.

2:40pm **GR+TF+NC-TuA4 Graphene on Graphite**, ***J.W. Choi***, Kyung Hee University, South Korea

Topmost graphne layer of graphite is investigated using scanning tunneling micropscopy and spectroscopy. Tunneling gap-distance, gap-voltage and bias polarity play an important role in the atomic image contrast and site-dependent tunneling spectra. The study revealed that the coupling and decoupling of the topmost graphene layer to the underlying graphite is occured because of the weak physical interaction between graphen layers, the electronically active and mechanically soft beta-carbon atoms of graphite and the strong tip-sample interaction.

3:00pm **GR+TF+NC-TuA5 Using Templates to Assemble Graphite Oxide (GO) and Graphene Nanostructures**, ***P.E. Sheehan***, *Z. Wei, J.T. Robinson, D.E. Barlow, E.S. Snow*, Naval Research Laboratory

Graphene and graphite oxide (GO) are new nanoscale building blocks that have generated widespread interest in both basic and applied research. The rapid, inexpensive, and reproducible generation of graphene and GO samples would expedite this work. To this end, we have directed the assembly of single-layered GO sheets using chemical templates patterned via micro contact printing.[1] Single-layer GO was inexpensively produced using the Hummer method and redispersed in water. Templates of 11-Amino-1-undecanethiol SAMS were created using microcontact printing. Unlike prior work in fullerene templating, the GO sheets could be captured electrostatically without the aid of surfactants. This process yields isolated, single-layer graphene sheets that are arbitrarily located on a patterned substrate. The electrostatic capture mechanism was verified by varying the pH to turn capture on and off. We will discuss the parameters (pH, time, etc.) that affect GO adsorption as well as the surprising resistance of the unpassivated Au substrate to adsorption of the GO sheets. Finally, the adsorbed GO and graphene were electronically and spectroscopically characterized to determine the effect of capture on the reduction process.

[1] submitted to Nano Letters.

4:00pm **GR+TF+NC-TuA8 Studies of Graphene Oxidation and Graphene Oxide Reduction by In-Situ FTIR**, ***L. Goux***, *R. Guzman, J.-F. Veyan, Y.J. Chabal*, University of Texas at Dallas

Graphene oxide (GO) is being investigated by the graphene community because it represents one of the most promising ways to produce graphene single sheets on a large scale.[1,2] Indeed graphene oxidation followed by exfoliation and reduction has been recently demonstrated to give single graphene layers in solution[3]. In addition, in any practical electronic device systems, electron transporting materials need to be controlled by insulating materials which can function as gate dielectrics or separator between device structures. Thus, the role of GO in graphene-based nanoelectronics may be comparable to that of SiO$_2$ in silicon-based microelectronics. We have therefore developed in-situ IR characterization to monitor graphene oxidation and GO reduction, in order to facilitate the development of graphene-based nanoelectronics. Graphene oxidation is being achieved using a remote oxygen plasma generator. We have designed a vacuum IR-cell (10^{-7} Torr base pressure), connected to the oxygen plasma and a Nicolet 6700 FT-IR spectrometer. Preliminary experiments have been carried out using HOPG. The GO reduction is performed in-situ by high temperature annealing in a Specac high temperature cell. In-situ FTIR studies of GO upon thermal reduction have shown a production of CO$_2$ gas concomitant with the disappearance of the vibrations associated to carboxyl, hydroxyl and peroxide groups in the 120°C-230°C temperature range. Interestingly the vibrational lineshape suggests that CO$_2$ is incorporated in GO. Around 290°C, there is a strong increase of the absorbance associated with structure changes of GO, resulting from an increase in scattering due to a higher refractive index. The change of refractive index most likely arises from an increase of electrical conductivity after reduction of GO.

[1] Stankovich, S. et al. Carbon 45, 1558–1565 (2007).

[2] Stankovich, S. et al. J. Mater. Chem. 16, 155–158 (2006).

[3] Li, D. et al. Nature Nanotechnology 3, 101 - 105 (2007).

4:20pm **GR+TF+NC-TuA9 Growth of Few Layer Graphene by Microwave Plasma Enhanced CVD**, ***R.G. Vitchev***, *A. Malesevic, A. Vanhulsel, R. Kemps, M. Mertens*, Flemish Institute for Technological Research (VITO), Belgium, *G. Van Tendeloo*, University of Antwerp, Belgium, *C. Van Haesendonck*, Catholic University of Leuven, Belgium, *R. Persoons*, Flemish Institute for Technological Research (VITO), Belgium

Graphene has recently attracted considerable attention as a potential material for nanoelectronic devices. A promising method for its mass production is microwave plasma enhanced chemical vapour deposition (MW PECVD). The main advantage of this technique is that few layer graphene (FLG) can be grown without the need of a catalyst on different substrates that can withstand high temperature (up to 700°C). However, the growth mechanism of PECVD synthesized graphene is not well understood. The aim of this work was to investigate the growth process of FLG deposited by MW PECVD on several substrates (quartz, silicon, platinum).

The resulting thin films were characterized by X-ray diffraction, scanning and transmission electron microscopy, Raman spectroscopy and angle resolved X-ray photoelectron spectroscopy (ARXPS). Three stages of film growth on silicon were identified by ARXPS: formation of a carbide layer on the substrate, deposition of an amorphous carbon layer and finally formation of a graphitic layer parallel to the substrate surface. It was established that crack edges in this graphitic layer serve as nucleation sites from which FLG flakes, only four to six atomic layers thin, grow perpendicular to the surface. This growth mechanism appears to be substrate dependent since no intermediate carbide layer was formed on both quartz and platinum surfaces. Furthermore, no amorphous carbon layer was detected on the platinum substrates, even for the shortest deposition time intervals.

4:40pm **GR+TF+NC-TuA10 Uniform Transparent and Conducting Solution Processed Graphene Thin Films for Large Area Electronics**, ***M. Chhowalla***, Rutgers University **INVITED**

The integration of novel materials such as single walled carbon nanotubes and nanowires into devices has been challenging. Similarly, although fundamental research on graphene has been prolific since its discovery, reports on making it technologically feasible for integration into devices have only recently appeared. In this presentation, a solution based method which allows uniform and controllable deposition of reduced graphene oxide thin films with thicknesses ranging from a single monolayer up to several layers over large areas will be described. The opto-electronic properties can thus be tuned over several orders of magnitude, making them useful for flexible and transparent semiconductors or semi-metals. The thinnest films exhibit graphene-like ambipolar transistor characteristics while thicker films behave as graphite-like semi-metals. Controllable p-type doping via exposure to SOCl2 vapor is also demonstrated. Cl doping leads to breakup of symmetry in ambipolar field effect characteristics, providing a route for unipolar devices. In addition, composite graphene/polymer thin film devices exhibiting on/off ratios >10 will also be reported. Collectively, our deposition method could represent a route for translating the interesting fundamental properties of graphene into technologically viable devices.

5:20pm **GR+TF+NC-TuA12 Electronic Manipulation in Graphene Formed by Proton-irradiated Method**, ***C.-H. Chuang***, National Taiwan University and National Synchrotron Radiation Research Center, Taiwan, *C.-H. Chen, H.-W. Shiu*, National Synchrotron Radiation Research Center, Taiwan, *X. Gao, M.B.H. Breese, F. Watt, S. Chen, A.T.S. Wee*, National University of Singapore, *M.-T. Lin*, National Taiwan University, Taiwan

Graphene is referred to the honeycomb lattice of carbon atoms formed as a 2D flat single layer. It is also the building block to construct 0D fullerenes, 1D carbon nanotubes, and 3D graphite in graphitic materials. Similar to carbon-based materials, the strong C-C bonding with sp^2 hybridization is stable and rigid in ambient atmosphere. In this letter, we introduce the simple method to modify its electronic character and use Scanning Photoemission Microscopy (SPEM) to study its electronic structure. The previous reports about ion- or proton-irradiated graphitic materials present the new physical and magnetic property, e.q. induced ferromagnetic behavior. The reasons are mainly related to the disorder lattice, the vacancy density, or hydrogen-absorbed carbon atoms in the graphene network. However, it is necessary to provide the evidence about electronic structure after proton irradiation. SPEM provides the spatial mapping image with different element and the chemical bonding environment of XPS at the individual location. As compared with the graphite, we can know the C 1s state of graphene is similar. After the proton-irradiated impact on the graphene, the irradiated area shows the broad FWHM of C 1s state and chemical shift of 0.4 eV up to the high binding energy. Besides, we find the satellite peak with binding energy 291 eV, related to π to π^* state transition, is decreased after irradiation. The observed result in our irradiation sample may be due to the lattice reconstruction of C-C bond. Our experimental findings open up a new field in electronic manipulation in graphene-based electronics.

Thin Film
Room: 302 - Session TF-TuA

Applications of ALD II
Moderator: S.M. George, University of Colorado

1:40pm **TF-TuA1 ALD of High-k Gate Dielectrics on Si and Alternative Substrates**, ***J. Kim***, *H.C. Kim, B. Lee, A. Hande, E.M. Vogel, M.J. Kim, R.M. Wallace*, University of Texas at Dallas **INVITED**

For future high performance semiconductor device applications, it is critical to achieve a high quality gate dielectric with a high dielectric constant and excellent interface properties with semiconductor substrates such as GaAs, InGaAs and graphene in addition to Si. ALD has been considered as one of the most appropriate deposition techniques for high-k gate dielectrics without significant damage due to energetic particles and plasma. Due to its surface reaction nature, it is important to understand effects of reactants, such as precursors and oxidants, in conjunction with substrates on both interface and dielectric properties. Various materials characterization techniques including XPS, HRTEM, AFM, XRD, SIMS and RBS are used to investigate the physical properties of ALD derived metal oxide (Al_2O_3, HfO_2 and La_2O_3) thin films on various substrates. In particular, our in-situ XPS half-cycle study provides an insight on variation of chemical composition and binding status at the both interface and dielectric during the first few cycles.

2:20pm **TF-TuA3 ALD of High Dielectric Material LaMO3 (M = Y, Yb, Er) Using Metal Formamidinate Precursors**, ***H. Li***, *D.V. Shenai*, Rohm and Haas Electronic Materials, *R.G. Gordon*, Harvard University

The study of ultrathin gate dielectrics has recently gained great attention due to the technological need to replace SiO2 films in the metal-oxide-semiconductor field-effect transistors (MOSFETs).[1] According to the International Technology Roadmap for Semiconductors (ITRS),[2] the implementation of high-k gate dielectrics with a dielectric constant between 10 and 20 will be produced by leading manufacturers by 2008 in order to meet both low leakage current density and performance requirements. Ternary rare earth oxides are emerging as promising candidates for these applications. As shown in earlier report,[3] lanthanum lutetium oxide films (LaLuO3) obtained by pulsed laser deposition (PLD) technique showed a high dielectric constant of 32, very low leakage current density, remaining amorphous up to 1000 ºC and excellent performance. Similarly atomic layer deposition (ALD) of ternary rare earth oxide films such as GdScO3 or LaScO3 also demonstrated the potential for substituting current high k material.[4] However Lu and Sc elements are much less abundant in earth compared to other rare earth elements. So the precursors based on Lu or Sc can be extremely expensive to manufacture. Finding less expensive metals while maintaining those unique properties is urgent. Y, Yb and Er are three rare earth elements which are similar to Lu and Sc in ionic radii, but are much less inexpensive because of their natural abundance. In this presentation, we report the Y, Yb and Er precursors based on formamidinate platform, which has been demonstrated to offer higher vapor pressure and higher thermal stability of the sources than commercially available conventional precursors.[5] We will also report the ALD growth using H2O and O3 as co-reactants within the acceptable window of deposition temperatures. The resultant films will be characterized by AFM, XRD, and TEM.

[1] Wilk et al, J. Appl. Phys. 2001, 89, 5243.

[2] International Technology Roadmap for Semiconductors: 2007 edition.

[3] (a) Lopes et al, Appl. Phys. Letts. 2006, 89, 222902.

[4] (a) Kim et al, App. Phys. Letts. 2006, 89(13), 133512/1-133512/3. (b) Wang et al, AVS 55th International Symposium, Boston, MA, 2008.

[5] Li et al, 8th International Conference on Atomic Layer Deposition, Bruges, Belgium, 2008.

2:40pm **TF-TuA4 Electrical Properties of Plasma-Enhanced Atomic Layer Deposition $HfO_2/HfO_xN_y/HfO_2$ Gate Oxide**, ***W.J. Maeng***, *H. Kim*, POSTECH, Korea Republic

Nitrogen incorporation produces several benefits in the performance of high k gate oxides. However, since too much nitrogen incorporation at the interface of gate dielectric results in device degradation, the proper amount of nitrogen incorporation with precise depth profile control is desirable. In this study, the microstructure and electrical properties of plasma enhanced atomic layer deposition (PE-ALD) HfO_2 gate oxides with nitrided middle layer ($HfO_2/HfO_xN_y/HfO_2$) were investigated. The nitridation of the middle layer was carried out by two different in situ processes; PE-ALD using N/O mixture plasma (denoted as HfON) and PE-ALD HfN using hydrogen plasma followed by oxidation during the consequent HfO_2 deposition (denoted as HfONO). Significantly better electrical properties were obtained for HfONO than HfON in terms of hysteresis, equivalent oxide thickness, and reliability. In addition, high nitrogen incorporation up to 10 at% with improved thermal stability was achieved for HfONO sample. The experimental results will be discussed based on the atomic bonding configurations analyzed by X-ray photoemission spectroscopy.

3:00pm **TF-TuA5 Improvement of the Electrical Characteristics of Amorphous $LaAlO_3$ Films Made By Atomic Layer Deposition**, ***Y. Liu***, *H. Kim, J.J. Wang, R.G. Gordon*, Harvard University, *H. Li, D.V. Shenai*, Rohm and Haas Electronic Materials

Amorphous lanthanum aluminum oxide ($LaAlO_3$) films were deposited on hydrogen-terminated silicon substrates by atomic layer deposition (ALD) at 300 ^{o}C. Capacitance-voltage measurements made from ALD $MoN/LaAlO_3/Si$ stacks showed humps especially at low frequencies, indicating traps for electrons or holes. Two sources of these traps were identified: impurities and oxygen vacancies. The number of traps was cut in half by careful purification of the La precursor to remove metallic impurities to below a total of 1 ppm. The remaining traps were effectively removed by adding an oxygen (O_2) exposure either after each ALD cycle or by a post-deposition O_2 treatment at 300 ^{o}C, without affecting the dielectric constant (κ~15). The O_2 treatment also lowered the leakage current by an order of magnitude, to 1 mA cm^{-2} for films with EOT = 1.3 nm.

4:00pm **TF-TuA8 In-situ Conductance Measurements during Transparent Conductive Zinc Oxide Film Growth using Low Temperature Atomic Layer Deposition**, ***J.-S. Na***, *G.N. Parsons*, North Carolina State University

Zinc oxide has been extensively studied for applications such as solar cells, flat panel displays, gas sensors etc., and is considered as an alternative to indium tin oxide due to its low-cost, non-toxicity, and chemical and thermal stability. For the flexible device and TFT applications, low growth temperature (<150 ^{o}C) or low carrier concentration ($<10^{18}$ cm^{-3}) is required. Here we report the low temperature atomic layer deposition (ALD) of zinc oxide using diethyl zinc and water as a precursor and reactant, respectively. We have developed a method to examine conductance in situ during ALD ZnO growth using two metal electrodes (Au/Cr) isolated by a thermally grown SiO_2 with a gap of 1 mm. Conductance was measured in situ during initial nucleation and steady state film growth at temperatures between 100-140 ^{o}C. The growth rate, electrical resistance, surface morphology, and crystallininty were also studied ex situ as a function of growth temperature and ALD cycles. At 120 ^{o}C the growth rate of ZnO ALD on SiO_2/Si was ~1.9 Å/cycles with ~3 cycles of incubation time and linear with the number of cycles. At 120 ^{o}C with 0.1V applied, the current was below the detection limit ($<10^{-11}$ A) for the first 42 cycles. The current increased exponentially from 10^{-11} to 10^{-7} A between 43 and 50 cycles and followed by percolation to 10^{-5} A. From 70 to 200 cycles the current increased linearly from 10^{-5} to 5×10^{-4} A. Interestingly, the effect of each reactant exposure on the conductance of ZnO film during growth was quite different. Specifically at 120 ^{o}C, both DEZ and water exposure dramatically increased the conductance of ZnO film at the exponential nucleation region. Meanwhile the DEZ exposure decreased and the water exposure increased the conductance of ZnO at the ohmic linear region. This technique shows a potential for in-depth understanding of the ALD ZnO growth process in situ and also how each reactant is involved in the defect formation related to the carrier concentration within the growing ZnO film.

4:20pm **TF-TuA9 ALD Noble Metal Oxides - Film Growth and Stability Studies**, ***M. Ritala***, *J. Hämäläinen, M. Heikkilä, K. Kukli, J. Niinistö, M. Kemell, M. Leskelä*, University of Helsinki, Finland

Noble metal oxide thin films gain interest over a broad range of application areas because of their attractive catalytic, optical, mechanical, electrical, and electrochemical properties. In integrated circuits, for example, high work function and structural similarity to high-k dielectrics make noble metal oxides potential electrode materials for capacitors and transistors. This presentation summarises our efforts in developing ozone based ALD processes for noble metal oxides. The consequences of the limited stability of noble metal oxides are also addressed using both high temperature XRD and chemical exposure experiments.

4:40pm **TF-TuA10 Increasing the Glass Cracking Resistance by Atomic Layer Deposition**, ***M. Putkonen***, *P. Soininen, M. Rajala*, Beneq Oy, Finland, *T. Mäntylä*, Tampere University of Technology, Finland

Infrared cut-off filters are used in CCD or CMOS sensors. Typically these filters are made onto separate glass sheets placed in front of the sensor. However, recently thinner and thinner glasses are used, for example in the wafer-scale integration, which causes increasing problems due to the cracking of the substrates. Cracking of the glass due to the nanometer-scale Griffith-like flaws[1] is well known problem. These tiny flaws are usually in the range of 10-20 nm at the surface and they act as a starting point where bigger cracks start to develop. There are some available strenghtening approaches, based for example on the coatings made by solution methods.[2] However, these relative thick coatings may require high post annealing temperatures in order to obtain desired properties without sacrificing optical properties. In this study we introduce ALD technique for improving the crack resistance of the glass. Previously ALD has been employed for example for thin film deposition onto deep microelectronic trenches as well as for coating nanometer scale features. Since ALD is highly conformal surface-controlled coating method, it is expected that the film growth will closely follow the structural flaws of the glass surface. We have utilised TMA/H_2O and SAM24/O_3 processes and studied the mechanical and optical properties of films. For example, thin films were deposited onto soda lime and D263T glass substrates measuring from 20x50 mm^2 to 1200x1200 mm^2. Typical film thicknesses were in the range of 10-30 nm, but thicker coatings were also evaluated. Batches of smaller pieces (20x50 - 100x100 mm^2) were deposited in Beneq TFS 500 ALD system whereas bigger samples were evaluated in P400A, P800 and TFS 1200 systems. Depending on the sample size, glass thicknesses from 0.3 to 3 mm were evaluated. ALD processing of large area glass sheets were evaluated in terms of film uniformity and optical properties. Glass strength was evaluated against different thin film processing conditions and film thickness. According to the four point bending tests significant improvement on cracking strength were obtained by using ALD coatings.

[1] A. Griffith, The phenomena of rupture and flow in solids, Phil. Trans. Royal Soc., A221 (1920) 163.

[2] K. Endres et. al., Enhancement of fracture strength of cutted plate glass by the application of SiO2 sol-gel coatings, Thin Solid Films 351 (1999) 132.

5:00pm **TF-TuA11 In Situ Gas Phase Absorption Measurements During Hafnium Oxide ALD**, ***J.E. Maslar***, *W.A. Kimes, J.T. Hodges, B. Sperling, D.R. Burgess, E.F. Moore*, National Institute of Science and Technology

In situ monitoring of atomic layer deposition (ALD) processes has the potential to yield insights that will enable improved efficiencies in film growth, in the development of deposition recipes, and in the design and qualification of reactors. In situ diagnostics potentially can be used to measure a number of parameters. Measuring precursor flux into the reactor is a relatively common application. However, such measurements are of limited value when trying to optimize deposition chemistry. Potentially more useful would be measurements of deposition precursor and product gas phase concentrations near the wafer surface. Such measurements would allow one to probe the properties of the near-surface thermal/gas velocity boundary layer that exists in many industrial ALD reactors. Since the properties of this boundary layer are strongly impacted by the state of the wafer surface, gas phase measurements in the boundary layer can provide information about the state of the wafer surface. In this work, semiconductor laser-based gas phase absorption measurements performed near the wafer surface are being investigated for use as in situ, real time diagnostics for ALD. The material system selected for investigation is hafnium oxide ALD using tetrakis(ethylmethylamino) hafnium (TEMAH) and water. Absorption measurements of water vapor were performed in the near-infrared (NIR) using a distributed-feedback (DFB) diode laser and employing a wavelength modulation detection scheme. Assuming complete reaction, the products of the TEMAH and water reaction are hafnium oxide and methyl-ethyl-amine, a volatile species under deposition conditions. Absorption measurements of methyl-ethyl-amine were performed in the NIR using an external-cavity diode laser (ECL) and employing an amplitude modulation detection scheme. In situ, time-resolved Fourier transform infrared spectroscopy measurements were used to compliment the laser-based measurements. Measurements were performed in a single-wafer, warm-wall reactor. Deposition precursor and product concentrations near the wafer surface were measured under a range of deposition conditions in an effort to correlate gas phase measurements with surface processes. The performances of the DFB laser-based and ECL-based measurement systems will be compared. In addition, efforts to model the observed concentration gradients using reactor-scale computational fluid dynamics models will be discussed.

5:20pm **TF-TuA12 Application of HRBS (High-resolution Rutherford Backscattering Spectrometry) to Elemental Depth Profiling of Advanced Gate Stack for Complementary Metal Oxide Semiconductor Devices**, ***C. Ichihara***, Kobe Steel, Ltd., Japan, *S. Yasuno*, Kobelco Research Institute Inc., Japan, *H. Takeuchi*, ATDF, *A. Kobayashi, S. Mure*, Kobe Steel, Ltd., Japan, *K. Fujikawa, K. Sasakawa*, Kobelco Research Institute Inc., Japan

Hafnium-based materials with high dielectric constant have started replacing conventional SiO_2-based materials as a gate dielectric for CMOS (complementary metal oxide semiconductor) devices at production level. Much of the effort has been made to develop gate stack structures without forming bulk defects and interface states, while maintaining compatibility with CMOS thermal budgets. It is thus very important to characterize the elemental depth profile of the gate stack accurately. As compared to conventional physical analyses such as SIMS, AES, XPS, and XTEM, High-resolution RBS (HRBS) has advantages in ultra-thin film characterization as it provides non-destructive and quantitative elemental measurements with a high depth resolution (up to sub-nm) and without special sample preparations. Using HRBS, we studied the change in elemental depth profile of ultra-thin HfSiO(N) films on Si. Three different interfacial layers (HF-last pre-cleaning; ~ 0.8 nm chemical oxide formed by wet cleaning; and ~1.4 nm thermally-grown SiO_2 film followed by plasma nitridation) were prepared prior to the growth of ~ 2 nm HfSiO film by ALD. For all of the as-deposited HfSiO film experiments, Si concentration was found to be slightly higher at the top surface than in the bulk HfSiO. It was also observed that the thickness of the interfacial SiO_x layer of the HF-last sample was similar to that of the sample with chemical oxide, indicating that the Si surface was oxidized during the ALD process. The samples were, then, spike-annealed in nitrogen ambient at 1070^{o}C. After the annealing, the accumulation of the Si at the top surface was enhanced for all the three samples, indicating the upward diffusion of Si species from the HfSiO film. The interfacial layer of the sample with chemical oxide was found to be the thickest of all the three different surface preparations after the spike annealing. Furthermore, the change in nitrogen profile was studied for the samples fabricated in two different processes (plasma-nitridation vs. NH_3 annealing) for the HfSiO films prepared on chemical oxide. The HRBS spectra revealed the difference of the nitrogen desorption during the spike-anneal between the two nitridation processes.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+AS+EM+TF-WeM

Electrochemical Storage
Moderator: S. Haile, Caltech, K. Thornton, University of Michigan

8:00am **EN+AS+EM+TF-WeM1 Molybdenum Oxide Nanoparticles for Improved Lithium Ion Battery Technologies**, ***A.C. Dillon***, National Renewable Energy Lab., *S.-H. Lee,* University of Colorado, *Y.-H. Kim,* National Renewable Energy Lab., *R. Deshpande,* Lam Research, *P.A. Parilla, D.T. Gillaspie, E. Whitney,* National Renewable Energy Lab., *S.B. Zhang,* Rensselaer Polytechnic Institute, *A.H. Mahan*, National Renewable Energy Lab. **INVITED**

Lithium-ion batteries are current power sources of choice for portable electronics. Further improvement of performance and simultaneous reduction in cost could allow for the deployment in hybrid electric vehicles or plug-in hybrid electric vehicles (PHEVs). The development of PHEVs will enable reduced oil consumption in the transportation sector. Importantly, PHEVs will also enable increased use of intermittent renewable energy resources such as solar and wind. By charging PHEVs during peak solar generation times, the load on the grid is effectively “leveled”, and the average output of coal-fired power plants will be decreased. Recent efforts for electric vehicle applications are focused on new anode materials with slightly more positive insertion voltages to minimize any risks of high-surface-area Li plating while charging at high rates, a major safety concern. The state-of-the-art anode is graphite with a reversible capacity of ~ 350 mAh/g and a potential of 0.1 V relative to lithium metal. Metal oxides have long been known as Li-insertion compounds and typically operate at higher potential than graphite. Unfortunately they suffer from poor kinetics and/or capacity fade with cycling, especially at higher rates. Hot-wire chemical vapor deposition has been employed as a scalable method for the deposition of crystalline metal oxide nanoparticles at high density. Under optimal synthesis conditions, only crystalline nanostructures with a smallest dimension of ~ 10 - 40 nm are observed. Anodes fabricated from crystalline MoO3 nanoparticles display both an unprecedented reversible capacity of ~ 630 mAh/g and durable high rate capability. Porous thin film nanoparticle anodes, deposited by a simple electrophoresis technique, show no degradation in capacity for 150 cycles when cycled at high rate (C/2 corresponding to one discharge in 2 hrs.). Micron sized MoO3 particles are shown to fail after several cycles, under the same conditions. Both x-ray diffraction and in situ Raman spectroscopy studies reveal that upon Li-ion insertion the crystalline nanoparticles become highly disordered. Density functional theory calculations elucidate the complex Li-ion insertion process and reveal a novel mechanism confirming the nanoscale, high-rate, reversible capacity despite the loss of structural order. The synthesis of these novel nanostructured materials and their potential for improving lithium-ion battery technologies will be discussed in detail.

8:40am **EN+AS+EM+TF-WeM3 Boron Oxynitride: An Emerging Dielectric for High Temperature Capacitor Applications**, *N. Badi,* ***S. Vijayaraghavan***, *A. Bensaoula,* University of Houston, *A. Tempez, P. Chapon,* Horiba Jobin Yvon, France, *N. Tuccitto, A. Licciardello,* University of Catania, Italy

Among the many technical challenges encountered in the development of high temperature electronics, the role of a passive component like capacitor is very important. Dielectric integrity at temperatures greater than 250 °C has however, up till now, been one of the major impediments to bringing out a capacitor with suitable performance characteristics at these high temperatures. In this work, we investigate applicability of boron oxynitride (BO_xN_{1-x}) thin films to fabricate capacitors for high temperature applications. Deposited BO_xN_{1-x} layers by a filamentless ion source assisted physical vapor deposition technique show a high thermal stability up to 400 °C and a very high breakdown voltage (BDV) above 400 V/µm. BO_xN_{1-x} samples of thickness varying from 70nm – 200nm were grown in a high vacuum reactor. Prototype capacitors with boron oxynitride dielectric and titanium metal electrodes have been fabricated on 3" Si wafers followed by electrical and thermal characterization. Preliminary results indicate a very small variation (~3%) of capacitance over the frequency range of 10 KHz – 2 MHz and <10% variation in capacitance for the temperature range of 25 °C-400 °C. The device electrical characteristics studies (capacitance, leakage current, breakdown voltage), as a function of temperature and frequency for (BO_xN_{1-x}) dielectrics with varying oxygen to nitrogen ratio, are currently underway and their results will be presented at the conference.

This research was supported in part by USDOE grant # DE-FG02-05ER84325 to Integrated Micro Sensors, Inc.

9:00am **EN+AS+EM+TF-WeM4 Improving Efficiencies of Electrochemical Systems Through Microstructure Optimization**, *H.Y. Chen,* University of Michigan, *J.R. Wilson, P.W. Voorhees,* Northwestern University, *S.B. Adler,* University of Washington, *S.A. Barnett,* Northwestern University, ***K. Thornton***, University of Michigan

The properties and performance of a wide range of materials depend on their microstructures. This is especially true in multifunctional, multiphase or composite materials in which different phases perform different functions. Therefore, controlling microstructures in these materials is one of the main routes for materials design to achieve optimal performance. Various simulation methods that can be applied to examine processing, property, and degradation during operation, including the phase-field simulations and finite element modeling, will be discussed. Through coupling of simulations of microstructural evolution and transport that use realistic microstructures, microstructural design for optimized performance is investigated. Specific examples will include microstructures found in solid oxide fuel cell electrodes and those resulting from phase separation.

9:20am **EN+AS+EM+TF-WeM5 Layer-By-Layer Approaches to Electrochemical Energy and Storage**, ***P.T. Hammond***, MIT **INVITED**

New advances in multilayer assembly have involved the development of ionically conductive multilayer thin films and the introduction of electrochemical functionality. These systems have allowed the formation of a range of ultrathin electrochemical devices including electrochromic displays, proton exchange membranes in fuel cells, and the use of these multilayers in other power and micropower devices. The use of this water based electrostatic assembly method has enabled the use of simple processing conditions, such as salt content and solution pH, to act as tools for the manipulation of ion and electron transport characteristics in the film, as well as the morphology of these unique nano-assemblies. Examples of this approach include the ability to integrate highly water soluble polymers with large sulfonic acid content into mechanically stable ultrathin films has led to new membranes with ionic conductivity approaching that of Nafion, and methanol permeability two orders lower, thus lowering fuel crossover and leading to large enhancements in methanol fuel cell performance with the application of nanometer thick thin films. On the other hand, the incorporation of both organic and inorganic nanoscale objects using the electrostatic assembly approach has enabled the incorporation of genetically engineering virus biotemplates in collaborations with the Belcher research group that have resulted in new developments in battery electrodes, and the integration of titania and other materials systems for reactive electrodes. Ultimately, the use of layer-by-layer systems have led to a range of organic and inorganic materials systems that have incorporated metal oxide nanoparticles, semiconducting carbon elements, and organic polymers to yield systems of interest for solar cells, capacitor/battery and electrochemical energy electrode and separator applications.

10:40am **EN+AS+EM+TF-WeM9 Material Solutions for Solid State Energy Storage**, ***L.F. Nazar***, University of Waterloo, Canada **INVITED**

The increasing demand for energy world-wide and inherent pressing environmental needs, have jump-started efforts to develop energy storage systems that can be coupled to renewable sources, and/or viable energy conversion systems. Traditional electrode materials for lithium-ion storage cells are typically crystalline, single-phase layered structures such as metal oxides, and graphitic carbons. These materials power billions of portable electronic devices in today’s society. However, large-scale, high-capacity storage devices capable of powering hybrid electric vehicles (HEV’s) or their plug-in versions (PHEV’s and EV’s) have much more demanding requirements. This in turn, means that demands are on chemists to create novel materials, and address fundamental scientific issues relating to mass (ion) and electron transport at rapid rates. Recently, nanostructured solid state materials comprised of two more compositions, are being increasingly exploited. These can take the form of “surface modified nanocrystallites”, or stuffed nanoporous materials. For example, we employ porous frameworks as electrically conductive scaffolds to encapsulate active electrode materials, where both components play a role in controlling the electrochemical performance. This presentation will provide an overview of how the nanostructured approach provides benefit over the bulk, using selected examples from a range of promising new solid state materials with targeted, and tuneable structures.

11:20am **EN+AS+EM+TF-WeM11 Platinum Nanorods as PEM Fuel Cell Electrodes**, ***M. Gasda**, R. Teki, T.-M. Lu, N. Koratkar, G. Eisman, D. Gall*, Rensselaer Polytechnic Institute

Platinum catalyst layers were deposited by magnetron sputtering from a variable deposition angle α onto gas diffusion layer (GDL) substrates and were tested as cathode electrodes in polymer electrolyte membrane (PEM) fuel cells. Layers deposited at normal incidence ($\alpha = 0°$) are continuous, and approximately replicate the rough surface morphology of the underlying GDL. In contrast, glancing angle deposition (GLAD) with $\alpha = 85°$ and continuously rotating substrates yields highly porous layers consisting of vertical Pt nanorods. At 0.40 mg/cm^2 total Pt loading, the rods are 100-500 nm long and ~300 nm wide, separated by 20-100 nm wide voids. The dramatic difference in microstructure is due to atomic shadowing during GLAD that causes Pt flux from highly oblique angles to preferentially deposit on surface protrusions, leading to nucleation and columnar growth on substrate mounds while surface depressions remain uncoated. Fuel cell testing at 70°C using Nafion 1135 membranes, Teflon-bonded Pt-black electrodes (TBPBE) at the anode, and atmospheric pressure hydrogen and air reactants shows a monotonic increase in performance of GLAD cathodes from 0.05 to 0.40 mg/cm^2 total Pt loading. Nanorod cells exhibit approximately 2x higher mass activity than continuous layers at 0.50V (corrected for iR, shorting, and gas crossover); for example, GLAD and continuous layers with approximately the same Pt loading (0.18 and 0.25 mg/cm^2, respectively) show 1.7 and 0.8 A/mg. In contrast, at low current density of 0.10 A/cm^2, the continuous layers (0.70 V with 0.25 mg/cm^2 Pt) outperform GLAD cells even with relatively high Pt loadings (0.65 V with 0.40 mg/cm^2 Pt). The GLAD cells' higher mass-specific performance at high current densities is due to their high porosity which facilitates reactant transport, while the low-current performance of the continuous layer is attributed to a higher active Pt surface area. The sputter-deposited electrodes exhibit a higher platinum utilization in comparison to TBPBE reference cathodes, with GLAD cells (1.7 A/mg) performing better than TBPBE (0.75 A/mg) at high current densities (0.50 V), while continuous layers (0.07 A/mg) outperform TBPBE (0.035 A/mg) at 0.80 V. These results indicate the promise of nanoengineering to boost catalyst utilization in PEM fuel cells.

Thin Film
Room: 302 - Session TF-WeM

Chemical Vapor Deposition
Moderator: P.D. Rack, University of Tennessee

8:00am **TF-WeM1 Growth and Functional Properties of Thin Film Oxides Synthesized under Photon Irradiation**, ***S. Ramanathan***, Harvard University **INVITED**

Thin film oxides play a key role in several advanced electronics and energy technologies such as alternate gate dielectrics, memory devices and functional membranes in energy generation. Developing novel routes for synthesis of oxide thin films with controlled structure and stoichiometry is therefore of great importance. In this talk, we will present experimental and modeling results from our on-going work on synthesis of ultra-thin oxides under photon irradiation with particular emphasis on structure-property relations. Model systems that will be discussed include ultra-thin fluorite-strucutred zirconia dielectrics synthesized by low temperature ultra-violet ozone oxidation and yttria-doped zirconia films grown by physical vapor deposition methods. The role of photon irradiation during oxide formation will be discussed in depth along with their impact on functional properties. Examples of applications of the processing technique in advanced electronic devices as well as solid oxide fuel cells will be presented.

8:40am **TF-WeM3 A Zone Diagram for Conformal Film Growth by CVD**, ***J.R. Abelson**, A. Yanguas-Gil, N. Kumar, Y. Yang*, University of Illinois at Urbana-Champaign

The field of thin film growth using physical vapor deposition has benefited enormously from the mechanistic insights provided by Thornton's zone diagram, which he introduced to this society in 1974. There has been no direct analogue for the case of chemical vapor deposition (CVD), presumably due to the multiplicity of chemical reactions and the wide range of experimental conditions associated with the use of different precursor molecules. One major advantage of CVD is the ability to deposit films with extremely good conformal (step) coverage, which is a requirement for the additive fabrication of many current and proposed nanoscale devices. We show that all conformal CVD processes share certain kinetic requirements and limitations. Each of these can be represented on a plot of precursor pressure vs. substrate temperature: threshold phenomena, such as the onset temperature for reaction, appear as a vertical or horizontal line; kinetic competitions, such as surface adsorption vs. desorption, appear as exponential slopes. The properties of the precursor molecule and the aspect ratio of the feature to be coated (represented by a trench) then define a polygonal figure on the (P,T) plot which may or may not allow for conformal growth. We further show that many of the kinetic coefficients can be represented in normalized form, which we present as a zone diagram for conformal growth by CVD. The usefulness of this construction is illustrated by analyzing well-known experimental systems, such as W or SiO_2 growth, and the recent results we have obtained for the low temperature CVD of HfB_2, CrB_2, TiB_2 and MgO. For all these systems, the underlying mechanism that affords good step-coverage is surface site-blocking due to adsorbed precursor molecules or reaction byproducts or co-reactants. The experimental results are consistent with the predictions of the zone diagram. We conclude by showing how the site-blocking processes, and thus the degree of conformal coverage, can be controlled through the addition of site-blocking agents, such that a precursor that normally does not afford conformal growth can be transformed into one that coats very deep features.

9:00am **TF-WeM4 Conformal Chemical Vapor Deposition of Metal Oxide Thin Films using Metal-Diboranamide Precursors**, ***A. Yanguas-Gil**, N. Kumar, S.R. Daly, Y. Yang, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

The N,N-dimethyldiboranamide (dmdba) ligand is used to synthesize a wide range of different alkaline earth, transition metal and rare earth metal compounds that have sufficient volatility to serve as precursors for the growth of complex materials by chemical vapor deposition (CVD). In this work, we report the successful growth of TiO_2, erbium-doped TiO_2, MgO, Y_2O_3, La_2O_3 and titanate complex oxides using water as a co-reactant at substrate temperatures as low as 225°C. The growth process is monitored in-situ using spectroscopic ellipsometry, and the films are characterized ex-situ by AES, RBS, SEM, XRD and AFM. The crystallinity of the films upon annealing is also studied. The results show that the metal center has a strong influence in the reactivity, surface chemistry and the vapor pressure of the precursor. The impurity concentrations in the films are below the AES and RBS detection limits, indicating that the dmdba ligand is efficiently released from the growth surface to the gas phase. Under suitable conditions the film growth is highly conformal, e.g. MgO films have been deposited onto trenches with 30:1 depth:width ratio with a step coverage (minimum to maximum thickness ratio) of 90%. The corresponding film growth rate is 5-100 times greater than that achievable using atomic layer deposition due to the uninterrupted nature of the CVD process. These results make the dmdba precursor family very attractive for the synthesis of complex oxide films by CVD.

9:20am **TF-WeM5 Chemical Vapor Deposition of WN_xC_y using Tungsten Piperidylhydrazido Complex: Deposition, Characterization and Diffusion Barrier Evaluation**, ***D.J. Kim**, O.H. Kim, T.J. Anderson, J. Koller, L. McElwee-White, C.L. Leu, J.M. Tsai, D.P. Norton*, University of Florida

The tungsten piperidylhydrazido complex $Cl_4(CH_3CN)W(NN(CH_2)_5)$ (designated as 1) was deposited by metal organic chemical vapor deposition (MOCVD) for growth of tungsten carbonitride (WN_xC_y) thin films in the temperature range 300 to 700 °C in the absence and presence of ammonia (NH_3). The effect of deposition temperature and NH_3 on the film microstructure, chemical composition, bonding states, growth rate, electrical resistivity, lattice parameter, and grain size were studied. The microstructure of films deposited with NH_3 was amorphous below 500 °C and polycrystalline at and above this temperature. The chemical composition of films deposited with NH_3 increased the nitrogen levels and decreased the carbon levels over the entire deposition temperature range as compared to films deposited without NH_3. The XPS results indicate that W is primarily bonded to N and C for films deposited at 400 °C, but at lower deposition temperature the binding energy of the W-O bond becomes more evident. Growth rates of films deposited with NH_3 varied from 0.6 to 4.2 Å/min. Diffusion barrier properties were investigated from $Cu/WN_xC_y/Si$ stacks consisting of 100 nm Cu deposited at room temperature by reactive sputtering on a WN_xC_y film deposited at 400 °C by CVD. XRD patterns, AES compositional depth profiling, and cross-sectional TEM imaging were used to determine the performance of the diffusion barrier. $Cu/WN_xC_y/Si$ stacks annealed at 500 °C for 30 min maintained the integrity of both Cu/WN_xC_y and WN_xC_y/Si interfaces. Hence, WN_xC_y thin films deposited at 400 °C are a viable material to serve as a Cu diffusion barrier to prevent interdiffusion and intermixing between Cu and Si. The film properties of thin films deposited with 1 and tungsten imido complexes $Cl_4(CH_3CN)W(NR)$ (R = Ph, ^{i}Pr, and allyl)[1] were also compared to provide insight into the effect of hydrazido and imido ligands on film properties.

[1] O. J. Bchir, K. M. Green, H. M. Ajmera, E. A. Zapp, T. J. Anderson, B. C. Brooks, L. L. Reitfort, D. H. Powell, K. A. Abboud, L. McElwee-White, J. Am. Chem. Soc. 127 (2005) 7825-7833.

9:40am **TF-WeM6 Conformality of Chemical Vapor Deposited Copper Oxide Thin Films in High Aspect Ratio Features for ULSI/MEMS Applications**, ***Y. Shimogaki***, *Y. Susa*, The University of Tokyo, Japan

Kinetics of chemical vapor deposition of copper oxide (Cu_2O) thin film using Cu(tmvs)(hfac) and H_2O_2 as precursors were investigated. Cu_2O films could be deposited at relatively low temperature, as low as 80°C, on various kinds of under-layers including thermal silicon oxide and TaN. Cu_2O films can be easily reduced to metallic copper thin films using formic acid (HCOOH) as reducing agent. This reduction process can be performed at low temperature of around 100°C. Thus, Cu_2O deposition and its reduction process combination can be a novel chemical route to make metallic copper film at low temperature. In this work, we examined the source precursor partial pressure dependencies of Cu_2O growth rate (G.R.) using cold wall type CVD reactor. G.R. showed non-linear behavior, know as Langmuir-Hinshelwood mechanism, against partial pressure of Cu precursor (P_{Cu}), while G.R. showed linear dependence against the partial pressure of H_2O_2 (P_{H2O2}). These kinetics suggest Cu_2O is formed via direct reaction of gas-phase H_2O_2 and adsorbed Cu precursor. The extendibility of this Cu_2O-CVD process to make conformal deposition onto high aspect ratio (HAR) features was systematically investigated. The film thickness profile within HAR-feature, like as trench, was analyzed by solving diffusion equation for precursor molecules. The consumption of the precursors by surface reaction, whose rate had been obtained from the above mentioned kinetic studies, was taken into account. The analysis suggested that film thickness non-uniformity was mainly derived from the consumption of H_2O_2. The Cu precursor concentration profile does exist in the HAR-features, however, due to the non-linear kinetic behavior of G.R. against P_{Cu}, its non-uniformity will not affect to the film thickness uniformity. Existence of gas-phase reaction to decompose H_2O_2 was also confirmed from the growth rate profile analysis. These kinetic information were integrated and extendibility of this Cu_2O-CVD process for conformal deposition onto HAR features was estimated. We could conclude that this process is suitable for ULSI interconnect and TSV applications with nearly 100% step coverage, but for MEMS applications, this process may have a limit. Step coverage of about 40% or less will be obtained for aspect ratio of 100, which may be sometimes required for MEMS applications.

10:40am **TF-WeM9 Structure and Morphology of Pentacene Film Grown on HOPG**, ***J. Götzen***, *D. Käfer, Ch. Wöll, G. Witte*, Ruhr-University, Germany

Previous studies have shown that the structure of organic semiconductor film depends sensitively on the interaction with the substrate. In this respect we have studied the film growth of pentacene onto highly oriented pyrolytic graphite which constitutes an interesting model system for a chemically rather inert but - in contrast to amorphous oxides – highly ordered crystalline substrate. Here we report a comprehensive characterization of the microstructure, morphology and thermal stability of pentacene films grown by OMBD onto freshly cleaved HOPG by employing STM, AFM, NEXAFS, XRD and TDS. Despite a rather weak, essentially van-der Waals-type substrate interaction pentacene molecules adsorb with their planes oriented parallel to the surface and form a commensurate monolayer due to the close match of the molecular carbon frame and the underlying graphite lattice. This packing motive, however, is not maintained in multilayer films where instead molecules in subsequent layers are tilted around their long axis. The multilayer growth is further characterized by the formation of individual crystalline islands exhibiting the Siegrist bulk polymorphism for rather different growth conditions (rate and temperature) and thus parallels the growth scenario observed previously for pentacene on Au(111)[1] In contrast films with upright oriented molecules were obtained if the graphite had been briefly sputtered before deposition and thus emphasizes the importance of micro-roughness on the resulting film growth.

[1] D. Käfer, L. Ruppel, G. Witte, Phys. Rev. B 75, 085309 (2007).

11:00am **TF-WeM10 Electrically Controllable Stationary Hadamard Shutter Exploiting the Semiconductor-To-Metallic Phase Transition of W-doped VO_2 Arrays**, ***M. Soltani***, *M. Chaker*, INRS-Énergie, Matériaux et Télécommunications, Canada, *E. Haddad, R.V. Kruzelecky, W. Jamroz*, MPB Communications Inc., Canada, *J. Margot*, Université de Montréal, Canada, *P. Laou, S. Paradis*, Defence R&D Canada-Valcartier

The well-known transmitting semiconductor (on) to the reflecting metallic (off) phase transition (SMT) of thermochromic VO_2 can be controlled by external parameters such as temperature, pressure, photo-carrier injection, photo-excitation, and an electric field. Also, the transition temperature (about 68 °C) of VO_2 can be controlled by metal doping such as W, Ti, Al, Mo, etc. Undoped and doped-VO_2 smart coatings are thus excellent materials for various switching applications such as IR uncooled bolometers, smart windows, all-optical, electro-optical and microwave switching devices. Here, we exploit the SMT characteristic of W(1.4 at. %)-doped VO_2 active layer in the fabrication of stationary Hadamard shutter arrays. The active layer was synthesized by reactive pulsed laser deposition. The micro-optical active slits were patterned by photolithography followed by plasma etching, while the lift-off process achieved the Au/NiCr electrodes onto the top of the individual micro-slit. This shutter consists of 16 active planar micro-optical slits for which both the infrared transmittance and reflectance switching can be controlled individually at room temperature by an external voltage. This allows performing any desirable on-off switching combinations. Both the electroreflectance and electrotransmittance switching of the individual slits were investigated at 1.55 µm. The transmittance switching was as high as 25 dB, while the reflectance switching was about 6 dB. In addition, the electrotransmittance switching modulation (on/off) was demonstrated at 1.55 µm by switching the individual slits by an external ac signal. This shutter can be used as individually programmable 16 multi-entrance slits (i.e., stationary Hadamard shutter) instead of the traditional single entrance slit of dispersive IR spectrometers. Thus, the role of the Hadamard shutter consists of multiplexing the incoming information into the output detector element arrays using binary coding. As results, enhancement of the signal-to-noise ratio and improvement of both the sensitivities and the resolutions of these spectrometers.

11:20am **TF-WeM11 Molecular Beams Tunable in Energy Yield Novel Growth Behavior in Small-Molecule Organic Semiconductors**, ***A. Amassian***, *S. Hong, T.V. Desai*, Cornell University, *S. Kowarik*, University of California at Berkeley, *J.E. Goose, A. Papadimitratos, V.A. Pozfin*, Cornell University, *A.R. Woll, D.M. Smilgies*, Cornell High Energy Synchrotron Source, *F. Schreiber*, Universität Tübingen, Germany, *P. Clancy, G.G. Malliaras, J.R. Engstrom*, Cornell University

The performance of organic electronic devices is closely tied to the packing structure and morphology of molecular semiconductors at the semiconductor-insulator interface, which in turn are intricately linked to molecular-scale processes operant during thin film growth. Tunable supersonic molecular beams have emerged as a versatile method to manipulate the state of incident molecules (e.g., kinetic energy, vibro-rotational states) and to promote novel growth behavior on the surface of the insulator (i.e., SiO_2). The growth of small-molecule thin films of pentacene and diindenoperylene from molecular beam sources tunable in kinetic energy (1 to 10eV) and flux was investigated in situ using synchrotron-based time-resolved X-ray reflectivity and grazing incidence X-ray diffraction techniques and ex situ by non-contact atomic force microscopy. Time-resolved X-ray scattering experiments reveal significant acceleration of the growth rate between the submonolayer and the multilayer thickness regimes. The acceleration of growth rate is not observed in thermal processes; it is operant when molecules are incident at hyperthermal kinetic energy and further enhanced by increasing the energy of molecules. Rate equation modeling of X-ray reflectivity data suggests that small-molecules incident at hyperthermal kinetic energy are trapped much more efficiently by a molecular monolayer formed on the surface of the "hard" insulator than by the bare insulator itself. Molecular dynamic simulations reveal that energetic molecules undergo a so-called "soft-landing" on molecular monolayers, during which can insert the molecular layer near step edges and transfer most of their kinetic energy to the "soft" molecular layer. Organic thin film transistors of pentacene and diindenoperylene fabricated from molecular beams tunable in energy exhibit significant increases – by a factor of five for pentacene and by an order of magnitude for diindenoperylene – of the field effect mobility in conditions of high kinetic energy. The relationship between the kinetics of growth and improved charge transport characteristics of conjugated small-molecule semiconducting thin films is discussed.

11:40am **TF-WeM12 Vanadium Oxide Thin Films for IR Imaging Bolometric Applications Deposited by Reactive Pulsed DC Sputtering**, ***N.M. Fieldhouse***, *S.S.N. Bharadwaja, M.W. Horn, S.M. Pursel, R. Carey*, Pennsylvania State University

Uncooled infrared focal plane arrays (IRFPAs) are the critical technology for night vision cameras needed for military and civilian applications. The two most widely used temperature sensitive imaging materials are vanadium oxide and amorphous silicon typically deposited by reactive ion beam sputtering and PECVD respectively. In this work, we report on vanadium oxide (VOx) films deposited by a reactive pulsed DC magnetron sputtering process using a pure vanadium metal target that are comparable to those presently used in commercial IRFPAs. The structural, microstructure and electrical properties were evaluated as a function of processing parameters such as substrate temperature, range of oxygen to argon (Ar:O_2) partial pressures ratio, and pulsed DC power. The VOx films deposited at various substrate temperatures between 30-400 °C over a range of Ar:O_2 partial pressure ratios exhibited distinct variations in their microstructure even though most of them appear amorphous using glancing angle X-ray diffraction. The critical electrical properties such as the temperature coefficient of resistance (TCR), resistivity and noise levels were found to be sensitive to film microstructure. Thin films of VOx (50-200 nm) were deposited with resistivity values between 0.1-100 ohm-cm and a TCR in the range of -1.1% to -2.4% K^{-1}. In particular, films grown at lower substrate temperatures with higher oxygen partial pressures have shown finer columnar grain structure and exhibited larger TCR and resistivity.

Wednesday Afternoon, October 22, 2008

Thin Film
Room: 302 - Session TF-WeA

Computational and Experimental Studies of Thin Films
Moderator: S. Gupta, The Ohio State University

1:40pm **TF-WeA1 Origination and Role of Compressive Stress at Ion Deposition of DLC-film**, ***V.E. Strel'nitskij***, *A.I. Kalinichenko, S.S. Perepelkin*, NSC "Kharkov Institute of Physics and Technology", Ukraine

The known approach to formation of compressive stress in thin films by ion bombardment[1] uses the formalism of the point-like thermal spike (PTS) to describe acceleration of kinetic processes responsible for stress relaxation. But the PTS model does not reflect adequately real thermodynamic conditions in vicinity of the ion path in the target material. It does not take into account the finitness of the initial volume of the energy release which depends on energy E of the ion and thermal properties of material. As a result the known formula for residual stress σ (E) in thin film under ion bombardment[1] matches with experimental data only by too high values of the activation energy of migration of defects U > 3 eV. Also σ(E) does not depend on the substrate temperature T_0. In this paper the rate of kinetic processes in carbon films at low-energy ion deposition in the model of the nonlocal thermoelastic peak (TEP)[2] of the ion is analyzed. The approximate expressions for temperature T, pressure P and the number of sp^2 to sp^3 transitions in the TEP depending on energy of the ion and substrate temperature T_0 were derived and applied for modification of the expression of σ(E).[1] Unlike the previous expression σ(E) the modified one depends on E in accordance with experimental data when U is closed to 0.3 eV (the typical value for the activation energy of interstitials). Also σ decreases substantially with T_0 in temperature range 300 to 600 K. Calculation of σ and T permitted determining "the initial locations" and "P,T- trajectories" of the ion TEPs on phase P,T- diagram of carbon[2] and investigating possibility of DLC formation depending on E and T_0. As the steady residual stress σ decreases with the substrate temperature increase from 300 to 600 K the initial locations and P,T- trajectories of TEPs shift preferably from the region of diamond stability to that of graphite stability. Such behavior which is pronounced for TEPs with energies E > 100 eV suggests that sp^2 – bound carbon forms preferably in TEPs of low-energy ions C^+ at temperature of deposition $T_0 > 600$ K. This conclusion agrees qualitatively with experimental data.

[1] C.A. Davis: Thin Solid Films 226 (1993) 30.

[2] A.I. Kalinichenko, S.S. Perepelkin, V.E. Strel'nitskij, Diam. Relat. Mater. 15 (2006) 365.

2:00pm **TF-WeA2 Phase Evolution in Sputter Deposited Hafnia-Titania Nanolaminates with Changing Architecture and Thermal Annealing**, ***M.C. Cisneros-Morales***, *C.R. Aita*, University of Wisconsin-Milwaukee

Thin film HfO_2 is a candidate for a high dielectric constant replacement material for SiO_2 in integrated circuits. The addition of TiO_2 to HfO_2 has shown promise for producing a $Hf_{1-x}Ti_xO_2$ ternary with an even higher dielectric constant than pure HfO_2 while maintaining thermal stability with Si. A convenient way of combining TiO_2 with HfO_2 in thin films is to sequentially sputter deposit them in a nanolaminate structure. In such a structure, interfaces are important in determining phase composition. The bulk pseudobinary HfO_2-TiO_2 temperature-composition phase diagram shows low miscibility between the end-point oxides. In this respect, the HfO_2-TiO_2 system is typical of an oxide nanolaminate in which there is a driving force for the formation of an interfacial mixed cation compound but there is no obvious kinetic path to achieve this structure via the formation of an interfacial crystalline substitutional solid solution. In this paper we examine the moderate temperature annealing behavior of HfO_2-TiO_2 nanolaminates with many different bilayer architectures. Multilayer stacks of HfO_2 and TiO_2 bilayers were grown on unheated fused silica substrates in a rf-excited multiple cathode reactor. The substrates were sequentially positioned under Hf and Ti targets and sputtered in 20 mtorr 80% Ar-20% O_2 discharges to build up the films. Four sequential annealing stages were carried out in laboratory air at the following temperatures: (I) 573 K, (II) 673 K, (III) 773 K, (IV) 973 K for 1 h each. The films were furnace cooled to room temperature and analyzed by double angle x-ray diffraction between annealing stages to obtain crystallographic data. The results show that the as-grown films are nanocrystalline and contain a mixed cation interface. This interface develops upon annealing into an orthorhombic $HfTiO_2$ phase adjacent to a titania layer, followed by an unusual metastable phase, monoclinic $Hf_{1-x}Ti_xO_2$ more remote from the interface. In nanolaminates with thicker HfO_2 layers, a simulaneous development of monoclinic HfO_2 occurs. The lattice parameters of this nanocrystalline intralayer phase, however, are greater than the expected bulk value, indicating dipole-dipole repulsion at the surface of a HfO_2 nanocrystal might be occurring.

2:20pm **TF-WeA3 Rapid Diffusion of Magic-Size Islands by Combined Glide and Vacancy Mechanism**, ***O.U. Uche***, *J.C. Hamilton*, Sandia National Laboratories

Monolayers of Ag on Cu(001) are well known to reconstruct forming a (10x2) reconstruction with Ag atoms packed hexagonally on the four-fold Cu(001) surface.[1] We have investigated the surface diffusion of hexagonally-packed Ag monolayer islands of various sizes on Cu(001) using computer simulation techniques. Our examination reveals a novel cooperative diffusion mechanism consisting of core glide coupled with the migration of edge vacancies. It should be noted that island diffusion is completely one-dimensional with the orientation determined by the (10x2) reconstruction of the diffusing island. In other words, rows of the hexagonal Ag lattice move along the hollow and bridge sites of the Cu substrate in the {110} type direction. In addition, we have observed magic-sized islands for which diffusion occurs much more rapidly as a result of their reduced diffusion barrier. In particular for a 169-atom hexagonal island, the activation energy for diffusion is smaller than the barrier for a single Ag atom hop. For this island size, diffusion occurs rapidly at temperatures as low as 200K. Molecular dynamics simulations suggest that the surface diffusion process displays non-Arrhenius behavior possibly resulting from the temperature-dependent lattice mismatch. Our findings should provide insight to future experimental research on the size distribution and shapes observed during the growth of thin films in similar systems.

[1] P.W. Palmberg and T.N. Rhodin, J. Chem. Phys. 49, 134 (1968).

2:40pm **TF-WeA4 The Influence of Oxygen Impurities on the Formation of Self-Assembled Nanostructures in Al/Al(110) Homoepitaxy**, ***Y. Tiwary***, *K.A. Fichthorn*, The Pennsylvania State University

Recent experimental studies of Al/Al(110) homoepitaxy show that self-assembled nano-structures can form due to an interplay between the kinetics of diffusion and deposition.[1] These "nanohuts" are characterized by smooth {111} and {100} facets. At temperatures between 330 and 500 K and for a deposition rate of 1 ML/min, the nanohuts emerge after about 10 ML have been deposited. Upon further deposition, these huts grow and self-organize, reaching average heights of 50 nm after 30 ML has been deposited. Understanding the formation of these features and developing the capability to control them in this and similar systems is both scientifically and technologically significant. To predict the formation and self-organization of these features, we employ first-principles calculations based on density-functional theory to study diffusion and atomic interactions on Al surfaces. We quantify many-body interactions between Al adatoms,[2] as well as the interactions between Al adatoms and isolated O impurities on Al(110). The interactions between Al and O atoms are expected to be especially important in the initial stages of growth, as oxygen is a common impurity on Al surfaces, even in ultra-high vacuum environments. We show that O impurities can significantly influence island nucleation and lead to entirely different growth modes than those observed in pure Al/Al(110) homoepitaxy. Using kinetic Monte Carlo, we simulate multi-layer growth under various conditions to predict the growth morphologies and understand the implications of surface impurities for self-assembled nanostructures.

[1] F. Buatier de Mongeot, W. Zhu, A. Molle, R. Buzio, C. Boragno, U. Valbusa, E. Wang, and Z. Zhang, Phys. Rev. Lett. 91, 016102 (2003).

[2] Y. Tiwary and K. A. Fichthorn, Phys. Rev. B 75, 235451 (2007).

3:00pm **TF-WeA5 A Formula for Increased Hardness and/or Ductility in TiN-based Thin Films and γ-TiAL Compounds**, *D.G. Sangiovanni*, ***V. Chirita***, *L. Hultman*, Linköping University, Sweden

TiN-based thin films, such as $Ti_{1-x}Al_xN$ and their alloys, are known to have excellent mechanical and thermal properties. In this paper we report the initial results of our ab-initio investigations of two novel ternary compounds, $Ti_{1-x}W_xN$ and $Ti_{1-x}Mo_xN$, obtained by alloying TiN with W, respectively Mo, in concentrations of up to 50%. The elastic constants as well as the bulk, shear and Young's moduli of these compounds were evaluated using density functional theory calculations within the generalized gradient approximation, and compared with the corresponding properties of TiN and $Ti_{1-x}Al_xN$. Significantly, we found that the addition of W and Mo resulted in substantial increases in bulk modulus values compared to TiN (up to 15%) and $Ti_{1-x}Al_xN$ (up to 30%). At the same time, we observed a dramatic decrease (up to 50%) in the values of C_{44}, and a reversal of the Cauchy pressure, C_{12}-C_{44}, from negative to positive, results indicative of significantly increased ductility in these compounds. Both of these trends are in total contrast to what is known for $Ti_{1-x}Al_xN$, which exhibits increased C_{44}/brittleness and lower bulk modulus values as the Al content is increased. We also investigated, in the same manner, the effects of alloying $Ti_{0.5}Al_{0.5}N$ with W and Mo, in concentrations of up to 6% and observed a similar trend in increasing hardness and ductility. However, in the case of quarternary TiAl(W/Mo)N, the impact of W and Mo addition was considerably more moderate, as the increase in bulk modulus, respectively decrease in C_{44}, were in the 5% range. As it will be shown, these results demonstrate and help understanding the mechanisms through which W and/or Mo additions modify the atomic bonding in these compounds, from a strong angular/directional character, towards a more metallic type of bonding. This type of electronic structure information is essential in designing compounds with different mechanical properties and tailoring them to a variety of applications.

4:00pm **TF-WeA8 Ion Implantation and Annealing Studies on VO_x Films Prepared by Pulsed dc Reactive Sputtering**, ***C. Venkatasubramanian****, M.W. Horn, S. Ashok*, The Pennsylvania State University

Vanadium oxide (VO_x) thin films find extensive use in room-temperature bolometers for IR imaging. It is desirable to control and modify the electronic properties of the material with treatments such as ion implantation and thermal annealing. In this work, we report on the modification of structural and electrical properties of VO_x thin films used in microbolometers. VO_x films of varying compositions were deposited by pulsed dc reactive sputtering of a vanadium target under different oxygen flow rates. The as-deposited resistivities of the films ranged from 0.1 ohm-cm to 100 ohm-cm and the temperature coefficient of resistance (TCR) values varied from -1.1 to -2.7 % K^{-1}. VO_x films used in microbolometer applications need to have a high TCR (> 2 % K^{-1}) and low resistivity values (1 -10 ohm-cm). But, typically, a high TCR is associated with a high resistivity. Hence ion-implantation followed by annealing was performed in order to examine trade-off between TCR and resistivity. Two species - Hydrogen (active) and Helium (inert) were chosen for implantation. Hydrogen is an active species well known for passivating defect states in a wide variety of electronic materials. Helium is an inert species and was chosen mainly to study the effects of bombardment on the film. The implanted films were annealed in an inert atmosphere to allow for redistribution of atoms, and then characterized by current-voltage measurements over a wide temperature range. The effect of thermal annealing alone was evaluated separately by annealing the unimplanted samples. In both cases, an order of magnitude change in resistance, and significant variations in TCR were observed. Further characterization has been done by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) to correlate these resistivity changes with the structure of the films.

4:20pm **TF-WeA9 Optical Properties and Structure of Magnetron Sputtered Vanadium Oxide Thin Films**, ***N.J. Podraza****, B.D. Gauntt, N.M. Fieldhouse, K.E. Wells, D. Saint John, E.C. Dickey,* The Pennsylvania State University*, R.W. Collins,* University of Toledo*, M.W. Horn*, The Pennsylvania State University

Vanadium oxide (VO_x) thin films have been used for the last twenty years as the imaging material in uncooled infrared imaging devices. The important material properties for this application are a high thermal coefficient of resistance (TCR), controllable resistivity (ρ), low electrical noise and process compatibility with standard IC fabrication. In this work, device quality VO_x thin films have been fabricated by single and dual-target pulsed dc magnetron sputtering. The deposition parameters of this novel technique include vanadium (V), vanadium dioxide (VO_2), or vanadium trioxide (V_2O_3) sputter targets which can be used individually or two targets simultaneously with separately variable power, variable total pressure, variable oxygen partial pressure, and variable substrate temperature. Variations in these parameters have been shown to result in films with TCR between 1.5 and 4.0 (-%/K) and ρ ranging from 0.1-100,000 Ω cm as measured by a four-point probe technique. The films produced in the region of device interest have been characterized with a wide variety of ex situ techniques to establish what role the deposition parameters play in the final structure and composition of the film, and the resulting effects of these characteristics on the electronic transport and optical properties. Transmission Electron Microscopy (TEM), Rutherford Backscattering (RBS), and Spectroscopic Ellipsometry (SE) have been used to characterize the nanocrystalline structure of these films, their bonding structure, the oxygen content in the film, and the dielectric function spectra ($\varepsilon = \varepsilon_1 + \varepsilon_2$) in the visible range (0.75-6.5 eV), respectively. By utilizing these complementary techniques, correlations between changes in the microstructure and composition determined by TEM and RBS, optical properties determined by SE, and electronic transport properties have been established.

4:40pm **TF-WeA10 Multi-Scale Modeling of Thin-Film Epitaxy**, ***K.A. Fichthorn***, Penn State University **INVITED**

Predicting, with first-principles accuracy, the nanostructures that form during thin-film epitaxy is a current challenge in multi-scale modeling. I will discuss our recent innovations in accelerated molecular dynamics and coarse-grained lattice techniques, which facilitate this task. I will highlight these methods in studies aimed at understanding the morphology in Al(110) homoepitaxy. This system exhibits a number of interesting growth modes as the temperature and deposition rate are varied, including the formation of nanohuts. The nanohuts, which have smooth (111) and (100) facets, arise from a sea of smaller mounds after several layers are deposited, in a bimodal growth mode. We illustrate how first-principles total-energy calculations with density-functional theory, accelerated (ab initio) molecular dynamics, and kinetic Monte Carlo can be extended to yield insight into diffusion, many-body interactions, and growth in this system. I will illustrate the role of oxygen impurities in promoting bimodal growth.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+EM+NS+P+A+T+V-ThM

Energy: Tools and Approaches
Moderator: S.P. Williams, Plextronics, Inc.

8:00am **EN+EM+NS+P+A+T+V-ThM1 Nano-Structured and Micro-Structured Semiconductors for Better Efficiency of Solar Cells**, ***C.-F. Lin***, *J.-S. Huang, S.-C. Shiu, J.-J. Chao, C.-Y. Hsiao, K.-H. Tsai*, National Taiwan University **INVITED**

The foreseeable depletion of fossil fuel and the global warming caused by the carbon dioxide had led to the increasing attention of alternative renewable energy, especially photovoltaic. Therefore, crystalline Si-PV devices are quickly spreading. Unfortunately, the large consumption of Si materials hinders their vast applications. Many efforts have been switched to developing thin-film PV devices. In this talk, we will discuss the use of nano-structured and micro-structured semiconductors that enable the fabrication of thin-film solar cells with improved efficiency. Several types of such thin-film solar cells will be discussed, including the organic-semiconductor-nanowire composite film, organic-semiconductor micro-structure composite film, nano-wire semiconductor thin film, and micro-structured semiconductor thin film. In the thin-film solar cells using organic-semiconductor-nanorod composite film, different types of semiconductor nanowires such as ZnO, Si, and GaAs nanowires are used to replace the accepter-type organics for two purposes: increasing the electron mobility and assisting the formation of nano-morphology for better inter link between the donor organics and acceptor materials. The fabrication procedures of those nanowires as well as the formation of the organic-semiconductor-nanowire composite film with controlled nano-morphology will be presented. For the other solar cells using nano-structured and micro-structured semiconductors, we will particularly describe the technique of nanowire/micro-structure transfer. In our approach, the nanowires and micro-structures are made from the bulk semiconductors or epitaxial semiconductors, so they will have much better crystal quality than the usual thin-film materials. In addition, after nanowires and micro-structures are transferred to other transparent substrates, the original wafer can be reused, so the material cost can be lowered considerably. In addition, it offers the advantages of the bending flexibility, not being limited by the brittle property of semiconductors. Furthermore, in comparison with current III-V tandem solar cells taken by monolithic approach, which requires lattice match and current balance, our approach enables mechanically stacking. Thus each cell could be designed individually to match the entire solar spectrum for optimal solar usage. Therefore, such new-type thin-film solar cells are expected to be potentially efficient and low cost.

8:40am **EN+EM+NS+P+A+T+V-ThM3 Endohedral Metallofullerenes as Improved Acceptor Materials for Organic Solar Cells**, *M. Drees*, Luna Innovations Incorporated, *R. Ross*, Georgetown University, *C. Cardona*, Luna Innovations Incorporated, *E. Van Keuren*, Georgetown University, *D. Guldi*, Friedrich-Alexander-Universitat Erlangen-Nurnberg, Germany, ***B.C. Holloway***, Luna Innovations Incorporated

Cost factors in inorganic solar cells have opened up a new path to less expensive manufacturing techniques using bulk heterojunction polymer/fullerene based solar cells. Using empty cage fullerene derivatives as the acceptor material, state-of-the-art organic photovoltaics currently display ~5% overall conversion efficiency. One of the main factors limiting the efficiency in organic solar cells is the low open circuit voltage. The open circuit voltage is governed by the molecular orbitals of the donor and acceptor material; therefore better matching of the orbitals will lead to improved voltages. Here we present a novel acceptor material based on Trimetasphere® carbon nanomaterials (TMS). Trimetaspheres® are endohedral metallofullerenes that consist of a trimetal nitride cluster enclosed in a C80 cage. First-generation Trimetasphere® carbon nanomaterial derivatives have been synthesized and show behavior consistent with C60 but with improved molecular orbitals. Electrochemical data suggests a maximum voltage increase of up to 280 mV over C60-PCBM-based devices and photophysical characterization of shows efficient and stable charge separation. Initial bulk-heterojunction devices have been synthesized with open circuit voltages that are 280 mV higher than reference devices using C60-PCBM and conversion efficiencies exceeding 3.1%.

9:00am **EN+EM+NS+P+A+T+V-ThM4 Morphology Study of Vacuum-Deposited Pentacene:C60 Mixed Thin Films for Photovoltaic Applications**, ***J. Xue***, *Y. Zheng, J.D. Myers, J. Ouyang*, University of Florida

The efficiency of organic photovoltaic (PV) devices has gained steady increase in past 20 years, showing a potential to provide clean and low-cost electrical energy in the near future. Bulk heterojunction (HJ) composed of nanoscale percolation of donor and acceptor phase have been demonstrated to improve the efficiency of organic PV device. Such improvement is attributed to the creation of a spatially distributed interface, which enhances exciton dissociation, and the presence of continuous conducting paths for efficient charge collection. However, ideal nanoscale percolation is not readily achievable. Therefore, understanding the morphology inside the bulk heterojuncion plays an important role on achieving efficient PV device. Here, phase separation in donor-acceptor (D-A) mixture composed of pentacene:C60 and how it contributes to a percolated morphology are studied. The pentacene:C60 mixed films are fabricated by co-deposition of two molecules with vacuum thermal evaporation (VTE) method. The mixing ratio of pentacene and C60 is controlled by varying the deposition rate of each species. X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to characterize the vacuum deposited pentacene:C60 mixed film. XRD patterns of pentacene:C60 mixed films indicate phase separation inside the mixture, which is reflected by appearance of characteristic diffraction peaks of thin film phase pentacene. SEM and AFM images reveal the change of surface morphology of the mixed films with varied mixing ratio and deposition rate, suggesting different degree of phase separation inside. Base on these information, PV devices are fabricated and their performance is investigated. It is found that by suppressing the phase separation between pentacene and C60 to nanoscale the PV performance is improved significantly. The open circuit voltage (Voc) and short circuit current (Jsc) increase from 0.45 V and 9.7 µA/cm2 in pentacene:C60 = 1:1 (by weight) device to 0.58 V and 1.3 mA/cm2 in pentacene:C60 = 1:5.5. All these suggest that degree of phase separation of molecular mixtures can be controlled by varying the process conditions, which may lead to new pathways to generate nanoscale percolation for application in efficient organic PV devices.

9:20am **EN+EM+NS+P+A+T+V-ThM5 Tailoring the Morphology of Organic Solar Cells with Surface Templates**, ***S. O'Donnell***, University of Virginia and The MITRE Corporation, *P. Reinke*, University of Virginia

One of the most important applications of fullerenes is their incorporation in organic solar cells, where they function as an electron acceptor in conjunction with photoactive molecules such as porphyrin. The photoyield is intimately linked to the morphology, which determines the efficiency of exciton diffusion and separation, and the effectiveness of charge transport to the electrodes. Control of the morphology across lengthscales, spanning the range from the molecule to the several hundred nm, is critical to optimization of solar cell functionality. We control the morphology by using tailored substrate templates on which we assemble ultrathin films with well-defined regions of acceptor and photoabsorber molecules. This approach enables us to measure the morphology and interface structure with atomic resolution with scanning probe methods, and to subsequently investigate the photocurrent distribution. A pattern with variable geometry is written on the surface of highly oriented pyrolitic graphite (HOPG), our model surface, with a focussed ion beam (Ga+, 30 keV ion energy), which creates regions with a high density of surface defects interspaced with largely undamaged graphite surface. The surface defect structure, its extension and density within the pattern is characterized prior to molecule deposition. Surface defects interact strongly with the fullerene molecules, and thus provide nucleation centers for the formation of fullerene islands whose position is in registry with the artificial pattern. The boundary of the ion damaged region serves as the primary nucleation center for the formation of C60 islands, whose shape is controlled by the pattern geometry and the diffusion length of the molecules. We will describe how the artificial pattern can be used to tailor the morphology across lengthscales and discuss the extension of this method to other, technically relevant surfaces such as quartz which possesses a natural patterning in the form of ledges. The complete 2D nanostructure can be built by deposition of fullerene on the templated HOPG, and the remaining "empty" graphite surface is then filled with photoabsorber molecules. We will show the movement of porphyrin molecules into the pattern, and how the interfacial region between fullerenes and porphyrins evolves, and discuss the resultant morphologies. This hierarchical assembly of organic solar cells will enable us to tailor morphologies and link them uniquely to the photophysical processes.

9:40am **EN+EM+NS+P+A+T+V-ThM6 Photoemission Studies of Lead Sulfide Nanocrystals in Organic Films,** ***A.T. Wroble****, D.J. Asunskis, A.M. Zachary, I.L. Bolotin,* University of Illinois at Chicago*, D.J. Wallace, M. Severson,* University of Wisonsin-Madison*, L. Hanley*, University of Illinois at Chicago

Lead sulfide (PbS) nanocrystals have shown potential for use in optoelectronic applications including photovoltaics. PbS nanocrystals are grown directly into polymers or organic oligomer matrices to control the size and surface chemistry of the resulting nanocrystals. Transmission electron microscopy is used to determine the size distribution of PbS nanocrystals in organic films grown by either colloidal synthesis in polymer solutions or gaseous deposition using a cluster beam deposition source. Both the colloidal and cluster beam deposition methods are described in detail. Various techniques in photoemission spectroscopy are then applied to these PbS nanocrystal-organic films. X-ray photoelectron spectroscopy (XPS) confirms that PbS nanocrystals are present. Soft-XPS using 200 eV photon energies available at a synchrotron radiation source provides surface sensitivity to observe the interaction of the PbS nanocrystal surface with the organic matrix and is compared to XPS results obtained using 1487 eV photon energy. Little or no bonding between the PbS nanocrystals and the organic phase is observed. The core of the nanocrystals are found to be 1:1 Pb:S, but their surfaces are enriched in Pb. Finally, core level binding energy shifts in XPS under simulated solar irradiation are used for contact-free evaluation of element-specific photovoltaic electrical response of these PbS nanocrystal-organic thin films.

10:40am **EN+EM+NS+P+A+T+V-ThM9 Rational Design of Nanostructured Hybrid Materials for Photovoltaics,** ***S.B. Darling****, I. Botiz,* Argonne National Laboratory*, S. Tepavcevic, S.J. Sibener,* The University of Chicago*, T. Rajh, N. Dimitrijevic*, Argonne National Laboratory

Efficient conversion of photons to electricity in organic and hybrid materials depends on optimization of factors including light absorption, exciton separation, and charge carrier migration. Bulk heterojunction devices target these processes, but disorder on the nanoscale results in inefficiencies due to exciton recombination and poor mobility. By rationally designing the morphology at appropriate length scales, one can enhance the effectiveness of internal processes and, therefore, the performance of photovoltaic devices. In this work, we have implemented this approach in two hybrid material systems—both of which may provide pathways to low-cost, large-area fabrication.[1] The first involves a rod-coil block copolymer which is used both as an optoelectronically active material and as a structure-directing agent to pattern active material into ordered nanostructures. The second system uses electrochemically prepared titania nanotube arrays in concert with in situ polymerization of electron-donating material. In both cases, the characteristic donor-acceptor length scale is controlled to be comparable to the exciton diffusion length throughout the active layer, and the domains are oriented perpendicular to the incident light direction to encourage efficient charge migration.

[1] Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract #DE-AC02-06CH11357. Parts of this work were also supported by the NSF-MRSEC at the University of Chicago.

11:00am **EN+EM+NS+P+A+T+V-ThM10 Electronic Energy Level Alignment in Dye Sensitized Oxide Surfaces,** ***S. Rangan****, J.P. Theisen, E. Bersch, R.A. Bartynski*, Rutgers University

We have used direct and inverse photoemission to measure the occupied and unoccupied electronic states of N3 dye and determine their alignment with the band edges of single crystal and nanostructured TiO_2 and ZnO substrates. In dye-sensitized solar cell applications, the HOMO-LUMO gap of the dye molecule determines the useful portion of the solar spectrum, and charge transfer of photoexcited electrons to the substrate depends on the alignment of the LUMO to the substrate conduction band edge. We have compared the N3 dye properties on well characterized rutile TiO_2(110) and wurtzite ZnO single crystal surfaces to adsorption on more technologically relevant TiO_2 anatase nanoparticle and ZnO nanorod substrates. Samples were prepared and passivated with a pivalate layer in UHV, then sensitized ex-situ in a solution of N3 dye in acetonitrile. STM measurements show that the pivalic acid forms an ordered overlayer on the TiO_2(110) surface and that the N3 dye molecules can be imaged after sensitization. For N3 on TiO_2(110) as shown below, our spectroscopic measurements show that passivation significantly reduces contamination (presumably from water in the ambient) and that the N3 HOMO occurs at 0.9 eV above the TiO_2 valence band edge, while the LUMO is found 0.5 eV above the conduction band edge. On ZnO , the N3 HOMO occurs at 1.3 eV above the ZnO valence band edge but the N3 LUMO occurs 2.1 eV above the conduction band edge, much higher than what is measured on TiO_2. Comparison with experimental and theoretical values from the literature will be discussed.

11:20am **EN+EM+NS+P+A+T+V-ThM11 Preparation of Nanoporous ZnO Photoelectrode using PEG Template for the Fabrication of Dye-Sensitized Solar Cells,** ***M.F. Hossain****, S. Biswas, M. Shahjahan, T. Takahashi*, University of Toyama, Japan

Recently, great attention has been paid to dye-sensitized solar cells (DSCs) due to their low fabrication cost. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO_2 electrode. Zinc oxide (ZnO) is a wide band gap semiconducting material with a similar band gap and electron affinity to those of TiO_2 and has been considered as an alternative material in DSCs applications. Among the various techniques for the preparation of ZnO photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates. In our present study, the nanoporous ZnO films were deposited on SnO_2:F coated glass by sol–gel technique with polyethylene glycol (PEG) as organic template, $Zn(CH_3COO)_2.2H_2O$ as precursor, ethanol as solvent and $NH(C_2H_2OH)2$ as chelating agent. The ZnO films have been characterized by the TG-DTA, XRD, SEM AFM, FTIR and UV-VIS systems. The surface morphology of the nanoporous ZnO films strongly depend on the $Zn(CH_3COO)_2$ concentrations, PEG contents and number of coatings. It was revealed from optical study that the dye absorption increases with the increase of PEG concentrations. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different ZnO thin films to evaluate the economic viability of this technique. The variation of photoelectric conversion efficiency of the solar cells, deposited with different $Zn(CH_3COO)_2$ and PEG concentrations are discussed with the analysis of different microstructure of the ZnO thin films and the corresponding dye-incorporations.

11:40am **EN+EM+NS+P+A+T+V-ThM12 Metal / Polymer Interfaces: Ca on Polyfluorenes,** ***J.A. Farmer****, J.H. Baricuatro,* University of Washington*, E. Zillner,* Universitaet Erlangen-Nuernberg, Germany*, J.F. Zhu,* University of Science and Technology of China*, C.T. Campbell*, University of Washington

Conjugated polymers are being investigated for use in organic photovoltaic devices and organic electronics due to favorable cost and ease of processing compared to devices based on inorganic materials. The synthetic tunability of polymer-based devices makes them applicable to many technological applications. The creation of cheap organic photovoltaic devices would significantly improve our ability to harness solar energy and curb the use of fossil fuels. The development of organic LED and organic electronics may give rise to flexible computer displays and hardware that could revolutionize human interaction with computing devices. Crucial to the performance optimization of these devices is understanding the interaction between the metal electrodes and the polymer. The structure and energetics of the interface between Ca and two polyfluorenes, poly(9,9-di-n-hexylfluorenyl-2,7-diyl) (PDHF) and poly(9,9-di-n-hexylfluorenyl-2,7-vinylene) (PDHFV), were studied in ultrahigh vacuum using adsorption microcalorimetry, and low-energy ion scattering spectroscopy. The initial sticking probabilities of Ca on pristine PDHF and PDHFV at 300 K were 0.40 and 0.53, respectively. The sticking probability of Ca on PDHFV began decreasing after ~0.06 ML, and then increased toward unity after ~0.24 ML. Because no similar behavior was seen on PDHF, this decrease in the Ca sticking probability on PDHFV is tentatively ascribed to the presence of the vinyl group. At submonolayer coverages on both polymers, the integrated Ca ISS peak area increased slowly below 1 ML, with a value less than 1 % of a saturated Ca surface at 300 K. These results indicated that most of the Ca at low coverages were below the surface, and not visible to ISS. Beyond 1 ML the Ca peak area increased, and ultimately a continuous Ca film formed at ~50 ML. Based on the variation of Ca peak area with coverage, Ca grows as 3D islands on these polymer surfaces. The heat of adsorption of Ca on PDHF at 300 K was initially 240 kJ/mol and 315 kJ/mol on PDHFV. The heat of adsorption of Ca on PDHF decreased to the heat of sublimation of Ca in ~0.25 ML; the heat of sublimation was reached by ~0.50 ML for PDHFV. The interesting thermodynamic and sticking behavior below 0.50 ML, where Ca is interacting strongly with specific adsorption sites on the polymer will be discussed, and related to the use of these polyfluorenes in device applications.

Thin Film
Room: 302 - Session TF-ThM

Evaporation, Pulsed Laser Deposition, and Molecular Beam Epitaxy
Moderator: J.M. Fitz-Gerald, University of Virginia

8:00am **TF-ThM1 Pulsed Laser Dewetting of Patterned Thin Metal Films: A Means of Directed Assembly**, ***Y.F. Guan,*** The University of Tennessee, Knoxville, *J.D. Fowlkes, A.V. Melechko, M.L. Simpson,* Oak Ridge National Laboratory, *P.D. Rack*, The University of Tennessee, Knoxville

One of the challenges of nanoscience and technology is understanding and controlling bottom up directed assembly of materials. A lot of work has been done studying the assembly of continuous thin polymer and metal films which reveal interesting dewetting phenomenon. While the break-up and pattern formation via dewetting of continuous thin metal and polymer films has been studied in detail, less work has been devoted to the dewetting and pattern formation of confined or patterned thin films. In this work, thin nickel films were patterned into various shapes and treated via nanosecond pulsed laser processing. The short liquid lifetimes offers a unique way to monitor the time dependence of the dewetting process and the subsequent pattern formation. Thin nickel films (30 nm) were evaporated onto electron beam lithography patterned PMMA coated (60 nm) silicon substrates. Thin nickel patterns of a variety of sizes of circles, squares, and triangles were achieved by a conventional lift-off process. The edges and vertices of the patterned shapes act as programmable instabilities which enable directed assembly via dewetting when the laser energy density is above the melting threshold. The pattern formations were monitored as a function of laser pulse and the retraction process was attributed liquid dewetting and a subsequent re-solidification. The calculated retraction velocity (83 m/s) and liquid lifetime (12.3 ns) were consistent with the measured nickel retraction distances. The lateral retraction and pattern formation was correlated to a two step process: 1) initially the surface tension drives the flow of the melted nickel films, and 2) a smaller contraction associated with the density difference between the liquid and solid when the liquid film solidifies. The vertices of the shapes had an initially larger retraction velocity which was attributed to an additional in-plane curvature. The reduced retraction rates at subsequent pulses were attributed to thickening of the front which reduces the curvature and enhances viscous dissipation. Acknowledgements: The authors acknowledge support from the Material Sciences and Engineering Division Program of the DOE Office of Science. And a portion of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

8:20am **TF-ThM2 Vacancy Ordered Screw Form (VOSF) and Layered Indium Selenide (In_2Se_3) Thin Films by Pulsed Laser Deposition**, ***E. Venkatasubramanian***, *F.S. Ohuchi*, University of Washington, *P. Nachimuthu, K.M. Beck*, Pacific Northwest National Laboratory

Indium Selenide (In_2Se_3) is an interesting material in the Chalcogenide family and has long been studied owing to its applications in Photovoltaics, optical waveguides and as battery material among others. It has recently garnered even more attention since being demonstrated as a viable phase change memory material with properties that could better GST. Device applications such as these require a film growth technique that is fast, has a high throughput along with the ability to make the desired composition relatively easily. Pulsed Laser deposition is one method that meets all the above criteria and it has also been widely used for making combinatorial samples and thus any optimization study could be done faster. In this work, we report the thin film growth of In_2Se_3 by Pulsed laser deposition. Here film deposition was carried out using a 355 nm Nd:YAG laser with a short 5ns pulse width, operating at 20 Hz. Films were subsequently characterized by X-ray diffraction, X-ray photoelectron spectroscopy and Scanning electron microscopy. Both single-phase VOSF and layered In_2Se_3 have been obtained exclusively by controlling the deposition conditions and post deposition in-vacuo annealing. The deposited films were found to be uniform and highly oriented along the c-axis. Film stoichiometry and thickness were evaluated by Rutherford Back Scattering and are in accordance with the formula unit and compare well with those obtained from vapor deposited films. Out of plane conductivity measurements were carried out with films deposited on TiN/Si and showed a large difference in conductivity between the amorphous and VOSF phases thereby supporting the use of PLD for growing thin films for Phase Change memory device applications.

8:40am **TF-ThM3 Electrical Conductivity and Thermopower of Ti_nO_{2n-1} Thin Films grown by Pulsed Laser Deposition**, ***N. Nguyen***, University of Washington, *A. Yamamoto,* Advanced Industrial Science and Technology Institute, Japan, *T. Chikyow,* National Institute for Materials Science, Japan, *F.S. Ohuchi*, University of Washington

Reduced titanium dioxide (TiO_2) in thin film forms are investigated as a new class of oxide materials for thermoelectric applications. Deposition of thin films was carried out at temperature of 800 °C and oxygen partial pressure of 10^{-7} torr on both $SrTiO_3$ (001) and $LaAlO_3$ (001) substrates by pulsed laser deposition (PLD). Initial X-ray diffraction characterizations indicate that thin films are crystallized into a mixture of polycrystalline and texture Magneli phases, Ti_nO_{2n-1} where n = 4, 5, 6… Electrical conductivity (Σ) and Thermopower (S) of the samples were measured over a temperature range from 10 K to 500 K, from which power factors ($S^2\sigma$) were evaluated as a function of temperature. It was found that Ti_nO_{2n-1} thin films deposited on $SrTiO_3$ yielded unusually large power factors, at room temperature and bellow. These values were at least several times larger than those found on Ti_nO_{2n-1} films deposited on $LaAlO_3$ and typical bulk thermoelectric materials such as $Na_xCo_2O_4$ and Bi_2Te_3 at room temperature, and by an order magnitude around T~100K. In addition, the thermopower from thin films deposited on $SrTiO_3$ exhibits large deviation from a small polaron hopping transport mechanism, suggesting that interface defects in a form of oxygen vacancies introduced during PLD play an important role in thermoelectric transport process.

9:00am **TF-ThM4 Effects of Pulsed Laser Deposition Conditions on the Growth of Ge Quantum Dot on Si(100)-(2x1)**, ***A. Er***, *H. Elsayed-Ali*, Old Dominion University

The growth of Ge quantum dots (QD) by pulsed laser deposition of Ge on Si(100)-(2x1) is studied. The samples were first cleaned by using modified Shiraki and IMEC methods and then transferred into the deposition chamber. The vacuum system was then pumped down, baked for at least 12 hours, and the sample was then flashed to 1100 °C in order for the 2´1 reconstruction to form. The experiment was conducted under a pressure ~1x10-9 torr. A Q-switched Nd:YAG laser (wavelength l = 1064 nm) with 10 Hz repetition rate was used to ablate a Ge target. Different substrate temperatures and ablation laser energy densities were used and were shown to affect the quantum dot morphology. In-situ RHEED and ex-situ STM and AFM were used to study the morphology of the grown QD. During deposition, the RHEED patterns changed from elongated streaks to spots. As we increased the ablation laser energy density or the substrate temperature, formation of RHEED spots occurred at less coverage. AFM scans show that the number of clusters and coverage ratio increases with the ablation laser energy density, while the average area of clusters decreases. As we increased the substrate temperature from 400±20 to 500±20 oC, the Ge QD morphology changed from the asymmetric hut shape to the symmetric dome shape. Also, a decrease in the number of clusters and coverage ratio was observed.

9:20am **TF-ThM5 Unique Initial Growth Mode for Rare-Earth Group-V Nanocrystals on III-V Semiconductors**, ***S.G. Choi***, *Y. Yan,* National Renewable Energy Laboratory, *B.D. Schultz,* International Technology Center, *C.J. Palmstrom*, University of California, Santa Barbara

Incorporation of rare-earth group-V (RE-V) compounds into III-V semiconductors has generated considerable interests as a result of their potential applications in thermodynamically stable metallic contacts to III-V semiconductors and metal-based novel electronic devices. It has recently been demonstrated that RE-V's in a nanocrystal (NC) form embedded in III-V semiconductor matrix can extend their applications to advanced photonic devices and high-efficiency thermoelectric devices.[1,2] High device performance relies upon the synthesis of heterostructures in a controlled manner, and therefore a good understanding of the structure for the growth front is of great importance. Even though early growth studies have shown that the formation of RE-V's on III-V semiconductors is not associated with any of the typical growth modes, details of their unique growth nature were not discussed until recently.[3,4] Our in-situ surface studies on ErAs/GaAs[3] and ErSb/GaSb[4] systems suggest that the incoming Er atoms displace the Ga atoms in the substrate and form ErAs and ErSb nanocrystals "within" the substrate surface rather than on top. After 3 – 4 monolayers deposition, RE-V NCs form a continuous layer and then grow via "layer-by-layer" modes for the remaining growth. We have used cross-sectional high-resolution High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) to study the ErSb NC formation as a result of 1 monolayer ErSb deposition on molecular beam epitaxially grown GaSb(001) surfaces. The HAADF-STEM studies clearly show the formation of ErSb NCs "within" the GaSb substrate surface consistent with the in-situ surface science studies and the embedded growth model.[3,4] In this presentation, we will correlate ex-situ cross-sectional HAADF-STEM results with in-situ reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoemission spectroscopy, and scanning tunneling microscopy studies to determine the unique formation mechanism involved during the growth of ErAs and ErSb NCs in III-V semiconductors. This work was supported in part by ARO and NSF-MRSEC. This abstract is subject to government rights.

[1] W. Kim, Phys. Rev. Lett. (2006).

[2] M.P. Hanson, Appl. Phys. Lett. (2004).

[3] B.D. Schultz, Phys. Rev. B (2006).

[4] B.D. Schultz, Appl. Phys. Lett. (2006).

9:40am **TF-ThM6 Growth and Characterization of Cuprous Oxide Nanoclusters on Strontium Titanate (100) Surface**, ***S.V.N.T. Kuchibhatla***, Pacific Northwest National Laboratory, *Z.Q. Yu*, Nanjing Normal University, China, *S. Thevuthasan, P. Nachimuthu, V. Shutthanandan, C.M. Wang, Y. Li, C.H. Henager, Jr., S.K. Sundaram*, Pacific Northwest National Laboratory

Growth of electronic materials as single crystals for a variety of uses can be limited by the lack of fundamental understanding of the nucleation, growth, and coalescence regime at the initial stages of the growth process. As a first step in comprehensively developing a knowledge database on the nucleation and growth of various materials, we have investigated the growth of cuprous oxide (Cu_2O) nanoclusters on $SrTiO_3$(100) substrate. There has been considerable interest in Cu_2O nanoclusters because they can be used effectively in chemical and photochemical applications due to their unique electronic transport properties. We have grown Cu_2O clusters using oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and the effects of deposition rate, substrate temperature, oxygen pressure, and deposition time were systematically studied. Structural, morphological, and chemical properties of these clusters were investigated using several surface and bulk interrogation methods. X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) measurements clearly demonstrated the complex nature of the copper oxide system due to the possibility of co-existing Cu(0), Cu(1), and Cu(2) phases in the clusters. Optimum deposition conditions were established to produce pure Cu_2O clusters. Atomic force microscopy (AFM) images clearly showed the growth of uniformly distributed epitaxial, faceted pure Cu_2O clusters on STO (100) with (100) orientation. Rutherford backscattering spectrometry (RBS) measurements have been used along with the AFM and transmission electron microscopy (TEM) measurements to compute the thickness of the films. The cluster size, shape and their preferred orientation were critically analyzed. It is observed that the surface morphology, cluster coalescence, and film formation are highly dependent on various growth parameters including growth rate, deposition temperature, and deposition time. Theoretical investigations have also been carried out to understand growth mechanisms and these results will be presented along with the experimental observations.

10:40am **TF-ThM9 Low Temperature Growth of High-Quality Indium Nitride on Si(100) by Femtosecond Pulsed Laser Deposition**, ***M.A. Hafez***, *H. Elsayed-Ali*, Old Dominion University

The growth and structural properties of indium nitride (InN) grown on Si(100) substrates by femtosecond pulsed laser deposition (fsPLD) are studied. Deposition InN on Si(100) is performed with an amplified Ti:sapphire laser (130 fs) at wavelength of 800 nm. Laser induced gas breakdown-assisted PLD is used to generate reactive nitridation from ammonia. Prior to InN growth, an intermediate two-dimensional layers of indium on Si(100) surface at substrate temperature of ~70 ^{o}C is performed by fsPLD under ultrahigh vacuum (low 10^{-9} Torr). In situ reflection high-energy electron diffraction (RHEED) is used during the deposition to monitor the structure and morphology of the film growth. The InN films are prepared at room temperature to a substrate temperature of ~350 ^{o}C. The grown films are examined by ex situ atomic force microscopy, scanning electron microscopy, and x-ray diffraction (XRD). RHEED and XRD analysis showed high-quality InN films grown on Si(100). The quality and structural properties of the InN films are improved by employing a low-temperature buffer layer and by the nitridation process. RHEED observation showed that InN grew on Si(100)-(2x1) surface by the Stranski-Krastanov mode. The growth mode and morphology of the InN films is influenced by the surface condition of Si(100) substrate. The kinetic effect of the PLD has a main rule in improving the initial layers and the formation of InN. The obtained results demonstrate the potential of the growth procedure for deposition of high quality InN epitaxial layers by fsPLD at reduced temperatures.

11:00am **TF-ThM10 Thin Films by Metal-Organic Precursor Plasma Spray**, ***D.L. Schulz***, *R.A. Sailer*, North Dakota State University, *J. Leach, R. Molz*, Sulzer Metco (US)

While most plasma spray routes to coatings utilize solids as the precursor feedstock, metal-organic precursor plasma spray (MOPPS) is an area that we have investigated recently as a novel route to thin film materials. Very thin films are possible via MOPPS and the technology offers the possibility of forming graded structures by metering the liquid feed. To date, liquid-based precursor plasma spray efforts have utilized solutions of metal salts or dispersed colloidal particles with a limitation of these approaches related to the fact that most of the plasma energy is expended toward evaporation/combustion of the solvent which starves this process of the energy required to promote film formation. The current work employs metal-organic compounds that are liquids at standard temperature-pressure conditions. In addition, these complexes contain chemical functionality that allows straightforward thermolytic transformation to targeted phases of interest. Toward that end, aluminum sec-butoxide (Al(OBu)3) and aluminum 3,5-heptanedionate (Al(hd)3) were used as precursors to alumina while triethylsilane (HSi(C2H5)3) and titanium tetrakisdiethylamide (Ti(N(C2H5)2)4) were employed for studies toward silicon carbide and titanium-nitride-carbide. In all instances, the precursors contain metal-heteroatom bonds envisioned to provide atomic concentrations of the appropriate reagents at the film growth surface thus promoting phase formation (e.g., Si-C bond in triethylsilane, Ti-N bond in titanium amide, etc.). Films were deposited using a Sulzer Metco Triplex Pro-200 Plasma Spray system under various experimental conditions using Design of Experiment (DoE) principles. The composition and morphology of these films was studied as a function of application conditions. Film compositions were analyzed by glancing incidence x-ray diffraction (GXRD) and elemental determination by x-ray spectroscopy (EDS). Silicon carbide and titanium-nitride-carbide films typically exhibited a continuous morphology with reasonable adhesion (i.e., passed tape pull adhesion test) while aluminum oxide films ranged from powdery to continuous but suffered from poor adhesion.

11:20am **TF-ThM11 Dependence of Fiber Texture on Composition in Au-SiO_2 Composite Thin Films**, ***D.I. Filoti***, *A.M. Brown, D. Carlson, J.M.E. Harper*, University of New Hampshire

We show that the evolution of metal fiber texture in sputtered metal-insulator composite thin films depends strongly on the composition through the presence of second-phase particles that interrupt normal metal grain growth. Using x-ray diffraction pole figures, we measured the strength of the Au(111) fiber texture as a function of composition in the Au-SiO_2 system, which phase segregates during deposition. For very low SiO_2 volume fractions less than 0.05, the Au has low resistivity and a strong (111) fiber texture similar to that of pure Au. For higher SiO_2 volume fractions up to 0.3, the strength of the fiber texture decreases rapidly with increasing volume fraction of SiO_2 second-phase particles, and the resistivity increases. For SiO_2 volume fractions greater than 0.3, the fiber texture is lost as the Au becomes discontinuous and the microstructure changes to randomly oriented Au islands within an insulating matrix of SiO_2, confirmed by resistivity and transmission electron microscopy measurements. We show that the rapid decrease in Au(111) fiber texture strength correlates with a reduction in Au grain size caused by Zener pinning of Au grains by second-phase SiO_2 particles. Grain boundary pinning by second-phase particles prevents the development of (111) fiber texture that usually occurs during normal grain growth. The result is a more rapid loss of fiber texture as a function of composition than can be explained only by the decreasing Au volume fraction.

11:40am **TF-ThM12 Phase Transformation Behaviors of SiO_2 Doped $Ge_2Sb_2Te_5$ Films for Application in Phase Change Random Access Memory**, ***S.W. Ryu***, *J.H. Lee, Y.B. Ahn, C.S. Hwang, H.J. Kim*, Seoul National University, South Korea

Phase change random access memory (PCRAM) has attracted a great interest because it satisfies various demands for nonvolatile memory devices.[1-3] PCRAM uses the reversible phase change between the crystalline and amorphous states of chalcogenide materials, such as $Ge_2Sb_2Te_5$ (GST), brought about by Joule heating. However, the high level of I_{res} has been the major obstacle to the further scaling of PCRAM because of the limited on-current drive capability of the cell transistor (<0.5 mA/µmm). There have been several reports on the improvement of the switching performance of GST achieved by doping it with various impurities, such as N,[4] O,[5] Si,[6] or SiO_2.[7] In the case of SiO_2 doped GST (S-GST), it was reported that the reset current is reduced by approximately 50% compared to that of undoped GST. [12] The improvement in the phase change characteristics of GST films was investigated by doping the GST films with SiO_2 using cosputtering at room temperature. As the sputtering power of SiO_2 increased from 0 to 150 W, the activation energy for crystallization increased from 2.1±0.2 to 3.1±0.15 eV. SiO_2 inhibited the crystallization of the amorphous GST films, which improved the long term stability of the amorphous phase. The melting point decreased with increasing concentration of SiO_2,which reduced the power consumption as well as the reset current.

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Tribology Focus Topic
Room: 205 - Session TR+SE+TF-ThM

Advances in Surface Engineering for Friction and Wear Control
Moderator: K.J. Wahl, U.S. Naval Research Laboratory

8:00am **TR+SE+TF-ThM1 Evaluation of Ti-In-N Films for Tribological Applications**, ***J.E. Krzanowski***, *M. Nowicki*, University of New Hampshire

Titanium nitride and indium have both found applications as tribological coatings. While TiN is used primarily for its high hardness and wear resistance, indium can be used as a solid lubricant layer. In this study, we have examined the concept of using co-deposited TiN-In films for tribological applications. Ti-In-N films have been deposited by RF co-sputtering of Ti and In in a nitrogen/argon atmosphere. By varying the power to the Ti and In sources, the In/Ti ratio in the film was varied. Films were deposited at DC substrate bias levels of -50V and -150V. In both cases, as the In/Ti power ratio was increased, the indium content increased, but in a highly non-linear manner. At lower power ratios, the films had a cubic TiN structure, but as the power ratio increased, there was an abrupt transition to a hexagonal structure. Near the transition point, the films could also be amorphous, depending on film thickness, and thicker films were more likely to be crystalline. Below the transition point, the film composition depended strongly on substrate bias, and films deposited at -150V bias exhibited significantly reduced indium contents. Tribolgical tests were conducted using a pin-on-disk test with an alumina counterface. Most films showed shorter wear lives compared to TiN alone. The friction coefficients were found to depend on the In content in the films, and it was also found that heating films for short times in the range of 100-250C reduced friction coefficients.

8:20am **TR+SE+TF-ThM2 Nanostructured Sulfur Doped CHx-TiB2 Coatings for Improved Mechnical and Friction Performance**, ***B. Zhao***, *Y.W. Chung*, Northwestern University

Hydrogenated amorphous carbon films are known to attain ultra-low friction performance only in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films results in ultra-low friction performance in both dry and humid environments. However, these films have a hardness of 7 - 10 GPa and an elastic modulus around 80 GPa, which are too low for some high stress applications. Formation of nanostructured coatings is known to improve hardness. With the aim to produce hard, low-friction coatings, we synthesized nanolayered and nanocomposite films of sulfur-doped hydrogenated carbon and titanium diboride using dual-target magnetron sputtering. Titanium diboride deposited by this method had a hardness >30 GPa. This paper will discuss the film structure and how such structure correlates with its tribological and mechanical properties.

8:40am **TR+SE+TF-ThM3 Latest Developments on the Family of C-alloyed TMD Self-lubricating Coatings**, ***A. Cavaleiro***, SEG-CEMUC - University of Coimbra, Portugal, *T. Polcar*, CTU Prague, Czech Republik, *M. Evaristo*, SEG-CEMUC - University of Coimbra, Portugal **INVITED**

Due to their layered structure and weak inter-layer bonding, transition metal dichalcogenides (TMD) exhibit very interesting physical and tribological properties. Among different TMD families (TmS2, TmSe2 and TmTe2, with Tm = Mo, W, Nb) MoS2 and WS2 have been the most intensively studied in last decades. They are now currently used either as oil additives or as thin self-lubricating coatings. The industrial applicability of these coatings is still very limited owing to their two main drawbacks: (1) the loss of the tribological performance in humidity-containing environments and, (2) the low load bearing capacity. Several solutions have been proposed to overcome these problems as, for example, alloying TMD coatings with other elements or compounds, such as C, Ti, Pb, and TiN. The concept of coatings based on TMDs alloyed with carbon was introduced in the 90´s and was based on the expected synergy between the excellent frictional behavior of TMD in vacuum/dry air and the tribological performance of C-based materials. Improved frictional performance of the W-S-C coatings could be achieved when the coatings were tested by environmental cycling from dry to humid air (FC - friction coefficient from 0.02 to 0.15). Successive changes in the sliding mechanisms based on the modification of the contact layers were assigned as responsible for this behaviour. The TMD+C solution was adopted by the authors for their research by studying its extension to other TMD-C systems. The aim of this talk was to present the latest developments achieved within TMD-C magnetron sputtering deposited coatings concerning di-selenides (Mo-Se-C and W-Se-C). Lower friction coefficient was achieved in comparison to previous deposited W-S-C coatings, particularly in humid air. FC was possible to be kept lower than 0.05 in all testing conditions. Tests were performed with contact stress as high as 1.5 GPa without destruction of the coating. The frictional and wear mechanisms under different operating conditions were studied by nanoscale analysis of the wear tracks. The tribological performance, whatever the testing conditions, was attributed to the formation of a thin tribolayer consisting exclusively of TMD platelets with the (002) plans oriented parallel to the sliding motion. C is removed from the contact area during the re-orientaion process, only playing a secondary role by increasing the coatings density, avoiding surface oxidation and improving the loading bearing capacity.

9:20am **TR+SE+TF-ThM5 Reduction in Friction and Micropitting by Coatings and Lubricants Containing Inorganic Fullerenes**, ***S.J. Bull***, *A. Oila*, Newcastle University, UK

Improvement in component performance by reduction in friction and wear has been the focus of considerable research over the last forty years. As products become more highly engineered and component size is reduced the significance of friction and wear is increased, particularly in terms of improvements in energy efficiency, and the need to develop materials with improved triboloigcal performance becomes critical. Nanostructured materials are one way whereby this might be achieved. Recent work has focussed on the development and assessment of nanomaterials and composites for triboloigcal performance. In particular, the use of inorganic fullerene-like materials in the form of coatings and nanoparticles (and as the reinforcement for nanocomposites) has shown a lot of promise for tribological applications. This talk will highlight the use of inorganic fullerene nanoparticles as additives for lubricating oils or coatings to achieve a significant increase in the operational life of rolling/sliding components such as gears.

9:40am **TR+SE+TF-ThM6 Tribology of Carbon Films in Hydrogen and Deuterium Gas Environments**, *A. Erdemir*, ***O.L. Eryilmaz***, Argonne National Laboratory

Recent systematic studies in our laboratory have shown that certain diamond-like carbon (DLC) films are able to achieve superlow friction and wear when tested in hydrogen-containing test environments. In the presence of deuterium, we were also able to achieve very low friction and wear on these films. In this study, we used a combination of controlled-environment atmospheric pressure and vacuum tribometers to further verify the critical effects of hydrogen and deuterium on friction and wear of such films; then we used imaging SIMS and XPS methods to ascertain the near surface chemistry of their sliding surfaces. The combined results of tribological tests and surface analytical studies revealed that there exist a close correlation between the chemical nature of sliding DLC surfaces and their friction and wear behaviour. Specifically, we found that in the presence of both hydrogen and deuterium, the sliding contact areas of carbon films were covered by a hydrogen and deuterium film (only a few Å thick). The wear rates and friction coefficients are much higher if tests were run in dry nitrogen or vacuum than in hydrogen and deuterium. Overall, we show that superlow friction behaviour of certain DLC films is largely controlled by gas-surface interactions.

10:40am **TR+SE+TF-ThM9 Tribomaterials for Spacecraft: Testing & Surface Chemistry**, ***J.R. Lince***, The Aerospace Corporation **INVITED**

The spacecraft environment is challenging for tribocoatings and lubricants used in devices in satellites and launch vehicles. Areas of concern include vibration during launch, thermal cycling on orbit, and the need to work effectively for missions up to twenty years in duration without lubricant replenishment. Especially challenging is the need for tribomaterials to withstand the vacuum of space during lengthy missions. Spacecraft tribomaterials must exhibit low vapor pressures, since evaporation of lubricants can result in loss from and premature failure of devices, as well as contamination of sensitive spacecraft components. A relatively small set of liquid lubricants meet the vapor pressure requirement – while also meeting performance requirements for current spacecraft applications – including synthetic hydrocarbons and perfluorinated polyalkylethers. Soft solid lubricants such as molybdenum disulfide (MoS_2) and polytetrafluoroethylene (PTFE) have been used traditionally. More recently, hard low friction coatings such as hydrogenated diamond-like carbon have shown promise for operation in vacuum with existing spacecraft lubricants, or even unlubricated operation in vacuum. These solid- and liquid-based tribomaterials show performance in vacuum that differs with that in air, nitrogen, or even with small partial pressures of oxygen and water. This is especially important for spacecraft hardware, because it is often prohibitive to test them in a space-like environment, including vacuum, before launch. As such, differences between non-vacuum and vacuum testing need to be understood in order to predict how lubricated devices will perform in space. This talk will focus on a series of recent studies done at The Aerospace Corporation that elucidate the effects of vacuum and other environments on the tribological performance of several important spacecraft tribomaterials. The emphasis will be on how varying environments affect the surface chemistry of the materials.

11:20am **TR+SE+TF-ThM11 Nano-Smooth Diamond Coatings on Various Alloys for Ultralow Friction in the Presence of OH-Containing Lubricants**, ***T. Gries***, CNRS - ICARE, France, *C. Matta, M.I. De Barros Bouchet, B. Vacher,* Ecole Centrale de Lyon, France, *S. de Persis,* ICARE - CNRS, France, *L. Vandenbulcke*, CNRS, France

Titanium alloys and titanium-coated alloys are important materials for aerospace, mechanical, chemical and biomedical applications; however their applications could be extended by improving their tribological behaviour. This can be done by using diamond-based coatings which are outstanding materials for changing their surface properties. We have shown that nano-smooth fine-grained diamond coatings could be deposited on these alloys at moderate temperature, equal to or lower than 600°C, from CH_4-CO_2 species. They are in fact duplex coatings with an external diamond film, a titanium carbide sub-layer and a diffusion solid-solution. These coatings exhibit particularly strong adherence with the substrates as shown by various mechanical tests and very high induced stresses without peeling off. They are first described in terms of sp^2-hybridized carbon contents relatively to the sp^3-carbon ones, a parameter which influences the structure and the intrinsic diamond properties (surface roughness in the 15-35 nm range, micro-hardness, Young's modulus and residual stresses). The whole is correlated to the plasma enhanced CVD process through the formation of different concentrations of the gaseous precursors in the plasma which include both radicals and stable species as revealed by molecular beam mass spectrometry and corroborated by kinetic calculations in the C-H-O plasmas. These coatings are studied by micro-Raman spectroscopy and their structure is revealed by TEM studies. A sp^2-C enriched layer is especially evidenced at their extreme surface by Energy-Filtered TEM on transverse cross-sections, a layer which is important for tribochemical reactions. While the friction coefficient is high under ultra high vacuum, ultra low friction is obtained in saline corrosive solution. Ultra low friction with no wear is also obtained with gas phase lubrication by glycerol under boundary lubrication regime, in conditions which permit a better identification of the friction mechanism from advanced surface characterizations. These studies allow concluding that lubrication of these diamond coatings by OH-containing molecules can permit new or improved applications in various fields. Some examples of ultra low friction and low wear are provided when nano-smooth diamond coatings or alumina are sliding on nano-smooth diamond in corrosive saline solution or in the presence of glycerol lubricant, a model of environmentally friendly molecules.

11:40am **TR+SE+TF-ThM12 Tribology of Nanocrystalline Diamond Coatings**, ***N.D. Theodore,*** North Carolina State University, *K.J. Wahl*, Naval Research Laboratory

The tribological behavior of several nanocrystalline diamond (NCD) coatings was compared to correlate compositional, structural, and chemical bonding differences to their friction performance. The diamond coatings were confirmed by X-ray diffraction (XRD) to be nanocrystalline with crystallite sizes ranging from to 4 to 60 nm. These diamond coatings could be differentiated from each other by their visible wavelength Raman absorption bands. Some coatings had a single strong peak at 1332 cm^{-1} typical of crystalline diamond bonding; others also had broad peaks at 1340 cm^{-1} and 1580 cm^{-1} characteristic of the D and G peaks in sp^2 hybridized carbon; and still others had additional peaks at 1135 cm^{-1} and 1470 cm^{-1}, which are commonly attributed to polyacetylene bonding. Reciprocating sliding tests using diamond counterfaces in controlled humidity environments resulted in low friction values for all coatings, between 0.02 and 0.09. The coatings exhibiting lower friction values possessed lower mean surface roughnesses, as measured using an atomic force microscope (AFM), smaller crystallite sizes, and increased amounts of non-sp^3 carbon content. Transmission Fourier transform infrared (FTIR) microscopy was used to examine the bonding chemistry in the coatings and wear tracks. The role of diamond coating microstructure, surface roughness, and bonding chemistry to the tribological behavior of NCD will be presented.

Biomaterial Interfaces
Room: 202 - Session BI+TF+MI+NS+NC-ThA

Plasmonics and Magneto/Plasmonics Aimed at Biosensing
Moderator: F. Höök, Chalmers University of Technology, Sweden

2:00pm **BI+TF+MI+NS+NC-ThA1 Optical Meta Materials and Nano Plasmonics*, X. Zhang***, University of California, Berkeley **INVITED**

Recent theory predicted a new class of meta structures made of engineered sub wavelength entities - meta "atoms" and "molecules" which enable the unprecedented electromagnetic properties that do not exist in the nature. For example, artificial plasma and artificial magnetism, and super lens that focuses far below the diffraction limit. The metamaterials may have profound impact in wide range of applications such as nano-scale imaging, nanolithography, and integrated nano photonics. I'll discuss a few experiments that demonstrated these intriguing phenomena. We showed, for the first time, the high frequency magnetic activity at THz generated by artificially structured "meta molecule resonance", as well as the artificial plasma. Our experiment also confirmed the key proposition of super lens theory by using surface plasmon. We indeed observed optical superlensing which breaks down so called diffraction limit. I'll also discuss nano plasmonics for imaging and bio-sensing. The surface plasmon indeed promises an exciting engineering paradigm of "x-ray wavelength at optical frequency".

2:40pm **BI+TF+MI+NS+NC-ThA3 Gold and Silver Nanocrescents as Tunable Substrates for Surface Enhanced Infrared Absorption Spectroscopy**, *R. Bukasov, **J.S. Shumaker-Parry***, University of Utah

Controlling the size, shape, and orientation of metal nanoparticles in order to tune and optimize the particles' optical properties for specific applications remains a challenge in the field of plasmonics. Tuning the localized surface plasmon resonance (LSPR) wavelength as well as the localized field enhancements is especially important for spectroscopy applications such as surface enhanced Raman spectroscopy (SERS) and surface enhanced infrared absorption spectroscopy (SEIRA). Although SERS has receive a lot of attention with the engineering of nanoparticle-based substrates, the activity in SEIRA development has been less, most likely due to the lack of tunable substrates for the IR spectral region. We describe the development of gold and silver nanocrescents as tunable substrates for SEIRA studies. We use nanosphere template lithography to fabricate gold and silver crescent-shaped structures which exhibit multiple, polarization-sensitive plasmon resonances that are tunable from the visible through the infrared. Large electromagnetic field enhancements are expected due to the sharpness of the crescent's tips and the ability to bring these sharp tips into close proximity to each other. Using the crescent-shaped structures as substrates, we demonstrate the importance of spectral tunability for maximizing signal enhancements in SEIRA. The nanocrescent area normalized SEIRA signal enhancement increases from 7,700 to 46,000 with an increase in the extent of overlap of the nanocrescents' LSPR frequency with the frequency of the probed molecular vibration. The broad tunability of the nanocrescents' LSPR properties makes the structures excellent candidates for a range of spectroscopic and sensing applications including SEIRA.

3:00pm **BI+TF+MI+NS+NC-ThA4 Use of Angle-Resolved SPRi for the Characterization of Protein Binding and Agglomeration Dynamics**, ***M.S. Golden**, J.A. Ruemmele, A. Whitty, R.M. Georgiadis*, Boston University

Transient protein-protein interactions are essential on almost every level of cellular function. In addition, protein aggregates play various roles in cell signaling pathways and have been implicated in the onset of many neurodegenerative conditions such as Alzheimer's disease. Although various structures of protein complexes have been widely studied, the mechanisms involved in protein binding events are not clearly understood, and the transient dynamics of this formation have proven difficult to study. Investigation of the mechanisms of protein agglomeration and binding, however, is essential to elucidating the role of these structures in diseases. Here we exploit the multi-array quantitative capabilities of angle-resolved surface plasmon resonance imaging (SPRi) to perform kinetic and thermodynamic measurements of protein-protein interactions. Specifically, the agglomeration and small molecule inhibition of Tumor Necrosis Factor (TNF) family members whose primary role is the regulation of immune cells is under investigation. Surface fabrication techniques coupled with multi-channel microfluidic delivery will be employed in order to introduce protein binding partners and small molecules to the surface. Effects of density, orientation, and heterogeneity of surface immobilized protein molecules on protein binding efficiency and kinetics will be investigated and optimum surface fabrication conditions will be identified. In addition, a unique multi-wavelength SPRi approach will be implemented to simultaneously determine dielectric constants and thicknesses of protein layers on a surface. These studies will therefore allow aggregate and nonaggregate structures at the surface to be clearly differentiated. The results of these fundamental studies will allow a broader understanding of how proteins act cooperatively.

3:20pm **BI+TF+MI+NS+NC-ThA5 Sensitivity Enhancement of Surface Plasmon Resonance Imaging by Nanoarrayed Organothiols*, P. Lisboa***, *A. Valsesia, I. Mannelli, P. Colpo, F. Rossi*, JRC-European Commission, IHCP, Italy

The implementation of sensor platforms providing high sensitivity of detection is a crucial step for the design of the new analytical device generation for biosensor developments. Designing platform with active/non-actives region at nanoscale has shown already a drastic increase of detection sensitivity.[1,2] The use of organothiols to create nanopatterns has been already studied showing that this type of chemistry is indicated to produce chemical contrasts for bio-applications.[3] In this work, the effect of organothiols-nanopattern in Surface Plasmon Resonance imaging (SPRi) detection was studied. The gold surface of the SPRi chip was divided in two areas, one modified with a chemical nano-contrast based in two different organothiols (thiolated polyethylene oxide (PEO) and Mercaptohexadecanoic acid (MHD) and the other modified uniformly with MHD. The SPRi study was based on the detection of the immunoreaction between Human IgG and anti-Human IgG (Ab specific) by comparing the results obtained with nanostructured and uniform carboxylic surface. First Human IgG was immobilised on the chip and after the recognition of different concentrations of anti-Human IgG was realised. The achieved SPRi signal was higher in the case of the nanostructured areas for all the tested concentrations. Since the active surface with carboxylic functionalities presented only 3% of the total area, one would expect the detection signal to be 3% of the signal obtained for the uniform MHD surface. The fact that the signal from the nanostructures is higher than in the MHD surfaces in SPRi detection is related to an amplification of signal due to the 2D crystalline character of the structures. This type of arrangement presents the geometry of a photonic crystal leading to the interaction between the Surface plasmon polaritron modes and the regular modulation of the dielectric constant of the surface above the gold film modifying the plasmon effect and consequently increasing the measured reflectivity. These results indicate that SPRi detection performance can be improved by the rational functionalisation of the prism surface with 2D crystalline nanopatterns. Moreover adhesive – nonadhesive nanopatterns are recognized to be good platforms for the correct immobilization of the biomolecules on biosensing surfaces.

References

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4:00pm **BI+TF+MI+NS+NC-ThA7 New Developments in Magneto-Plasmonic Devices*, C. Clavero***, *J.R. Skuza, K. Yang, R.A. Lukaszew*, College of William and Mary **INVITED**

In recent years Surface Plasmon Resonance (SPR) sensors have been extensively used in bio-sensing applications. SPR is a charge density oscillation at the boundary between a metal and a dielectric material that gives rise to highly confined fields at the interface. As a consequence the SPR excitation condition is very sensitive to changes in refractive index in the dielectric medium and hence to bio-molecules adsorbed at the metal surface. Nevertheless, the required detection sensitivity for low concentrations of small molecules exceeds current SPR sensors. A new kind of sensors combining plasmonic and magneto-optical (MO) properties, i.e. magneto-plasmonic devices, is being actively investigated. In particular, Au-Co-Au trilayers have been found to increase sensitivity in this type of biosensors.[1] This is due to MO activity enhancement in the Co film caused by the high electro-magnetic field created by SPR.[2] We will report on Au-Co-Au thin film tri-layers grown on glass using UHV magnetron sputtering. The optimization of growth conditions and accurate control of films thickness is critical to achieve a remarkable increase in MO activity and hence in overall sensitivity. A practical issue in these multilayer systems is the bad adhesion of Au to glass causing degradation of the sensor when exposed to a water flux. We will show how to circumvent this problem by inserting Cr or Ti thin buffer layers. A different approach to magneto-plasmonic materials, namely fabrication of Au-Co nano-composite materials in thin film form, will also be presented. These materials are expected to exhibit enhanced MO response due to localized surface plasmon resonances (LSP) within the Co nano-particles and also considerable reduction of light absorption associated with ferromagnetic materials thus increasing the overall sensitivity of the bio-sensor. Parameters such as shape, size and inter-particle distance can be tuned to control the optical and magnetic properties of the material. Au-Co nano-composite materials in thin film form were obtained by magnetron sputtering co-deposition of Au and Co where parameters such as Au and Co concentration, deposition temperature and film thickness were accurately controlled. Finally, different optical configurations for the excitation of the surface plasmon resonance will be discussed.

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4:40pm **BI+TF+MI+NS+NC-ThA9 Grafting Thermoresponsive Polymers on Gold Nanoparticles with Atom Transfer Free Radical Polymerization**, ***S. Chakraborty***, *V.H. Perez-Luna*, Illinois Institute of Technology

Thermoresponsive polymer brushes on colloidal gold were formed through Atom Transfer Free Radical Polymerization (ATRP) of N-isopropylacrylamide (NIPAAM) in aqueous media. In this approach, the “grafting from” technique was used with Atom Transfer Radical Polymerization (ATRP) to grow polymer chains from the surface of gold nanoparticles (~20nm). ‘Grafting from’ using the ATRP technique enables more uniform/homogenous coverage of polymer chains on the surface of gold nanoparticles. Other advantages of ATRP are the growth of polymer chains without chain termination or chain transfer and that the presence of an active initiator site at the end of the growing polymer chain facilitates synthesis of block copolymers. In the present work, PNIPAAM was grown from the surface of nanoparticles with the help of 2-bromopropionyl bromide as the initiator. The reaction was carried out at room temperature under inert atmosphere and aqueous conditions. The system was found to exhibit thermoresponsive behavior with increase in temperature above 32oC. This behavior could be exploited to develop aggregation based assays. The hybrid polymer-gold nanoparticle system was characterized using Optical Absorption Spectroscopy, Fourier Transform Infra-Red Spectroscopy (FTIR) and Dynamic Light Scattering (DLS). These analytical techniques confirmed the growth of polymer chains in the reaction scheme yielding the final product. The ability to make block copolymers with this metal-polymer hybrid system opens up a wide range of applications such as drug delivery systems, detection assays and bioseparations.

5:00pm **BI+TF+MI+NS+NC-ThA10 Reconfigurable Core-satellite Nanoassemblies as Molecularly-Driven Plasmonic Switches**, *D.S. Sebba, J.J. Mock, D.R. Smith, T.H. LaBean*, ***A.A. Lazarides***, Duke University **INVITED**

Colloidal metal nanoparticles support localized surface plasmon resonances that are sensitive to the presence of molecules, materials, and other polarizable particles that assemble in their near fields. Biomolecule nanoparticle conjugates have been implemented in various molecular detection applications in formats that allow monitoring of plasmonic response. Each specific format has vulnerabilities as well as advantages. For instance, monolayers of immobilized particles functionalized with receptors respond sensitively to target molecules and can be used to track kinetics, but are equally sensitive to non-specific adsorbates, a disadvantage shared with traditional, thin film surface plasmon resonance (SPR). Other formats, such as target induced particle aggregation offer strong plasmon modulation, but involve a complex bulk phase process that presents a significant barrier to quantitative interpretation of the optical data. Here, we report plasmon modulation in pre-formed, few particle assemblies linked by reconfigurable DNA nanostructures. The investigation is motivated by the potential of reconfigurable few particle assemblies to provide control of plasmon coupling, and ultimately, to yield a signal that is distinguishable from plasmonic variations associated with non-specific interactions. In the coupled system upon which we report, DNA nanostructures tether satellite particles to a core particle of like or unlike composition. The DNA nanostructures use duplex DNA to control interparticle separation and are responsive to target strands that modulate interparticle helix length. The reconfigurable assemblies are characterized structurally using dynamic light scattering and transmission electron microscopy and optically using elastic scattering spectroscopy. We demonstrate that DNA nanostructures provide molecular control of interparticle separation by correlating measured plasmonic signals with simulated signals derived from models based upon measured structural parameters. In order to study the sensitivity of core-satellite spectral response to colloid material properties, single assembly scattering spectroscopy and multi-color CCD image analysis are used to monitor perturbation of the core plasmon resonance induced by assembly of satellites of various composition.

Advanced Surface Engineering
Room: 204 - Session SE+TF+NC-ThA

Glancing Angle Deposition (GLAD) II
Moderator: D. Gall, Rensselaer Polytechnic Institute

2:00pm **SE+TF+NC-ThA1 Glancing Angle Deposition at the Nano-Bio Interface**, ***Y. Zhao***, University of Georgia **INVITED**

Glancing angle deposition (GLAD) technique is a physical vapor deposition method to design three-dimensional nanostructures by programming the vapor incident angle and substrate azimuthal rotation. This method offers large area growth of aligned nanorod arrays with additional capability of self-alignment. There is almost no limitation on materials that can be fabricated into desired nanostructures. With recent advance in a multilayer deposition procedure, one can design complex and multifunctional heterogeneous nanostructures. In addition, with a co-deposition system of two or more sources, novel nanocomposites or doped nanostructure arrays can be produced, which results in nanostructures with different morphology. Here, I will highlight our recent progress in multi-component nanorod array fabrication and their potential biological applications. We find that aligned silver nanorod array substrates can be used as a high sensitive virus and bacteria sensor base on surface enhanced Raman spectroscopy (SERS) principle. This SERS based sensor can be used to detect the molecular fingerprints of several important human respiratory viruses including respiratory syncytial virus, rhinovirus, adenovirus, human immunodeficiency virus, influenza virus, and bacteria, with high sensitivity and selectivity, and to discriminate between different virus/bacterium strains. Using a unique multilayer deposition configuration, catalytically driven nanomotors have been fabricated and demonstrated, which can directly convert chemical energy into mechanical energy. This device holds a great potential to mimic smart biological systems via hybrid organic-inorganic nanostructures.

This work was supported by NSF, NIH, and ARL.

2:40pm **SE+TF+NC-ThA3 Growth and Characterization of Magnesium, Magnesium Alloy, and Doped TiO_x Sculptured Thin Films (STFs)**, ***S.M. Pursel***, *M.W. Horn, B.A. Shaw*, The Pennsylvania State University

Bioabsorbable materials such as magnesium, which is essential for cellular function, have recently been studied for use in heart stents, bone plates and screws, and dental and orthopedic implants. However, the use of vapor deposition to form non-equilibrium magnesium alloys has had little if any commercial interest even though certain properties of these alloys, namely corrosion resistance, can be improved. Engineering of surface morphology using dip coatings and etching has been used in biomedical materials to enhance certain application specific surface properties. Sculptured thin film (STF) technology potentially provides a path to merge the advantages of non-equilibrium alloy formation and engineering nanoscale surface morphology. We present here our results utilizing a vapor co-deposition scheme to improve nucleation and corrosion properties of magnesium alloys. By utilizing co-deposition with materials such as titanium, yttrium, zirconium, and others the growth mode of magnesium can be modified and the solid solution limit can be surpassed leading to an improvement in corrosion resistance. Characterization of the growth of magnesium alloy thin films has been done utilizing various alloying elements, substrate temperatures, post-deposition treatments, and substrate positions (to deposit STFs). The results point towards a growth mode controlled by crystallization effects that are not common in higher melting temperature materials. The results of the study are presented in terms of x-ray diffraction data, microscopy analysis of growth evolution, and corrosion testing. We will also present results that extend our work on TiO_x chiral STFs utilizing the circular Bragg phenomenon (CBP) for sensor applications. The CBP is observed in the circularly polarized transmission spectrums of chiral STFs as a stop band for co-handed light. The location and shape of this stop band is dependant on the material properties among other factors. Using an impurity material from a second source may allow added sensitivity for sensor applications while maintaining STF morphology and function.

3:00pm **SE+TF+NC-ThA4 Performance and Response Time of Nanostructured Relative Humidity Sensors**, ***M.T. Taschuk***, *J.J. Steele, M.J. Brett*, University of Alberta, Canada

Applications requiring relative humidity (RH) measurement will require differing sensitivity, range of humidity operation, and response times. These properties are determined by the properties of the sensing medium: material, porosity, surface area, pore size distribution and morphology. We have been investigating the use of glancing angle deposition (GLAD) for the fabrication of RH sensors with interdigitated electrode (IDE) substrates.[1,2] While GLAD offers some significant advantages for RH sensors, there remain a number of open questions regarding the underlying physics of GLAD RH sensor performance and response time. The response of our devices depend on the extremely large low frequency dielectric constant of water adsorbed to metal oxides, which can results in a three order of magnitude change in capacitance as RH is increased from 0 to 100%. We have recently employed an electromagnetic model with simple dielectric mixing laws to compare our device performance with literature values for dielectric constants[2]. Further work is ongoing to include structural effects in the dielectric mixing laws to improve accuracy. Response time varies with the size and nature of pores in our sensors, which in turn relies on column properties such as diameter and surface roughness. Experimental values for response time of the GLAD RH sensors have been reported, but a neither a model nor thorough study of response time as a function of deposition angle and film thickness has been presented. Constructing a model for our devices requires an understanding of the diffusivity of GLAD films, the interaction between water vapour and TiO2, and the electromagnetic behaviour of IDE devices. In this paper we characterize the performance and response time of GLAD RH sensors as a function of film thickness and deposition angle. The microstructure column radius as a function of film thickness and deposition angle is investigated. A 1D numerical model describing response time of our devices is developed, which includes diffusion, adsorption and IDE physics. The modeling results are compared with our experimental data, and demonstrates that response time of our sensors is dominated by adsorption.

[1] J.J. Steele, G.A. Fitzpatrick, and M.J. Brett. IEEE Sensors Journal, Vol. 7:955 – 956, 2007.

[2] J.J. Steele, M.T. Taschuk, and M.J. Brett. IEEE Sensors Journal, (In Press), 2008.

3:20pm **SE+TF+NC-ThA5 Patterned Ag Nanorod Arrays as SERS Substrates by Template Mediated Oblique Angle Deposition**, ***Y. Liu****, Z. Zhang, Y. Zhao*, University of Georgia

Surface enhanced Raman scattering (SERS) is widely used in the analytical, biomedical, clinical, environmental, and security applications. The practical application of a SERS-based sensor requires an efficiency SERS substrate which can not only provide a high enhancement factor, but also be uniform, stable and reproducible. In this work, a highly ordered, uniform and periodic patterned Ag nanorod arrays as SERS substrates are fabricated by combining electron beam lithography (EBL) and oblique angle deposition (OAD) techniques. Two dimensional nano Au post arrays with different separations are fabricated by EBL. There are only very weak SERS signal can be detected after the Au post arrays are treated by a 1 μL 10^{-4} M BPE (trans-1,2-bis (4-pyridyl) ethene) droplet. However, after a layer of ~ 400 nm Ag nanorods are deposited on those BPE treated Au post array, strong SERS signals have been obtained. Furthermore, the SERS intensities become more than 8 times stronger, after the Ag arrays are further treated by a droplet of 1μL 10^{-5} M BPE. These results demonstrate that most SERS signals could come from the molecules adsorbed on the side surfaces of the Ag nanorods, rather than the ends. The SERS signal is also strongly dependent on the separation of the Au posts. A numerical calculation on the electric field enhancement has been carried out to confirm this result.

4:00pm **SE+TF+NC-ThA7 Quantification of Porosity and Deposition Rate of Nano-Porous Films Grown by Oblique Angle Deposition**, ***D.J. Poxson****, F.W. Mont, M.F. Schubert, J.K. Kim, E.F. Schubert*, Rensselaer Polytechnic Institute

We propose analytic formulas accurately predicting the refractive index and film thickness of obliquely deposited thin films for a given incident angle. Recently, it was shown that accurate control of the refractive index of physical-vapor deposited thin film materials can be achieved through the use of oblique-angle deposition. Refractive index tunability and low refractive index (low-n) films are highly desirable for a variety of optical applications. For example, broadband antireflection coatings, omni-directional reflectors, distributed Bragg reflectors, optical micro-resonators, light-emitting diodes, photovoltaic solar cells, and optical interconnects. While the qualitative tenets of oblique-angle deposition were demonstrated over a century ago, no quantitative formulas for the porosity and deposition rate have been described in the literature. In this work, we propose a model relating the porosity and deposition rate of a material to its vapor flux incidence angle for oblique-angle deposition. Our model is based upon geometrical arguments, employs a single fitting parameter, and takes into account surface diffusion. We have measured the refractive index and thickness for SiO_2 and indium tin oxide (ITO) nano-porous films deposited over a wide range of deposition angles ($0° < \theta < 90°$). The porosity of a material is determined from the measured refractive index. Comparison of experimental SiO_2 and ITO porosity values and deposition rates with theory reveals excellent agreement. The theoretical model allows for the predictive control of refractive index, porosity, and deposition rate for all deposition angles, potentially a very useful tool in the development of high quality low-n optical coatings. Furthermore, given the set of basic assumptions used, we expect these formulas to be valid for a wide range of materials.

4:20pm **SE+TF+NC-ThA8 Sculptured Thin Films from Aluminum**, ***E.B. Schubert****, T. Hofmann, D. Schmidt, M.M. Schubert*, University of Nebraska-Lincoln

Three-dimensional (3D) structure design of chiral materials on the nanoscale is a current demand in modern material science and engineering and various intriguing applications are foreseen for example in the fields of optics, electromechanics or electromagnetic. Glancing angle deposition is a method which allows for "bottom-up" fabrication of 3D shaped and tailored chiral nanostructures arranged in sculptured thin films (STF). We will present an investigation of the growth of STF's from aluminum on highly p-type doped silicon substrates by using either ion beam sputtering or electron beam evaporation. Various growth schemes have been used to obtain films with different nanostructure shapes such as posts, plates, screws or spirals. The films have been characterized regarding their optical and electrical properties by means of 4x4 Mueller-Matrix ellipsometry, IR spectroscopic ellipsometry and electrical measurements. Whereas Mueller-Matrix Ellipsometry reveals an optical response which can be related to the symmetry of the three-dimensional nanostructures,[1] the IR data give hint to electron or lattice absorptions. We found that the IR optical response depends on the shape of the nanostructures. STF's from aluminum plates for example show a strongly metallic behavior, whereas films containing Al spirals show multiple resonances, with a periodic spectral distance of 7.2 THz between neighboring absorption features. The IR optical data for the Al nanocoils are discussed in terms of coupled inductance and capacitance pairs, where the inductance is formed from the coil itself and the depletion layer capacitance is created on the footprint of the metallic Al coil with the highly p-type doped Si substrate. A Drude-like background term, which accounts for free carriers in the aluminum nanospirals was also used during sample regression. It is found, that resistivity and free mean path of the electron depends of the shape of the Aluminum nanostructures as well. This behavior is verified by electrical measurements under dc conditions.

[1] D. Schmidt, E. Schubert, and M. Schubert, phys. stat. sol. (a) 205, 748 (2008).

4:40pm **SE+TF+NC-ThA9 Mueller Matrix Ellipsometry Studies of the Optical Properties and Structure of Serial Bi-Deposited Titanium Oxide Sculptured Thin Films**, *N.J. Podraza, S.M. Pursel,* The Pennsylvania State University, *R.W. Collins,* University of Toledo, ***M.W. Horn***, The Pennsylvania State University

In this work, titanium oxide (TiO_2) chiral sculptured thin films (STFs) are fabricated using serial bi-deposition (SBD) electron beam evaporation and studied using Mueller matrix ellipsometry (MME). Chiral STFs are of interest for a wide range of applications in optoelectronic devices such as photovoltaics, microelectronic devices, microcavities, biological sensors, and bioabsorption devices. These films can be described as assemblies of upright, parallel, helical columns. Their helicoidal morphology, being periodic, engenders the circular Bragg phenomenon: circularly polarized light couples to the helices present in the film, if the handedness of the light and the STF coincide, resulting in enhanced reflectance in the Bragg regime spectral range. TiO_2 STFs fabricated using SBD are of particular interest for fundamental studies due to its high bulk index of refraction and films prepared using this technique can be fabricated to exhibit Bragg resonances in the visible spectral range at wavelengths ~450-650 nm. Although normal incidence transmission and reflection measurements can demonstrate this behavior, it is often impossible to discern the various optical and structural properties of optically anisotropic materials like STFs. MME, however, allows us to extract each of the principal indices of refraction (n_x, n_y, n_z) as well as the microstructural parameters such as film thickness and the initial polar and in-plane orientation of the helices. The complete Mueller matrices for SBD TiO_2 STFs are measured using a dual-rotating compensator spectroscopic ellipsometer over a spectral range from 250-825 nm in transmission mode at normal incidence ($\Theta_i = 0^0$) and non-normal incidence ($5 \le \Theta_i \le 55^0$). The normal incidence measurements provide the principal indices of refraction and the microstructure, while the non-normal incidence measurements allow us to monitor the blue-shift in the Bragg resonance with increasing angle of incidence. The fundamental understanding gained from MME is expected to provide assistance in further engineering and optimizing these types of materials for specific applications requiring control of the Bragg resonance feature.

5:00pm **SE+TF+NC-ThA10 Low Hydrogen Desorption Temperature of Hydrided Pd Coated Novel Mg Nanoblades**, ***F. Tang****, T. Parker, H.-F. Li, G.-C. Wang, T.-M. Lu*, Rensselaer Polytechnic Institute

We grew Mg nanoblades standing nearly vertically on the substrates by oblique angle vapor deposition. The thickness of the nanoblades along the vapor incident direction ranges from ~15 nm to ~30 nm at a vapor incident angle ~75^o, while the width perpendicular to the incident vapor direction is as wide as a few hundred nm.[1] These novel nanoblade structures have several advantages over the bulk materials for hydrogen storage: such as a large surface-area-to-mass ratio of ~60 m^2/g and ultrathin thickness (~22 nm), which will significantly enhance the kinetics of hydrogen absorption/desorption. The spacing between the nanoblades can also accommodate the large volume change (Mg ↔ MgH_2) during hydrogenation/de-hydrogenation processes. We have studied hydrogenation/de-hydrogenation properties of ultrathin Mg nanoblades coated with Pd as a catalyst, using in situ temperature desorption spectrum (TDS), ex situ scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Pd coated Mg nanoblades were hydrogenated at a pressure of 1 bar with substrate held at ~333 K for ~15 hours. The de-hydrogenation property of the hydrided Pd/Mg/Pd nanostructure was characterized in situ by TDS, which showed that the hydrided nanostructure has a low hydrogen desorption temperature at ~365 K. Through a combinational microstructure by TEM and TDS analyses of hydrided nanoblades as well as hydrided nanoblades covered with additional Mg layers, we found that the effect of Pd catalyst on reducing the hydrogen desorption temperature is significantly stronger than the conventionally proposed grain size and strain effects. The ex situ SEM images showed that the hydrided Pd/Mg/Pd and hydrided Pd/Mg (one sided Pd coating) nanoblades became highly curved. Various shapes such as circular, helical or spiral have been formed in the hydrided Pd/Mg nanoblade films. The formation of these curly structures could be related to the strain induced by the partial decomposition of MgH_2 after the sample was exposed to air. The understanding of hydrogenation/de-hydrogenation properties of Pd coated Mg nanoblades could help us in designing promising nanoscale metal hydrides for hydrogen storage with low desorption temperatures. FT was supported by the NSF award 0506738 and TP was supported by the DOE (education) GAANN P200A030054.

[1] F. Tang, T. Parker, H.-F. Li, G.-C. Wang, and T.-M. Lu, J. of Nanosci. and Nanotechnol. 7, 3239 (2007).

5:20pm **SE+TF+NC-ThA11 Improving Stiffness of Silicon Chevrons by 1.2 MeV Ar^{+8} Ion Irradiation**, ***R. Nagar***, Indian Institute of Technology Delhi, *C. Patzig, B. Rauschenbach*, Leibniz-Institute of Surface Modification Leipzig, Germany, *P. Kumar, D. Kanjilal*, Inter-University Accelerator Centre, India, *B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi

Five-armed silicon chevrons were grown by oblique angle ion beam sputter deposition on Si(111) substrates pre-patterned with 260 nm diameter silica spheres and 500 nm diameter polystyrene spheres. The patterning spheres self-assemble in hexagonal network, act as nucleation sites, and control the dimensions as well as the distance between the growing chevrons. The chevron arms are about 500 nm long, 350 nm wide and 200 nm thick with odd numbered arms making an angle of about 45° and even numbered arms an angle of about 55° from the vertical. In order to tailor the mechanical strength of the chevron coatings, the samples were irradiated with 1.2 MeV Ar^{+8} ions at liquid nitrogen temperature at different fluences of 10^{15}, 10^{16} and 10^{17} ions/cm^2. The range of Ar ions in the amorphous Si matrix as determined by the simulation code SRIM is about 1.1 µm. Therefore, the Ar ions traverse the complete length of the chevrons before getting implanted in the Si(111) substrate. The spring constant of the chevrons was determined by force-distance spectroscopy using an atomic force microscope. Results show that the spring constant of the irradiated Si chevrons grown on 260 nm diameter silica spheres increases from 480 N/m for pristine to 1320 N/m for a fluence of 10^{16} ions/cm^2. For chevrons grown on 500 nm diameter polystyrene spheres, an increase from 370 N/m for pristine to 1325 N/m for fluence of 10^{17} ions/cm^2 is observed. Thus, irradiated chevrons are stiffer as compared to pristine ones. Finite element analysis of chevrons provides an insight into the dynamics of the resulting deformations when the chevrons are loaded. The modeling establishes that for these odd-armed chevrons a vertically downward load results in a torque about the base of the chevrons. The load produces a significantly larger lateral stress/displacement relative to the vertical, thus making them more robust to the loading force. Investigations by micro-Raman and glancing angle X-ray diffraction suggest that the Ar irradiation fosters a transformation from amorphous to poly-crystalline Si. The improved mechanical strength of the chevrons indicates that ion irradiated chevron coatings are capable of withstanding higher loads as compared to pristine coatings without getting delaminated.

Thin Film
Room: 302 - Session TF-ThA

Thin Films for Displays and Flexible Electronics
Moderator: J. Grace, Kodak

2:00pm **TF-ThA1 Thin Film Challenges for Flexible Displays and Electronics**, ***R. Ma***, *M. Hack, J. Brown*, Universal Display Corporation **INVITED**

In this paper, after a brief review of the history and current status of flexible displays and electronics, we will discuss in detail the development of one of the most challenging devices, a flexible full color active matrix organic light emitting diode (OLED) display. We will focus in the three areas: ultra-thin flexible TFT backplanes, rugged thin film barrier protection, and the flexibility of the overall system. The use of flexible substrates generates two main challenges: the handling of the flexible substrates and the compatibility of TFT process to substrate property. Both semiconductor and TFT-LCD industries are built on rigid substrates so the traditional process can't be applied directly to flexible substrates. Mis-match of thermal properties between substrates and TFT materials/process will result failed backplanes. We have chosen thin metal foils as the substrates for flexible displays because of their excellent thermal, mechanical and permeation barrier properties and good flexibility. Metal foils as thin as 25 mm have been used and planarization process has been developed. Another key challenge is to develop a flexible thin film permeation barrier. OLEDs degrade as a result of exposure to atmospheric oxygen and water. Working with Professor Wagner's team at Princeton University, we have identified a flexible, highly impermeable barrier layer that is deposited from environmentally-friendly and inexpensive precursors in a single-chamber reactor. The lifetime of OLEDs encapsulated with the layers exceeds the industrial target of 1,000 hours and also the lifetime of conventionally sealed glass packaged OLEDs. Many materials are used in a flexible AMOLED: organic, inorganic and metallic systems. We have studied the characteristics of such materials and developed an initial system to study the mechanical flexibility of the integrated device. We will present the required material building block properties and present recent results on ultra-thin (< 50 µm) flexible OLED displays. Flexibility results on these displays show that they operate when conformed to a tight diameter of only 5 mm.

2:40pm **TF-ThA3 Roll-to-Roll Plasma Enhanced Chemical Vapor Deposition of Graded Ultra-high Barrier Coatings on Polymer Substrates**, ***M. Yan***, *R.A. Zhao, D.J. Smith, C.L. Jones, P.A. Mcconnelee, A.G. Erlat, A.R. Duggal, T.P. Feist*, GE Global Research

The use of plastic film substrates for organic electronic devices promises to enable new applications, such as flexible displays and conformal lighting, at low cost through high volume roll-to-roll fabrication. Unfortunately, presently available substrates cannot yet deliver this promise because of the challenge in achieving the required combination of optical transparency, impermeability to water and oxygen, mechanical flexibility, and high temperature capability. In this contribution, we describe our roll-to-roll (R2R) plasma enhanced chemical vapor deposition (PECVD) process development and performance of a unique graded transparent ultra-high gas barrier coating on top of plastic substrate which is aimed at meeting this challenge.

3:00pm **TF-ThA4 Latest Innovations in Large Area Web Coating Technology via PECVD Source Technology**, *M.A. George, J.E. Madocks, J. Morris*, ***H. Chandra***, General Plasma

In this paper we discuss the latest results of our development of large area PECVD source technologies for flexible substrates. A significant challenge for flexible displays is the economical application of thin films for use as vapor barriers, transparent conductive oxides, optical interference thin films and thin film silicon. Here at General Plasma we have developed two innovative PECVD source technologies that provide an economical alternative to low temperature sputtering technologies and enable some thin film materials not accessible by sputtering. The Penning Discharge Plasma (PDP™) source is designed for high rate PECVD depositions on insulating temperature sensitive web.[1] This technology has been utilized to deposit SiO2 and SiC:H for barrier applications.[2] The Plasma Beam Source (PBS™) is useful for deposition on conductive or rigid substrates or for deposition of thin films that are sensitive to the high ion bombardment flux inherent to the PDP technology. We have developed thin film processes in our laboratory for deposition of SiO2, SiC:O, SiN:C, SiN:H and thin film silicon via this PBS source.[3] We discuss the patented source design, plasma physics and chemistry of the deposited thin films.

[1] J.Madocks; "High Rate PECVD Source for Flexible Substrates", Proceedings of the Society of Vacuum Coaters, pp 187, 2003.

[2] V. Shamamian, L. Zambov, U. Pernisz, S. Kim, S. Perz and G. Cerny, "Progress in the Development of SiC:H Alloy Film on Flexible Substrates for Extremely Low Moisture Permeability Applications", Proceeding of the Flexible Displays and Manufacturing Conference, 2006.

[3] M.A. George, P. Morse, J. Morris, H. Chandra and J. Madocks, "Deposition of Silicon Oxide, Silicon Nitride and Silicon Carbide Thin Films by New Plasma Enhanced Chemical Vapor Deposition Source Technology", Conference Proceedings of the Assoication of Industrial Metallizers, Coaters and Laminators (AIMCAL), 2007.

3:20pm **TF-ThA5 Low Damage Sputter-Deposition System for the Deposition of TCO Films on Organic Films**, *H. Lei, K. Ichikawa, T. Uchida, **Y. Hoshi***, Tokyo Polytechnic University, Japan

We examined damages produced in organic materials during sputter-deposition of electrode film by measuring a change of photo-luminescence (PL) intensity of organic light emitting materials and developed a low damage sputter-deposition system. MEH-PPV as polymer and BAlq3 as small molecule were used for the light emitting materials. We compared the damages produced in the deposition of electrode films(ITO) by using different types of sputtering systems, i.e., a facing target sputtering (FTS) system and a conventional planar rf-magnetron sputtering (rf-MS) system. By using FTS system, decrease in PL intensity was suppressed remarkably compared with the using of rf-MS. In addition, removing the bombardment of high energy secondary electrons to the film surface was very effective to reduce the damages of the organic films. Furthermore, reduction of kinetic energy of deposition particles to the organic film surface by increasing sputtering gas pressure was necessary to reduce the damages of the organic films. Finally, we could deposit ITO films on the organic films without damages by using a FTS system, where bombardment of high energy negative oxygen ions, high energy secondary electrons, and high energy deposition particles to the organic film were completely removed.

4:00pm **TF-ThA7 Sputter Deposition of Highly Flexible ITO on Polymeric Substrates**, *M. Yan, A.G. Erlat, **B. Scherer**, P.A. Mcconnelee, A.R. Duggal, T.P. Feist*, GE Global Research

This contribution describes a novel modification to conventional DC magnetron sputtering setup to make highly flexible, conductive and transparent indium tin oxide (ITO) coatings on polymeric films. Such high quality ITO coated polymeric film serves as an ideal substrate for flexible optoelectronic devices such as organic light emitting diodes (OLED), photovoltaics, organic electrochromic devices, and the like. The uniformity and flexibility of ITO coatings on plastic substrates were dramatically improved by inserting a shadow mask between substrate and ITO sputter target and critically positioning the mask to block a spatial region of the sputtering target material from depositing on the substrateIn addition, ITO sputtering process repeatability was improved by preconditioning sputter chamber after cleaning.

4:20pm **TF-ThA8 Thermally Stable Very Thin Ag Films for Electrodes**, ***M. Kawamura**, D. Fukuda, Y. Inami, Y. Abe, K. Sasaki*, Kitami Institute of Technology, Japan

Low resistivity metals such as Cu or Ag have been paid attention for substituting Al alloy films as gate, source, and drain electrodes in LCD-TFT. Though Ag features with the lowest resistivity among all metals, some serious demerits, e.g. agglomeration by heating, are known. Improvements of thermal stability of Ag thin films have been attempted by especially alloying the Ag films, but it is difficult to preserve its low resistivity due to impurity scattering effect in some cases. We have showed a result of structural modification, where very thin Al oxide layer (about 3 nm of thickness) were introduced at top and bottom of the Ag films (about 95 nm), namely Al/Ag/Al structure. This structure showed excellent stability on surface morphology and electrical resistivity even after annealing at 600ºC in vacuum. The resistivity of the film was also as low as that of bulk Ag. Next, reduction of Ag layer thickness down to 50 nm was attempted. The resistivity and morphology of the film were degraded slightly but remarkably superior to those of pure Ag films, and also those of Cu thin films with the same size. Consequently, it is found that the modified Ag films show excellent electrical properties and can be used at elevated temperatures.

4:40pm **TF-ThA9 High Rate Sputtering Deposition of Silicon Oxide Thin Films from New SiO_2:Si Target Composition**, ***Q.H. Fan,*** Wintek Electro-Optics Corp, *L.Q. Zhou,* University of Michigan, *D. Stevenson*, Wintek Electro-Optics Corp.

Silicon oxide thin films are widely used in flat panel displays as well as optical and large area architectural type coatings. Two sputtering techniques are commonly used to deposit silicon oxide thin films. For the highest density SiO_2 films RF sputtering using quartz targets is normally preferred. For large area coating at high rates reactive sputtering using silicon targets and either DC or AC type power supplies is the most common method. RF sputtering results in high quality films but relatively low deposition rates. Reactive sputtering from silicon targets has higher deposition rates but lower film quality. In addition reactive sputtering using planar targets has process stability issues due to target poisoning. The ideal process would combine the high rates of reactive sputtering with the film quality of RF sputtered SiO_2 films from quartz targets. We have successfully developed a conductive SiO_2:Si target (patent pending) that achieves this goal. This target composition can be sputtered using DC, AC or RF power supplies. Using this new target it is possible to reach deposition rates that are at least three times higher than typical RF sputtered SiO_2 films from quartz targets. Further, the SiO_2 film quality that can be achieved is comparable to RF sputtered films from quartz targets. In this paper, we present details of the conductive SiO_2:Si target as well as the resulting SiO_2 film properties and deposition rates that have been achieved. In addition we also provide our preliminary analysis of the deposition process mechanism that enables such high deposition rates and film quality when SiO_2:Si targets are used.

5:00pm **TF-ThA10 Recent Development of Low Temperature Plasma Enhanced CVD of Transparent Conducting Oxide in Photovoltaic Applications**, ***H. Chandra**, M.A. George, S. Higgins, P.L. Morse, J.E. Madocks*, General Plasma Incorporated

Transparent conducting oxide (TCO) is a key component for photovoltaic and display applications. Indium tin oxide (ITO) is the best known TCO material with regard to electrical and optical properties. However, ITO is prohibitively expensive for economical production for these applications. One candidate to replace ITO as TCO material is fluorine-doped tin oxide. It is stable at high temperature, economical to produce and less reactive compared to other TCO materials such as zinc-oxide based TCO[1]. The bulk resistivity of tin oxide films deposited with conventional method (PECVD, spray pyrolysis, atmospheric pressure CVD) is as low as $2x10^{-4}$ Ohm-cm.[1] However, the deposition temperature is typically above 350°C which has limited use for temperature sensitive processes such as quantum dots based solar cells or large area plastic substrates. We have developed a novel PECVD system to deposit tin oxide at lower temperature (below 200°C) while achieving good conductivity. Our tin oxide films have bulk resistivity below $4x10^{-3}$ Ohm-cm at 200°C which is lower than conventionally deposited films at the same process temperature. Furthermore, the linear PECVD source used in this process is scalable to several meter-wide web substrates with film uniformity better than 3%. The deposition rate is typically 200-400 nm-meter/minutes more than an order of magnitude higher than competing sputtering technologies. The scalability to large area with excellent uniformity coupled with high deposition rate is important for economical production of TCO layer. In the present work, we will discuss the PECVD source used in the process, electrical properties (carrier concentration and mobility), optical properties and microstructure of the deposited tin oxide and other TCO thin film materials.

[1] W. Beyer et al., "Transparent conducting oxide films for thin films silicon photovoltaics," Thin Solid Films 516, 147 (2007).

5:20pm **TF-ThA11 Field-Effect Mobility Enhancement of Organic Thin Film Transistors on Flexible Substrates with Organosilanes-based Surface Modification**, *C.G. Takoudis, **L. Jiang**,* University of Illinois at Chicago, *J. Zhang, D.R. Gamota*, Motorola

In Organic Thin Film Transistors (OTFTs), the performance is profoundly affected by organic semiconductor crystal formation or organic structure ordering. As it is known, the ability of conjugated molecules to transport charge due to the π-orbital overlap of neighboring molecules provides their semiconducting and conducting properties. The self-assembling or ordering of these molecules enhances this π-orbital overlap and is the key to improvements in carrier mobility. Since the semiconductor materials are deposited on dielectric layer, the surface chemical and mechanical properties of dielectric materials do affect the alignment and the crystal formation of semiconductor. For industrial applications requiring large area coverage, structural flexibility, and low cost, such as printed electronics, each layer is printed on the flexible plastic substrate, so that the dielectric materials have to be printable. In this work, poly(4-vinyl phenol-co-methyl methacrylate) (PVP-PMMA) was used as dielectric cross-linked at 200ºC by mixing with p- Tolyltrimethoxysilane (TTMS) on polyimide substrate, and Aluminum deposited on the polyimide as gate. The carbon ink could be printed on the cross-linked PVP-PMMA to form source and drain. Solution processed bis(triisopropylsilylethynyl) (TIPS) pentacene was deposited either by drop casting or rod coating and the field effect carrier mobility of 10^{-3} ~10^{-5} cm^2/V•s were obtained. The resulting structures and systems were also characterized with differential scanning calorimetry and atomic force microscopy.

Thin Film
Room: Hall D - Session TF-ThP

Aspects of Thin Films

TF-ThP1 Surface Roughness of Amorphous Carbon Nitride Films Prepared by rf-Reactive Sputtering, *S. Kikuchi, M. Aono, N. Kitazawa,* ***Y. Watanabe***, National Defense Academy, Japan

Amorphous carbon nitride (a-CNx) thin films were deposited on silicon single crystal substrates by rf-reactive sputtering method using a graphite target, and after deposition the films were exposed to oxygen plasma so as to be modified on their surface. The effect of the substrate temperatures, deposition time and oxygen plasma treatment on the surface roughness has been studied. The substrate temperature was varied from room temperature to 853 K and the deposition time was changed from 10 to 180 min. Oxygen gas of about 20 Pa was discharged by rf-power and oxygen plasma was generated. Plasma treatment time was changed from 10 to 60 sec. Film composition and the chemical bonding states were analyzed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). Film surface was observed by atomic force microscopy (AFM). AFM observations has revealed that the as-deposited film surface is uniformly covered with particle-like features in the early stage of deposition and the surface changes to be covered with broccoli-like features with increasing the deposition time and correspondingly the root-mean square roughness (RMS) increases from about 0.5 to 7 nm after 180-min deposition, while the RMS slightly decreases with the substrate temperature under the constant deposition time of 10 min. After exposure to oxygen plasma, the film surface was etched selectively and the RMS increases with the plasma treatment time. It should be mentioned that the etching behavior depends on the film deposition temperatures. XPS studies have shown that the bonding states between carbon and nitrogen change with the deposition temperature. This change may be related to the different etching behavior against oxygen plasma.

TF-ThP2 Nanotribological Properties and Degradation of Ionic Liquid Films on Magnetic Tapes, ***M. Palacio***, *B. Bhushan*, The Ohio State University

New magnetic tapes with ultrahigh storage density are expected to encounter increasingly more intolerant head and tape path materials, such that the fatty acid mixtures and fluorocarbons that are currently used as tape lubricants may no longer provide adequate wear protection. Ionic liquids are promising as lubricants for magnetic tapes because of their desirable thermal properties. Characterizing the nanotribological properties and degradation of ionic liquids is a crucial step in evaluating the potential of these novel materials as the next generation lubricant for tapes. In this study, commercial AME tape was lubricated with two ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) and 1-butyl-3-methylimidazolium octyl sulfate (BMIM-$OctSO_4$), and were investigated for the first time with atomic force microscopy. The adhesive and friction properties of the ionic liquids were compared to the perfluoropolyether (PFPE) lubricant Z-TETRAOL. Tape durability studies were conducted by running the lubricated tape samples to failure. The tape life of the lubricated samples was compared to historical data on MP and ME tapes.

TF-ThP3 Influence of Re-Deposition on Particle Generation, ***C.F. Lo***, Praxair Electronics

In physical vapor deposition (PVD), depending on the target material, target design and sputtering conditions, the bombarded atoms may re-deposit on to the lower erosion zone of the sputtered target. Due to difference in structure between the sputtering target and re-deposited layer, flaking may occur mainly induced by mismatch of coefficient of thermal expansion, resulting in particles generation and causing defects on substrate. Micro-arcing at the tip of re-deposited nodules is another potential particle source in target sputtering. In this report, re-deposition of many materials used for the semiconductor devices, such as Cu, Ti, Ta, W, WTi, W-Silicide and Cr, were discussed. Direct and indirect evidences of flaking and micro-arcing acting as particle sources to substrate are also presented in this report.

TF-ThP5 Synthesis of SiGeC Alloy by the Modified Ablation Laser Technique*, ***J.G. Quiñones Galván***, *F. de Moure Flores, E. Mota Pineda, S. Cerón Gutiérrez,* CINVESTAV-IPN, Mexico, *A. Hernández Hernández,* Escuela Superior de Física Matemáticas-IPN, Mexico, *M. González Alcudia,* CICATA-IPN Unidad Altamira, Mexico, *J.J. Araiza Ibarra,* Universidad Autónoma de Zacatecas, Mexico, *M. Meléndez Lira*, CINVESTAV-IPN, Mexico

SiGeC has been the subject of interest because of the possibility of control the stress associated to the deposit of SiGe/Si heterostructures but also for the possibility to modify the SiGe properties to produce light efficiently. However, the major problem to deposited this alloy in the whole range of compositions is the low solubility of carbon in SiGe. We present the results of the characterization of SiGeC alloys produced by the modified ablation laser technique in which the desired SiGeC alloy composition target is prepared by ball milling[1]. The target is prepared as a powder of the right composition and subject to the ablation process. Films of the $Si_{1-x-y}Ge_xC_y$ alloys were prepared with $0.1<x<0.3$ and $0<y<0.1$. Samples were characterized by X ray diffraction, atomic force microscopy, IR, Raman and photoluminescence spectroscopies. The results are discussed in function of the amount of substitutional carbon.

* This work is partially funded by CONACyT- Mexico.

[1] M. González-Alcudia, A. Márquez-Herrera, M. Zapata-Torres, M. Meléndez-Lira and O. Calzadilla-Amaya, Adv. in Tech. of Mat. And Mat. Proc. J. 9, 81 (2007).

TF-ThP6 Surface, Interface, and Bulk Characterization of ALD Cu Films and PVD Dielectric Films, ***L. Zhang***, *K. Lloyd, G. Blackman, L. Bao, J. Thompson, M. Plummer, D. Brill, J. Ryley, D. Reardon*, DuPont

Surface and interface properties of thin films play an important role in a variety of existing and emerging industrial applications, including the development of semiconductor devices, surface coatings, heterogeneous catalysts, polymers, biological materials, and medical devices. Among these applications, the surfaces and interfaces of these materials often control device or part performance, therefore quantitative chemical and structural characterization in the near surface region are critical to quality. This presentation will cover two topics. The first part will focus on the applications of applying integrated methods/techniques to characterize surface roughness, film quality and thickness of ultrathin copper films prepared by the Atomic Layer Deposition (ALD) process. The second part of the presentation will discuss the surface and interface characterization of dielectric films prepared by the Physical Vapor Deposition (PVD) method.

TF-ThP7 Characteristics of the Top-Emitting Organic Light-Emitting Diodes Based-on the Electronic Structure of the BaO-on-Alq3 Interface, ***J.T. Lim***, *G.Y. Yeom*, Sungkyunkwan University, Korea

Top-emitting (TE) type of organic light-emitting diode (OLED) have been actively developed in recent years, to improve aperture ratio to the top cathode direction in active matrix (AM) displays. Therefore, developing thin semitransparent conducting cathodes (STCCs) have become one of the essential key-element technologies to obtain a high light out-coupling of the devices. In this study, STCC of the BaO/Ag (20 nm)/ITO (100 nm) structure were used to fabricate the TEOLED. The TEOLED structure is consisted of glass/Ag (150 nm)/tin-doped indium oxide (125 nm)/4,4',4"-tris[2-naphthylphenyl-1-phenylamino]triphenylamine (2-TNATA, 30 nm)/4,4'-bis[N-(1-napthyl)-N-phenyl- amino]-biphenyl (NPB, 18 nm)/tris(8-quinolinolato)aluminum (III) (Alq3, 62 nm)/BaO (x nm)/Ag (20 nm)(x: 0, 0.5, 1, and 1.5 nm)/ITO (100 nm). The device with 0.5-nm-thick BaO showed the highest driving performance as the luminous efficiency of 2.7 % and the maximum luminance of 47000 cd/m2, compared with other devices. The driving performance of these devices can be explained by analyzing as electronic structures of the BaO-on-Alq3 interface. In the ultraviolet photoemission spectroscopy (UPS) study, the barrier height of an electron injection (ΦnB) from the BaO/Alq3 interface to the Alq3 layer is increased with increasing the coverage of BaO on Alq3. In the X-ray photoemission spectroscopy (XPS) studies of the O, N, and Ba core levels, the staged interface reaction of two steps was observed, which shows the formation of stable radical anion at low BaO coverage of below 0.5 nm.

Alq_3. cd/m^2. φ_n^B.

TF-ThP8 Influences of Ceria-Mixed Abrasive Slurry on the Oxide-Chemical Mechanical Polishing, ***S.J. Han***, *Y.K. Lee, S.W. Park,* Chosun University, Republic of Korea, *Y.J. Seo,* Daebul University, Republic of Korea, *W.S. Lee*, Chosun University, Republic of Korea

In this paper, we have studied the chemical mechanical polishing (CMP) characteristics of mixed abrasive slurry (MAS) retreated by adding of ceria (CeO2) abrasives within 1:10 diluted silica slurry. The slurry designed for optimal performance should produce reasonable removal rates, acceptable polishing selectivity with respect to the underlying layer, low surface defects after polishing, and good slurry stability. The modified abrasives in MAS are evaluated with respect to their particle size distribution, surface morphology, and CMP performances such as removal rate and non-uniformity. As an experimental result, we obtained the comparable slurry characteristics compared with original silica slurry in the viewpoint of high removal rate and low non-uniformity.

TF-ThP9 Improvement of Tetra-Ethyl Ortho-Silicate Oxide - Chemical Mechanical Polishing Characteristics According to the Cerium Oxide Dispersion Time*, **Y.K. Lee**, S.J. Han, S.W. Park,* Chosun University, Republic of Korea*, Y.J. Seo,* Daebul University, Republic of Korea*, W.S. Lee*, Chosun University, Republic of Korea

CMP (chemical mechanical polishing) process has been attracted as an essential technology of multi-level interconnection. However, the COO (cost of ownership) is very high, because of high consumable cost. Especially, among the consumables, slurry dominates more than 40 %. So, we focused how to reduce the consumption of raw slurry. In this paper, CeO2 abrasive was added de-ionized water (DIW) and pH control as a function of KOH contents. And then, we have discussed the CMP characteristics as a function of abrasive dispersion time. We have also investigated the possibility of CeO2 - mixed abrasive slurry for the oxide CMP application. Note: Requested a Poster Session.

TF-ThP10 Influence of Ar/O_2 Gas Ratio on the Performance of Sputtered-Deposited TiO_2 Electrodes for the Application of Dye-Sensitized Solar Cells*, M.F. Hossain, **S. Biswas**, M. Shahjahan, T. Takahashi*, University of Toyama, Japan

Dye-sensitized solar cells (DSCs) have attracted great interest because of their potential application as a cost effective and alternative to the p-n junction solar cells. Conventional technology of DSCs employs colloidal films of titanium oxide (TiO_2) to which a ruthenium dye is attached. In such conventional processes, porous TiO_2 electrode also gives rise to several undesired characteristics, such as low conductivity and charge density and non-uniform over the large area. Reactive magnetron sputtering is a very promising technique for large-area uniform coating to preparation high quality TiO_2 thin films with strong adhesion to substrate and it has potential to control the crystallographic phase and micro-structure through the process of modification of different sputtering parameters. In this study, an effort has been made to fabricate the DSCs with sputter-deposited TiO_2 electrode. Nanoporous TiO_2 electrodes were successfully deposited on SnO_2:F coated glass substrate by facing target reactive sputtering technique with 500 W dc input power, 2.0 Pa sputtering pressure and various sputtering Ar/O_2 gas ratios such as, 8:2, 7:3 and 6:4. Ruthenium complex based-dye was used to sensitize these electrodes and carbon paste on SnO_2:F coated glass was used as a counter electrode. The amount of dye incorporation was found to be highly dependent on the microstructure of the film with various gas ratios, as apparent from optical measurements. The surface morphology of the films has been observed by atomic force microscope and field emission scanning electron microscope. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different TiO_2 thin films to evaluate the economic viability of this technique. The variation of photoelectric conversion efficiency of the solar cells with TiO_2 electrodes deposited at various gas ratios is discussed with the analysis of different microstructure of the TiO_2 electrodes and the corresponding dye-incorporation.

TF-ThP11 Electronic Structure of Self-Assembled Sm Nanostructure on HOPG Studied by Photoemission Spectroscopy*, **G. Kutluk**, M. Nakatake, H. Namatame, M. Taniguchi*, Hiroshima University, Japan

Small change in the electronic structure of lantanide-based compounds may lead to quite distinct alteration in physical properties, and such systems have considerable technological interest since they are being used in e.g., microelectronic industry, in catalysis, and in strong permanent magnets. Sm may be of particular interest from a fundamental point of view since two different isoenergetic states may coexist. Relatively small change in chemical environment may induce a change in the valence states. In order to limit (or prevent) interface alloy formation between substrate, the HOPG (highly oriented pyrolytic graphite) was chosen as substrate. HOPG surface is very inert, and therefore sample cleaning is much less time-consuming compared to other substrates. Oxygen chemisorption on Sm overlayer can be more easily studied using graphite surfaces than on oxide surfaces, since there is no background oxygen signal on graphite surfaces. Metallic properties of HOPG allow electron spectroscopy and microscopy experiments without surface charging problem. In situ photoemission spectroscopy on Sm overlayers on HOPG in coverage regime 0.2~10Å were performed at room temperature in an ultrahigh vacuum (UHV) with base pressure of $1x10^{-10}$ torr. The resonance photoemission spectra indicate that the divalent feature was observed for the coverage below than 1.0Å, and the trivalent structures are enhanced for films coverage exceeding the 1.0Å. The oxidization of Sm overlayers even in an UHV environment cannot be avoided during measurement, however that is not only due to the residual oxygen species attacking to Sm normally, the VUV (Vacuum ultraviolet) light also take a part of stimulating the oxidization process, that has been observed from valence band spectra. And the morphology of Sm overlayer was evaluated by AFM (atomic force microscopy). A self-assembled nanostuctures of shower of cherry blossoms shape (island shape) dominate the morphology of Sm overlayer in a lower coverage regime below than 1.0Å. The Sm overlayers were deposited on to HOPG in an UHV chamber with base pressure of 3x10-10 torr, and transferred to measurement chamber without exposing to the atmosphere. The coverages of Sm films were monitored by a quartz-crystal microbalance. The VUV light supplied from monochrometor BL-7 was employed for the photoemission spectroscopy at Hiroshima synchrotron radiation research center (HiSOR)

TF-ThP12 The Influence of N-dopping for Titanium Dioxide Thin Films on Photo-functional Properties*, **K. Tanaka**, I. Takano*, Kogakuin University, Japan

TiO_2 is anticipated as one of materials which are alternative for existing solar cell technology based on silicon. TiO_2 shows relatively high reactivity and chemical stability under UV light whose energy exceeds the band gap of 3.2 eV in the anatase crystalline phase. The sun can provide an abundant source of photons. however, UV light accounts for the only small fraction (～5 %) of the sun's energy compared to the visible region (45 %). Many techniques have been examined to achieve this purpose, including the doping of TiO_2 with transition metals (such as Cr, Fe, Ni, V), but these doped materials suffer from thermal instability and an increased number of carrier recombination centers. Many research groups proposed to replace Oxygen by another anionic species (such as C, P, S, N, F) rather than incorporating transition metals into TiO_2. Especially, Nitrogen-doped TiO_2 is often used to improve the photocatalytic properties of TiO_2 in order to achieve visible light response.[1] In this study, the Nitrogen-doped TiO_2 film has been prepared by reactive magnetron sputtering using a Ti target in an Ar/N_2+O_2 gas mixture. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic change of a methylene blue solution was applied to a photocatalytic property. Light irradiation to the TiO_2 film in a methylene blue solution was carried out using a commercial sterilizing lamp as ultraviolet light and a commercial fluorescent lamp as visible light. Transmittance of a methylene blue solution was measured by a spectro photometer. Furthermore, photocurrent between the TiO_2 film and a platinum electrode was measured by a volt-ampere characteristic using an unresisted ammeter in a KCl solution of 0.5 mol/ℓ. In the case of the Nitrogen-doped TiO_2 film, the higher photocatalytic property and photocurrent under a sterilization lamp were obtained at N_2 gas flow rate of 0.6 sccm and 0.4-0.5 sccm, respectively. In the case of a fluorescent lamp, the photocatalytic property showed lower transmittance and photocurrent as compared with that of a sterilization lamp. But transmittance and photo current showed the maximum value at N_2 gas flow rate around 0.5 sccm, so Nitrogen-dope effect was confirmed under a fluorescent lamp.

[1] R.Asahi, et al.; Science, 293(2001)269.

TF-ThP13 The Structural, Electrical and Optical Properties of ATO Films Prepared at Room Temperature by Radio Frequency Magnetron Sputtering for Transparent Electrodes*, **S.U. Lee**,* Sungkyunkwan University, Korea*, W.S. Choi,* Hanbat National University, Korea*, H.J. Kim, B. Hong*, Sungkyunkwan University, Korea

Antimony-doped tin oxide (ATO) films were prepared on a 7059 Corning glass substrate by the radio frequency (RF) magnetron sputtering method using a SnO2 target mixed with Sb of 6 wt% at room temperature. The working pressure was varied from 5 to 15 mTorr in steps of 5 mTorr, and the RF power was varied from 100 to 175 W in step of 25 W at room temperature. The thickness of the deposited ATO films was about 150 nm ± 10. X-ray diffraction (XRD) measurements showed ATO films to be crystallized with a strong (101) preferred orientation as the RF power increased. The spectra revealed that the deposited films were polycrystalline and they retained the tetragonal structure. The grain size, which was 23.2 nm, was calculated from the XRD spectra using the Scherrer equation. ATO film deposited at a working pressure of 5 mTorr and RF power of 175 W showed the lowest resistivity of 8.6 x 10^-3 ohm.cm and the optical transmittance was 86.5 % in the visible range.

TF-ThP14 Interface Control Effect of Nitrogen-doped Diamond-like Carbon by Ion Beam Assisted Deposition Method*, **K. Harada**, I. Takano*, Kogakuin University, Japan

DLC (Diamond-like Carbon) constituting a class of new materials is an amorphous carbon including hydrogen and has similar properties of matter with a diamond. DLC film was formed by the ion beam evaporation method in the early 1970's,[1] and after that has been manufactured by various methods such as CVD (Chemical Vapor Deposition) or PVD (Physical

Vapor Deposition). Because the representative mechanical property of DLC is to show the high hardness and low friction coefficient, DLC is applied in various filed such as motor parts or tools. Also the electric properties of DLC are anticipated as a field emission source. In this study, mechanical properties were investigated about the interface between the DLC film and the substrate controlled by the ion beam assist. The ion beam assisted deposition method has many parameters on the film formation condition in comparison with other dry process methods. Therefore this method was anticipated in production of new characteristics such as a high adhesion film. The interface control was performed by changing two procedure. The first process was performed by an accelerating voltage of 12 kV with a current density of 40 μA/cm^2 to obtain the high hardness property. The second process was performed by an accelerating voltage of 5 kV with a current density 40 μm/cm^2 to obtain the low friction property. An N_2^+ ion beam and a C_7H_8 gas atmosphere were used on this ion beam assisted deposition method. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and Raman spectroscopy. The hardness was measured from an indentation method with a Knoop indenter. The friction coefficient was measured for an SUJ2 ball with a constant load 0.98 N until the sliding distance reached a length of 10m. As for the sample formed the mixing layer at the first process, mechanical properties were improved in the hardness and the friction coefficient. The Knoop hardness of the film showed 23 GPa. The sample formed using both of first process and second process showed 0.194 in the friction coefficient, because mechanical properties were improved by the interface condition. The depth profile of the mixing layer showed gradual change of C and Fe (as substrate material) in comparison with a sumple without mixing layer.

[1] S. Aisenberg , R. Chabot : J. Appl. Phys., 42, 2953 (1971).

TF-ThP15 In Situ Spectroscopic Ellipsometry Studies of the Oxidation of Nickel Thin Films, *J. Rhim, S. Lee, H. Jeong,* Hanyang University, South Korea, *D. Kim,* Ewha Womans University, South Korea, *I. An*, Hanyang University, South Korea

Nickel oxide film is an attractive material for electrochromic devices as well as resistance random access memory devices. In this work, e-beam evaporated nickel films are thermally oxidized in oxygen ambient at various temperatures. In situ spectroscopic ellipsometry is employed to study the oxidation process of nickel films. The optical and microstructural properties of nickel oxide films are deduced and these are compared with the electrical properties. When the nickel film is not fully oxidized, the optical properties of nickel oxide show the inclusion of nickel element. This film shows low resistivity and poor switching characteristics.

TF-ThP16 Study of Vanadium Oxide Thin Films Deposited by Pulsed DC Sputtering using a V_2O_3 Target, *K.E. Wells, S.S.N. Bharadwaja, M.W. Horn*, The Pennsylvania State University

Uncooled infrared focal plane arrays (IRFPAs) are the critical technology for night vision cameras needed for military and civilian applications. The two most widely used temperature sensitive imaging materials are vanadium oxide and amorphous silicon typically deposited by reactive ion beam sputtering and PECVD respectively. For future applications requiring higher speed and/or sensitivity, materials with high temperature coefficient of resistance (TCR) may be desirable. In this work, vanadium oxide thin films were made at room temperature by reactive pulsed DC (225 kHz) magnetron sputtering of a V_2O_3 target with 200 W power. Total pressure and partial pressure of oxygen were varied during deposition to determine their effects on the films properties. The TCR and resistivity values of the films were in the range of -3 to -5% (K^{-1}) and 10- 200 kΩ-cm respectively. Both Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM) data established that the microstructures of the films follow the structure zone model with increased columnar size as total pressure is increased. Spectroscopic ellipsometry analysis indicated significant variation in the dielectric functions in the VO_x films with similar electrical properties. We attribute this variation to either differences in porosity or oxygen content. The crystallinity of the films, evaluated by High Resolution Transmission Electron Microscopy (HRTEM) studies, was found to be substrate dependent. Films deposited for various durations with the same deposition parameters showed a lower resistivity with increased thickness.

TF-ThP17 Atomic Layer Deposition of Lanthanum Based Oxides for High-K Gate Dielectrics, *A. Hande, B. Lee, H.C. Kim, R.M. Wallace, J. Kim,* The University of Texas at Dallas, *X. Liu, M. Rousseau, J. Yi, D.V. Shenai, J. Suydam*, Rohm and Haas Electronic Materials, LLC.

Lanthanum oxide (La_2O_3) is gaining importance as one of the promising high-k candidates due to its superior properties such as a high dielectric constant (~27), large band gap and high electrical breakdown field strength. However, the hygroscopic properties of La_2O_3 leads to the formation of lanthanum hydroxide ($La(OH)_3$) which causes deterioration of electrical properties such as, permittivity. Additionally, several studies have reported that a La based CVD process result in a high C concentration in the deposited films. In order to overcome these issues, we investigate two different processes; one is alternating layers of La_2O_3 and Al_2O_3 to form nano-laminate ($La_xAl_yO_3$) structures and the other is employing ozone as the oxidant. In this study, we deposited $La_xAl_yO_3$ films using atomic layer deposition (ALD) on H-terminated p-type Si (100) substrate using tris(N,N'-diisopropylformamidinato) lanthanum, $La(iPrfAMD)_3$ as the La precursor while water and ozone employing as the oxidant. The physical properties of the deposited La-oxide using various characterization techniques such as HR-TEM, XPS, and XRD as well as electrical characteristics will be presented. Particularly, our in-situ XPS half-cycle study provides an insight on chemical composition modulation based on different process sequence. Acknowledgement: Rohm and Haas Electronic Materials, LLC. for financial support and Toshiba Mitsbushi Electric Industrial Systems Corporation (TEMIC) for providing a ozone generator (OP-H250 LT) for a high concentration ozone.

TF-ThP18 Integrated UHV/ALD Reactor for Growth of Oxide Materials, *K. Pradhan, A.E. Wierzbinski, P.F. Lyman*, University of Wisconsin-Milwaukee

We have constructed a novel chemical reactor for controlled growth of crystalline oxide layered structures using Atomic Layer Deposition. The instrument operates in the viscous flow regime, and the design is based heavily upon that of Elam, Groner, and George.[1] However, we have interfaced this reactor to an existing UHV analytical chamber. The combination allows us to investigate not only the as-grown films, but also to study, on an atomic scale, the intermediate reaction sequences. Moreover, we can use established UHV techniques to prepare a well-defined starting surface for subsequent growth, and are able to modify the substrate at arbitrary points in the growth sequence. Initial results on the growth of ZnO films will be reported.

[1] J.W. Elam, M.D. Groner, and S.M. George, Rev. Sci. Instrum. 73, 2981-2987 (2002).

TF-ThP19 Annealed Multilayer Thin Films of Al_2O_3-Y_2O_3 Using Atomic Layer Deposition, *J.C. Rowland, M. Davidson, P.H. Holloway, J. Jones*, University of Florida

Multilayer thin films consisting of alternating layers of amorphous Al_2O_3 and Y_2O_3 were prepared using Tris(2,2,6,6,-tetramethyl-3,5-heptanedionato)yttrium(III), $AlCl_3$, H_2O, and O_3 as precursors in an atomic layer deposition system with a substrate temperature during growth of 500^{o}C. The thicknesses of each layer ranged from 0.5-10nm depending on the number of precursor pulses with a resulting multilayer stack thickness of 10-100nm. Time-resolved X-ray diffraction spectra were taken as a function of annealing temperature from 20^{o}C to 1200^{o}C. Results above 500^{o}C show crystallization of the amorphous films into mixed phases of Al_2O_3, Y_2O_3, $Y_4Al_2O_9$ (monoclinic), and $YAlO_3$ (perovskite type). The resulting microstructure shows a dependence on the anneal temperature and thickness of the individual as-deposited Al_2O_3 and Y_2O_3 films. Optical and electrical properties of the films are correlated with the growth and processing conditions.

TF-ThP20 Deposition and Etching of Hexagonal and Cubic Boron Nitride, *M. Darnon, D.A. Neumayer, G. Gibson, Y. Zhang*, IBM Research

Boron nitride is a material presenting a high thermal conductivity, a low dielectric constant and a high young modulus. Those properties make it a good material to be used in integrated circuits technologies. We present here a process to deposit cubic or hexagonal boron nitride from a high density plasma. The deposition is performed using an ultima high density plasma chamber from Applied Materials. We also present the etching properties of both phases of Boron Nitride using halogenated plasmas. The etching is performed in a DPS chamber from Applied Materials, using a 20 mTorr plasma, with 500W of source power and 100W of bias power. During the deposition, phase formation is found to be critically dependant on diborane, nitrogen and argon gas ratios and the bias utilized during deposition. Cubic boron nitride formation is found to be favored at the deposition/sputtering regime. A density of 2.9 g/cm^3 for cubic boron nitride and of 1.8 g/cm^{3}for hexagonal boron nitride is measured by XRR. The etch rate of hexagonal boron nitride is measured by ellipsometry. HBr/Ar plasmas present a very low etch rate (21nm/min). Addition of 25 sccm of Cl_2 into the plasma doubles the etch rate. Fluorine-based plasmas etch much faster boron nitride than Bromine- or Chlorine-based plasmas. An eth rate of 146 nm/min is obtained using CF_4/Ar, and the etch rate increases up to 511 nm/min with SF_6/Ar plasma. The substitution of CF_4 by a polymerizing gas such as CH_2F_2 leads to a decrease of boron nitride etch rate. The etch rate of cubic boron nitride is also measured. A ratio of 1.2 between hexagonal and cubic boron nitride etch rates is always obtained. Since the density ratio is 1.6, we can say that the structure of cubic boron nitride enhances its etch yield compared to hexagonal boron nitride. Thanks to the deposition and etching processes presented here, the integration of boron nitride in microelectronics technologies can be considered.

TF-ThP21 Enhancement of Crystal Growth in μc-Si:H Thin Film Deposition by H Radical-Assisted Magnetron Sputtering and the Plasma Diagnostics, *K. Fukaya, **K. Sasaki**, A. Tabata,* Nagoya University, Japan*, N. Knake*, Ruhr-Universität Bochum, Germany

Silicon thin films are promising materials for TFTs and solar cells. It is desirable to deposit Si thin films with good electrical characteristics onto various substrates such as a glass at a low temperature. Magnetron sputtering deposition is useful to prepare silicon thin films because of the advantage in not using explosive gases and consequently, a low equipment cost. We measured the Si atom density in rf magnetron sputtering plasmas with a Si target and Ar/H_2 mixture gas by laser-induced fluorescence (LIF) spectroscopy. As a result, we found that the sputtering yield in the Ar/H_2 mixture discharge was higher than that in the pure Ar discharge. This suggests that sputtering in the Ar/H_2 mixture discharge is not simple physical sputtering but a process similar to reactive ion etching (RIE). Since the products of RIE are not Si atoms but molecular species SiH_x (typically SiH_4), the deposition mechanism similar to PECVD would be expected in magnetron sputtering of a Si target with the assist of chemical reactivity of H atoms. The objective of this work is to develop a new Si sputtering deposition system employing an H radical source. We expect the enhancement of the RIE effect by injecting additional H radicals produced in an ICP radical source. We prepared Si thin films by using simple sputtering with Ar/H_2 mixture gas and H radical-assisted sputtering. In the case of the simple sputtering, an amorphous film was deposited at a low gas pressure of 5 mTorr. The crystalline volume fraction (X_c) increased with the gas pressure from 10 to 200 mTorr, and was saturated at gas pressures above 200 mTorr. In the case of the H radical-assisted sputtering, the X_c increased steeply with the gas pressure from 3 to 5 mTorr, and was saturated at gas pressures from 5 to 500 mTorr. It should be noted that the films deposited by the H radical-assisted sputtering crystallized even at gas pressures below 3 mTorr, where the film deposited by the simple sputtering did not crystallize. This result may be attributed to both or one of the following two effects. One is the supply of H radicals produced in the radical source to the growing film surface. The other effect is the enhancement of the production of molecule species SiH_x by the RIE effect. The increases in the densities of molecular species SiH_x may result in the enhancement of the H coverage on the growing film surface.

TF-ThP22 Fabrication and Characterization of ZnO:(Ag-nano-particles) Thin Films Deposited by Spray Pyrolysis, *G. Alarcon, J. Guzman-Mendoza, M. Aguilar-Frutis, E. San Martín-Martínez, L. Ortega,* CICATA, IPN, Mexico*, **C. Falcony***, CINVESTAV-IPN, Mexico

Zinc oxide thin films with and without the addition of silver (Ag-nano-particles or AgNO3) were deposited using the ultrasonic spray pyrolysis technique using Zn(acac), in the temperature range from 400 to 550 ºC. The optical, structural and electrical properties of the films deposited were studied. The addition of silver was performed through either a solution containing a dispersion of Ag nano-particles or an AgNO3 solution, sprayed in parallel to the Zn containing aerosol. A comparison between both types of films, as well as with those without silver will be presented. The films resulted dense and transparent in all the cases. The as deposited photoluminescence characterization of the films was measured at room temperature presenting the characteristic peaks 514 and 390 nm associated with ZnO. The electrical characterization of the films was carried out by means of Impedance Spectroscopy. In addition, a structural characterization consisting of X-ray diffraction, energy dispersive spectroscopy, and scanning electron microscopy was also performed in the films.

TF-ThP23 Growth Rate Induced Epitaxial Orientation of Cerium Oxide Thin Films on Sapphire (0001), ***P. Nachimuthu**, S.V.N.T. Kuchibhatla, F. Gao, V. Shutthanandan, M.H. Engelhard,* Pacific Northwest National Laboratory*, Z.Q. Yu,* Nanjing Normal University, China*, C.M. Wang,* Pacific Northwest National Laboratory*, S. Seal,* University of Central Florida*, S. Thevuthasan, W. Jiang*, Pacific Northwest National Laboratory

Cerium oxide based materials are widely used in catalysis, solid oxide fuel cells (SOFCs), and for microelectronic applications. Performance of this functional oxide in various applications is dependent on the crystallographic planes of ceria and their participation in various chemical reactions. High-quality ceria (CeO_2) films were grown on sapphire, (Al_2O_3), (0001) substrates using oxygen plasma-assisted molecular beam epitaxy. The epitaxial orientation of the ceria films has been found to be (100) and (111) at low (< 8 Å/min) and higher growth rates (up to ~30 Å/min), respectively. Reflection high energy electron diffraction (RHEED) measurements show that CeO_2 (100) film grows as three-dimensional islands, while CeO_2 (111) proceeds with layered growth. In CeO_2(100) films, although the growth appears to be 3-D island growth, Rutherford backscattering spectrometry (RBS) measurements along channeling geometry clearly demonstrates that the films have high crystalline quality in comparison to CeO_2(111) films. X-ray diffraction (XRD) measurements show that there are three in-plane domains in the CeO_2 (100) film and those are attributed to the three-fold symmetry in Al_2O_3 (0001) surface. Molecular dynamics (MD) simulations have been carried out to understand the stability of different orientations of ceria on the sapphire (0001) substrate. The experimental observations have been supported very well by the simulations. Excellent oxygen sub-lattice match between sapphire and ceria are proposed as a major driving force for achieving high quality epitaxial films, as opposed to oriented, polycrystalline films. High resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) measurements have been carried to study the structure and surface morphology of the ceria films. X-ray photoelectron spectroscopy measurements were used to find the oxidation state of cerium in the as-grown films.

TF-ThP24 Preparation of Very Thin GZO Transparent Electrodes with a Low Resistivity by a VAPE Method, ***T. Minami**, T. Miyata, T. Ito, Y. Honma*, Kanazawa Institute of Technology, Japan

Although transparent conducting impurity-doped ZnO thin films with a low resistivity have been prepared even on low temperature substrates, there is still a problem of the resistivity of the deposited films considerably increasing as the thickness is decreased, irrespective of the deposition methods used. This paper describes the improvements in the thickness dependence of resistivity as well as in other properties obtained in very thin low resistivity Ga-doped ZnO (GZO) thin films prepared using a newly developed vacuum arc plasma evaporation (VAPE) method. It should be noted that in film preparation by VAPE, the substrate normally must rotate or travel linearly during the deposition in order to improve distributions in film thickness and electrical properties across the substrate surface. In this work, however, the substrate remained fixed at a specific position during each deposition. The relative position between the flow direction of the arc plasma and the substrate surface and the VAPE method deposition conditions were optimized to further improve the thickness dependence of the resistivity in transparent conducting GZO thin films deposited on glass substrates. It was found that the obtained resistivity of GZO films deposited with a thickness below about 50 nm at a pressure of 0.15 Pa was strongly dependent on the substrate position relative to the arc plasma flow; it also was affected by the substrate temperature and the Ga content doped into deposited films. In addition, the obtainable resistivity is related to the crystallographical structure, crystallinity and surface morphology of deposited GZO thin films. A resistivity as low as $5X10^{-4}\Omega$cm was obtained in GZO thin films prepared with a thickness of approximately 30 nm under the optimized substrate position and deposition conditions.

TF-ThP25 Relationship Between Oxide Targets and Properties of Impurity-doped ZnO Thin Films Deposited by DC Magnetron Sputtering, ***J. Oda**, T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

This paper describes the relationship between the targets used and the obtained properties of transparent conducting impurity-doped ZnO thin films prepared by a dc magnetron sputtering (dc-MS) deposition method using various sintered oxide targets. The oxide thin films were deposited on glass substrates using a dc-MS apparatus with various sintered impurity-doped ZnO targets; both the target and substrate were fixed during the depositions. In this work, we used various commercially available high-density sintered impurity-doped ZnO disk targets (diameter of about 150 mm). All thin films were prepared with a thickness in the range from 30 to 200 nm; the substrate temperature was controlled to a constant 200ºC during sputtering depositions. It was found that the amount of observable arcing generated during the sputter deposition was considerably dependent on the targets used; in addition, it always increased as the supplied dc power was increased. The obtained minimum resistivity (the resistivity near the substrate location that corresponds to the target center) and the spatial distribution of resistivity on the substrate surface in deposited impurity-doped ZnO thin films were both dependent on the targets used; the varied target properties included density, resistivity and the kind and content of doped impurity. In addition, the film thickness dependence of the obtained resistivity and the stability of the resistivity during long term tests at high temperature in a highly moist environment were considerably affected by the targets used. Improvements in the thickness dependence and the distribution on the substrate surface of resistivity were successfully obtained by varying the target properties. The obtained improvements in deposited films will be discussed on the basis of the relationship between the properties found in both the deposited films and the targets used.

TF-ThP26 Transparent Conducting Si-co-doped AZO Thin Films Prepared by Magnetron Sputtering Using AZO Powder Targets Containing SiC, ***J. Nomoto**, T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

Transparent conducting impurity-doped ZnO thin films are the best, and only practical, indium-free candidate suitable as a substitute for indium-tin-oxide (ITO) thin films used as transparent electrodes in liquid crystal displays (LCDs). However, they have not yet been used practically in LCD applications because of important obstacles such as a spatial distribution of resistivity and insufficient stability of resistivity in impurity-doped ZnO thin films prepared on low temperature substrates by conventional magnetron sputtering depositions. For the purpose of resolving these problems, we have demonstrated a new sputtering deposition technique that was developed to improve both the spatial distribution and the stability in resistivity; transparent conducting Al- and Si-co-doped ZnO (AZO:Si) thin films were prepared on glass substrates at approximately 200°C by rf magnetron sputtering using a powder mixture of ZnO, Al_2O_3 and carborundum (SiC) as the target. The SiC content was varied, but the Al_2O_3 content was held constant. It was confirmed that the Al and Si contents (Al/(Al+Zn) and Si/(Si+Zn) atomic ratios) in the deposited thin films are approximately equal to those of the powder targets used, but carbon was not detected in all the deposited films. It was found that the spatial distribution of resistivity improved as the Si content of deposited films was increased up to approximately 0.75 at.%; the resistivity of deposited films decreased at the location on the substrate surface corresponding to near the erosion area on the target. This decrease in resistivity is attributed to increases of both carrier concentration and Hall mobility. Thus, the improvement of resistivity distribution obtained in the newly developed sputtering deposition technique may be due to a reducing effect originating from the carbon produced by sputtering the SiC containing AZO target during the film deposition. In addition, it was found that the stability of resistivity during long term tests at a high temperature in a highly moist environment of Si-co-doped AZO thin films is better than that of non-Si-co-doped AZO films prepared with the same thickness under the same deposition conditions.

TF-ThP27 Transparent Conducting AZO Thin Films Prepared Using Oxide Targets Sintered by Millimeter-wave Heating, ***T. Miyata***, *Y. Hara, K. Okada,* Kanazawa Institute of Technology, Japan, *H. Abe,* Fuji Dempa Kogyo Co. Ltd., Japan, *T. Minami*, Kanazawa Institute of Technology, Japan

In this paper, we describe the preparation of transparent conducting Al-doped ZnO (AZO) thin films by magnetron sputtering deposition (MSD) and pulsed laser deposition (PLD) using AZO targets sintered with a newly developed millimeter-wave (28GHz) heating technique. For the purpose of evaluating the millimeter-wave-sintered AZO targets, AZO thin films were prepared with various thicknesses on glass substrates at a temperature of 100-300°C by MSD or PLD using an AZO target sintered for about 30 min at a temperature of approximately 1250°C in an Ar gas or air atmosphere. For comparison, additional AZO thin films were prepared by MSD or PLD using an AZO target sintered for 5 h with a conventional furnace. The Al content (Al/(Al+Zn) atomic ratio) in sintered AZO targets was varied in the range from approximately 1.5 to 6 at.%. It was found that the obtainable resistivity of AZO thin films deposited using a millimeter-wave-sintered AZO target was less than or comparable to that produced in AZO films deposited using a furnace-sintered AZO target prepared with the same temperature and Al content. AZO thin films prepared with a thickness above 100 nm by PLD exhibited a low resistivity on the order of 2X10^{-4}Ωcm. Using either type of target preparation, the obtainable resistivity of the deposited AZO films increased as the thickness was decreased; the thickness dependence of the obtainable resistivity in AZO thin films deposited using a millimeter-wave-sintered AZO target was comparable to that found in AZO films deposited using a furnace-sintered AZO target. Although the obtained resistivity and other properties in deposited AZO thin films were affected by the deposition method used, these properties were relatively independent of the sintering technique of the targets. It can be concluded that the newly developed energy saving millimeter-wave heating sintering technique is very well suited for producing sintered oxide targets.

TF-ThP28 Study of Semiconductors III-V, IV-VI and II-VI Films Growth by PLD-M System, ***M. González-Alcudia***, CICATA-IPN, México, *M. Meléndez-Lira,* CINVESTAV-IPN, México, *O. Calzadilla-Amaya,* Universidad Habana, Cuba, *M. Zapata-Torres*, CICATA-IPN, México

This research seeks to develop improved and innovative growth technique (pulsed laser deposition modified: PLD-M) for growing thin films based on III-V elements, such as Si and Ge, or II-VI elements, such CdS, CdTe and Tellurides. In addition, on advanced semiconductor alloy combinations such as CdTe/PbSnTe or other promising materials. Compared them with conventional growth of pulsed laser deposition for films, concerning microstructural properties. Films with different droplets morphology could be obtained under mild conditions. The films were characterized by X-ray diffraction (XRD) and SEM. The radius of droplets formed during single pulse irradiation is the rKH ≈ 0.05 - 5 μm. Our experiment shows that source materials and reaction temperature play important roles in forming the objective products and controlling their morphologies. By this method, it is possible to prepare at low temperature, films with good chemical homogeneity.

TF-ThP29 Mutual Inductance Characteristics of a Thin Film Planar Loop, ***G.A. Topasna***, *D.M. Topasna, F.R. Powell*, Virginia Military Institute

We present a model of the mutual inductance of a thin film planar loop that is flux linked to a short straight wire. The mutual inductance is dependent on the geometry of the planar loop as well as its location relative to the wire. Our calculations provide closed-form and numerical solutions for various geometries. Calculations for the induced emf in the loop are compared to experimental measurements for various configurations.

TF-ThP30 Room Temperature Photoluminescence from CdTe Nanocrystals Embedded within a SiO_2 Matrix Deposited on Silicon Employing Reactive RF Sputtering, ***E. Mota-Pineda***, *M.A. Melendez-Lira*, CINVESTAV IPN Mexico

CdTe nanocrystals embedded in a SiO2 matrix were fabricated by radio frequency sputtering employing the texture of a SiO2 layer as template. The SiO2 film texture was controlled through the partial pressure of O2 (OPP) in the working atmosphere. The CdTe crystallinity is better for the samples synthesized on the rougher SiO2 films. Room temperature photoluminescence spectra showed a signal at 1.74 eV, related to the CdTe nanoparticles, for the samples that shown better crystallinity. Additional photoluminescence signals at 1.65 eV and 1.68 eV could indicate recombination process at the nanoparticles/matrix interface. These results indicate that the employed methodology allows to obtain room temperature light emitting CdTe nanoparticles in a single step. After thermal annealing all samples presented light emission related to quantum confinement; the photoluminescence emission can be controlled from 1.69 eV to 2.15 eV by an appropriate adjust of the OPP.

TF-ThP31 The Influence of Pt Layers on the Corrosion Resistance of TiAl/TiAlN Multilayers, ***M. Flores***, Universidad de Guadalajara, Mexico, *J. Avalos*, UAM-I, Mexico, *L. Huerta, R. Escamilla*, UNAM, Mexico

In this work we report the results of studies of the influence of Pt layers on the corrosion resistance of TiAL/TiALN multilayers deposited on 316L stainless steel. The multilayers were deposited by magnetron sputtering using targets of TiAL and Pt. The thickness of the Pt layers was from 50 nm to 500nm. The corrosion was studied using open circuit potential measurements and potentiodinamyc polarizations in ringer solutions. The results indicate that the corrosion resistance of TiAL/TiAlN multilayers is improved when Pt layers are deposited. The structure of multilayers was studied by means of XRD analysis. It was found that Pt layer has a strong influence on the structure of subsequent TiAlN layer. The corroded surface was studied by means of SEM and EDS. Pitting corrosion was observed in TiAl/AlTiN multilayers analyzed samples. RBS depth analysis was useful to determine the composition of each film and for modeling the interface characteristics through the heterostructure.

TF-ThP32 Characterization of Metal Oxide Electrical Properties for Band Engineered Catalysis, ***M.C. Kratzer***, *E.G. Seebauer*, University of Illinois at Urbana-Champaign

There is good reason to believe that the properties of semiconducting metal oxide catalysts can be improved when designed according to the principles of microelectronic devices. Since oxide semiconductors support space charge, it is possible for surface electronic properties to couple to bulk electronic properties. As a consequence, catalyst surface reactivity can be modified via electronic "band engineering," wherein the electronic properties of the underlying bulk alter the oxidation state of active sites at the free surface or modify the electric field in the space charge region adjacent to the surface. For example, hydroxyl group acidity on the TiO_2 surface can be tuned via the electron richness of the semiconductor, which can be manipulated via controlled doping. Current metal oxide catalyst synthesis methods do not permit doping with the requisite control for the band engineering approach, partly due to problems with measuring majority carrier type and concentration. Such determinations are difficult for metal oxides because the contacts employed for four-point-probe measurements need to obey Ohm's Law but, in practice, behave as diodes. The present work describes new methodology to solve this metrology problem, using TiO_2 as an example metal oxide. The approach involves synthesis of a thin film of the semiconductor on a silicon substrate by chemical vapor deposition or atomic layer deposition. A Schottky diode structure is then fabricated on the film to obtain the doping concentration from high frequency C-V measurements. For TiO_2, this approach has been implemented with aluminum contacts to the TiO_2 and InGa eutectic alloy contacts to the underlying silicon. The novelty of the structure lies in its compatibility with oxide semiconductors having widely varying doping levels, and the use of easily applied electrical contacts. Oxide thickness, uniformity, and crystal structure can be precisely tailored to suit the subsequent choice of reaction chemistry. A wide variety of fabrication issues have been characterized, including surface and interface preparation, contact metal type, and method of contact deposition. Detailed I-V measurements confirm diode-like behavior that is free from spurious artifacts and amenable to standard Mott-Schottky analysis. Values for the depletion width, barrier height, and series resistance are reported for the example case of TiO_2 synthesized from titanium tetraisopropoxide and O_2.

TF-ThP33 Deposition and Characterization of Bi doped $Ge_2Sb_2Te_5$ Thin Films for Phase Change Random Access Memory Application, ***J.H. Lee****, S.W. Ryu, Y.B. Ahn, C.S. Hwang, H.J. Kim*, Seoul National University, South Korea

Among the next-generation resistance based memories, PcRAM stores the digital data as different resistances of the phase change material between amorphous and crystalline phase. Although PcRAM has superior performances, there are still critical issues to be resolved i.e. reducing high amorphization current,[1] enhancing slow crystallization speed. $Ge_2Sb_2Te_5$ is the most well known phase change material for PRAM. Attempts has been made to improve the phase change properties of $Ge_2Sb_2Te_5$ by doping various elements and compounds such as N,[2] O[3] and SiO2.[4] In this report $Ge_2Sb_2Te_5$ was manipulated by doping Bi. Incorporation of Bi into $Ge_2Sb_2Te_5$ thin film was performed in two ways. First, by cosputtering Bi_2Te_3 and $Ge_2Sb_2Te_5$. Second, by sputtering $Ge_2Bi_2Te_5$ and $Ge_2Sb_2Te_5$ simultaneously. By cosputtering Bi_2Te_3 and $Ge_2Sb_2Te_5$, Bi was successfully incorporated into the lattice, which was confirmed by shifts in XRD peak positions compared to those of undoped $Ge_2Sb_2Te_5$. Cosputtering $Ge_2Bi_2Te_5$ and $Ge_2Sb_2Te_5$ guaranteed fixed atomic percentage of Ge and Te in the film with varying Bi contents. When the amorphous Bi doped $Ge_2Sb_2Te_5$ films crystallized by thermal annealing at about 150 °C, the resistivity of the film was reduced over 3 orders of magnitude, which was sufficient for device application. The Bi doped $Ge_2Sb_2Te_5$ films showed lower amorphization voltage without having to increase the crystalline resistance and demonstrated faster crystallization speed than those of $Ge_2Sb_2Te_5$.

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TF-ThP34 Dynamic Scaling and Optical Study for Optimization of Thermally Evaporated Ag Thin Films on Glass, ***J.R. Skuza****, C. Clavero, R.A. Lukaszew*, College of William & Mary

Noble metal (e.g. Ag, Au) thin films, also in nano-structured form, have recently been the subject of intense research for their possible applications (e.g. chemical and biological sensors, PV devices, etc.). Thermal evaporation is a suitable thin film deposition method that yields high quality Ag thin films. For example, reproducible production of thermally evaporated Ag thin films with tunable surface plasmon resonance wavelengths has been demonstrated with precise control of the deposition parameters.[1] Thus, understanding the growth dynamics of Ag thin films onto glass substrates by thermal evaporation and correlating these with optical properties is of great interest to link specific growth parameters to their desired properties. The surface of a film growing under non-equilibrium conditions often develops in agreement with the concept of dynamic scaling, where scaling exponents (e.g. α, β) can be used as the spatial and temporal signatures of highly complex growth processes.[2,3] Here, we present a scaling analysis study on the surface morphology of thermally evaporated Ag thin films on glass substrates observed with atomic force microscopy. We find a dramatic change in the scaling exponents as a function of deposition rate, suggesting that there exists an optimum deposition rate in the range of studied values. This implies that there are competing mechanisms during the growth, such as the interaction energy of the adatoms and the substrate and their dynamics on the surface during the early stages of growth. Furthermore, these changes affect the microstructure and also have a profound effect on the optical properties, and in this case, we find that the optical properties of the Ag thin film approach bulk values at the optimum deposition rate.

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TF-ThP35 Study of Slope Distribution with Mathematical Molding on Au(111) Thin Film Growth, ***A. Gonzalez-Gonzalez****, J.L. Sacedon, E. Rodriguez-Cañas,* Instituto de Ciencia de Materiales de Madrid (CSIC), Spain, *J.A. Aznarez,* Instituto de Fisica Aplicada (CSIC), Spain, *E. Vasco*, Instituto de Ciencia de Materiales de Madrid (CSIC), Spain

In the present work two statistical methods of growth front analysis, the minimalist analysis and the mathematical molding, are compared. The minimalist method, previously developed,[1,2] is able to give a statically complete description of the surface, based in a linear limited sampling. It includes the capability to interpret the distribution of slopes at the border of surface protrusions. At difference the mathematical molding method allows to extend the sampling to all the image points and its handling is automatic. Applications of both methods on growth fronts of Au(111) thin films are presented. Thin Au films were thermally evaporated on Au epitaxied /mica substrates at 373K substrate temperature, resulting in a out of equilibrium mound growth (up to 60nm thick) on extended single crystalline plates. Atomic Force Microscopy (AFM) measurements were carried out to investigate the morphology of the films using high aspect ratio tips (nominal tip radius of 2 nm) to achieve high lateral resolution (estimated to be less than 3 nm). The molding algorithm is based on adaptive numerical interpolations of the AFM-measured surfaces by polynomial methods, the extended sampling results are coherent and can be interpreted with the set of parameters and shapes used in the minimalist method, allowing a better statistical determination. Using this method, we have investigated the evolution of the surface slopes with the film thickness and we were able to correlate slope distribution with terrace selected slope models and crystalline facets shaping the surface features.

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