Thin Film

Room: 613/614 - Session TF-MoM

Atomic Layer Deposition and Applications

Moderator: G.N. Parsons, North Carolina State University

8:40am **TF-MoM3 Conformal Polymeric Thin Films via Initiated Chemical Vapor Deposition**, *S.H. Baxamusa, M. Gupta, **K.K. Gleason***, Massachusetts Institute of Technology **INVITED**

Conformal surface modification of high aspect ratio micro- and nano-structures is desirable for a range of applications ranging from microelectronics to textiles. In this work, initiated chemical vapor deposition (iCVD) is demonstrated to conformally deposit thin polymer films (<500 nm) at high growth rates (up to 100 nm/min). The iCVD technique is a low energy process (0.01 W/cm^2) that fully retains the pendent functionality in the deposited polymer films, a result that has been demonstrated with more than 40 different vinyl monomers. The iCVD method is particularly valuable for creating ultrathin layers of insoluble polymers. For the process, initiator and monomer vapors simultaneously flow into a vacuum where decomposition of the initiator results in free-radical polymerization of the monomer on the substrate. As iCVD relies on neutral chemistry, directional effects on deposition typically associated with the electric fields in plasma processes are avoided. Step coverage of trenches in silicon substrates by polymeric iCVD coatings will be shown to depend on the ratio of monomer to initiator. A kinetic model highlights the surface-driven nature of iCVD polymerization and that is analogous to free radical polymerization in the bulk phase, albeit on the surface. The iCVD process is often absorption limited and hence cool (~25 ºC) substrates are essential for rapid film growth. From an applications perspective, low substrate temperatures are favorable for the coating of thermal sensitive materials, including paper, plastics, fabrics, and membranes. The iCVD process can be used to functionalize membranes with high aspect ratio (80:1) pores with a hydrophobic polymer coating. X-ray photoelectron microscopy data confirmed the presence of the iCVD coating on the topside and backside of the membranes and electron microprobe analysis confirmed the presence of the coating along the pore wall. Additionally, the iCVD process has been demonstrated conformally to coat carbon nanotube forests and microparticles. Superhydrophobic surfaces (contact angles >175 degrees) result from surface modification of nanostructured substrates by iCVD PTFE and polymerized perfluoroalkyl ethyl methacrylate.

9:20am **TF-MoM5 Nanolaminate Gas Diffusion Barriers on Polymers with Exceptionally Low H_2O Permeabilities**, *A.A. Dameron, **S.M. George***, University of Colorado at Boulder, *P.F. Carcia, R.S. McLean*, DuPont Research and Development

Flexible, ultrathin gas diffusion barriers are required for the protection of organic electronics, e.g. organic light emitting diodes (OLEDs) in flexible displays. Existing barriers provide insufficient protection from permeating H_2O and O_2 gases. Our earlier work demonstrated that a low water vapor transmission rate (WVTR) of ~1 × 10^{-3} g/m^2/day could be achieved on polyethylene naphthalate (PEN) and Kapton using Al_2O_3 ALD films with thicknesses of ~25 nm. These H2O transmission rates are not low enough to meet OLED requirements. The Al_2O_3 ALD films also degrade over time with exposure to H_2O vapor. To lower the H_2O transmission rates further and to protect the Al_2O_3 ALD films, we have used additional layers in combination with the ~25 nm Al_2O_3 ALD layer. The additional layers were one layer of silicon nitride with a thickness of >60 nm deposited by plasma-enhanced chemical vapor deposition (PE-CVD) or one layer of SiO_2 with a thickness of ~60 nm deposited using rapid SiO_2 ALD. Both of these additional layers in combination with the ~25 nm Al_2O_3 ALD layer reduced the measured WVTR to ~1 × 10^{-4} g/m^2/day. When deposited on top of the Al_2O_3 ALD film, these silicon-containing layers also protect the Al_2O_3 ALD film from H_2O exposure. Nanolaminates of Al_2O_3 ALD and SiO_2 ALD should further reduce the WVTRs. These nanolaminate films are fabricated by alternating the Al_2O_3 ALD and SiO_2 ALD to create 2 bilayers, 3 bilayers or higher numbers of bilayers. Tests of multiple bilayer nanolaminate structures of Al_2O_3 ALD and SiO_2 ALD on Kapton have yielded extremely low WVTRs of 5 × 10^{-5} g/m^2/day using the HTO testing technique. These exceptionally low WVTRs are approaching the range that is necessary for OLED devices in flexible displays.

9:40am **TF-MoM6 Atomic Layer Deposition for Passivation and Corrosion Protection of Metal Substrates**, ***S.I. Sneck***, Beneq, Finland

The unique features of Atomic Layer Deposition; capability to produce highly conformal pin-hole free films on complex structures and excellent adhesion to most surfaces, have been utilized mainly by the semiconductor industry. However, these properties are often highly appreciated by many other industries as well. As an example, silver industry has recently started using ALD to protect silver jewelry from tarnishing. Tarnishing is mostly caused by airborne sulfur compounds forming black silver sulfide on the surface of a silver object. In this application, the most important criteria are invisibility and anti-tarnish properties of the coating. A uniform 10nm thick aluminum oxide layer increases the tarnishing time by two orders of magnitude while being invisible to human eye. The same method can also be applied to other silver products as well as other metals, including copper and copper containing alloys. In addition to passivation of silver and copper based products, more demanding anti-corrosion coatings can be done on stainless steel and other common construction metal parts used in extreme conditions. Relatively low growth rate of ALD compared to other thin film techniques can be compensated with large batch size, since ALD is one of the easiest thin film processes to scale-up. ALD films can also often be much thinner compared to films prepared with other thin film techniques, for example if certain barrier properties are required. This is due to higher film uniformity and fewer pin holes in ALD films. Even though most work with ALD has been done on silicon and glass substrates, metal substrates offer many applications for ALD, since complex shaped parts are often made of metal. By careful selection of coating structure, it is possible to combine anti-corrosion coatings with other functions, including decorative and wear resistant functions.

10:20am **TF-MoM8 Combinatorial Atomic Layer Deposition of Nanolaminates**, ***W.L. Gladfelter**, T. Moersch, L. Zhong, B. Luo*, University of Minnesota **INVITED**

Nanolaminates of HfO_2 and SiO_2 were prepared using atomic layer deposition methods. Successive exposure of substrates maintained at 120 or 160°C to nitrogen flows containing $Hf(NO_3)_4$ and $(^tBuO)_3SiOH$ led to typical bilayer spacings of 2.1 nm with the majority of this being SiO_2. Combining the $Hf(NO_3)_4/(^tBuO)_3SiOH$ ALD with ALD cycles involving $Hf(NO_3)_4$ and H_2O allowed the systematic variation of the HfO_2 thickness within the nanolaminate structure. This provided an approach towards controlling the dielectric constant of the films. The dielectric constant was modeled by treating the nanolaminate as a stack of capacitors wired in series. The nanolaminate structure inhibited the crystallization of the HfO_2 in post-deposition annealing treatments. As the HfO_2 thickness decreased, the preference for the tetragonal HfO_2 phase increased. Nanolaminates of SiO_2 with compositionally graded mixture of HfO_2 and ZrO_2 were deposited using a combinatorial ALD process. Exposure of repeated cycles of co-dosed alkoxide precursors $Hf(O^tBu)_4$ and $Zr(O^tBu)_4$ with counter-reactant pulses of $Si(O^tBu)_3(OH)$ formed films of uniform thickness (±5%) and uniform silicon oxide concentration. The hafnium and zirconium concentrations exhibited smooth graduation across the film from 18% - 82% (per Hf and Zr metals basis). Self-limiting deposition rates of 1.5 nm/cycle were measured, and a linear relationship of film thickness to number of deposition cycles was observed, both consistent with a true ALD process. Elemental analysis by Rutherford backscattering spectrometry, thickness measurements by ellipsometry, capacitance measurements, electron microscopy, X-ray reflectivity and X-ray diffraction results were used to map the composition and determine the film microstructure. Deposition of mixed films of SrO and HfO_2 were deposited by the related combinatorial chemical vapor deposition process using $Sr(tmhd)_2[HN(CH_2CH_2NMe_2)_2]$, where tmhd = 2,2,6,6-¬tetramethylheptane-3,5-dionato, as the strontium precursor and $Hf(O^tBu)_4$ as the HfO_2 source. XRD showed that films with low Sr concentrations, e.g. < 15% Sr, exhibited a crystalline phase consistent with Sr-stabilized cubic hafnia. Films with higher Sr contents were amorphous. The dielectric constants of the films increased as the proportion of the cubic phase increased. A maximum value of 25 was obtained for the film with a Sr/(Sr + Hf) ratio of 0.07. We will report on our attempts to extend this CVD process to ALD.

11:00am **TF-MoM10 Combinatorial Strategy to Address the Complexities of Surface Chemistry and Multicomponent Materials in Atomic Layer Deposition**, ***L. Henn-Lecordier**, E. Robertson, P. Banerjee, G.W. Rubloff*, University of Maryland

While atomic layer deposition (ALD) shows unique promise for highly controlled deposition of super-conformal thin films, its perfection and practice are limited by (1) reactant dose (inter)dependencies that reflect deviations from perfect self-limiting reaction and (2) the numerous permutations of stoichiometry that must be investigated to exploit ternary and higher materials systems. We have developed a combinatorial ALD approach to efficiently address these challenges. A wafer-scale (4- OD) substrate-heated ALD mini-reactor delivers reactant gases across the wafer, maintained in a small reactor volume to achieve short cycle times. Downstream mass spectrometry reveals the ALD surface chemistry in real time, enabling direct observation of reaction product generation as a function of dose, as well as direct thickness vs. time determinations during nucleation and growth stages of the ALD process.[1,2] With increasing dose, nominally complete surface saturation conditions are observed. As reactant dose is decreased, incomplete surface coverage is expected and identified, which corresponds to across-wafer depletion conditions in the cross-flow geometry of the mini-reactor. By achieving such depletion, various combinations of reactant dose ratios for binary constituents provide a combinatorial gradient library for ALD process recipe optimization. Results for Al_2O_3 deposited by ALD from TMA and H_2O demonstrate the ability to create linear thickness gradients across the wafer. This combinatorial synthesis is coupled with post-process electrical characterization of MIS capacitors using I-V and C-V measurements automated to assess several hundred devices across the wafer, complemented by wafer maps of thickness and composition. Together these directions reflect an effective strategy for evaluating and optimizing ALD process recipes as well as extending the approach to ternary systems, e.g. Hf aluminates. Work supported in part by MKS Instruments.

[1] "Real-time observation and optimization of tungsten ALD process cycle", W. Lei, L. Henn-Lecordier, M. Anderle, Gary W. Rubloff, M. Barozzi, and M. Bersani, J. Vac. Sci. Technol.B 24 (2), 780-789 (Mar/Apr 2006).

[2] "Real-time sensing and metrology for atomic layer deposition processes and manufacturing", L. Henn-Lecordier, W. Lei, M. Anderle, and G.W. Rubloff, J. Vac. Sci. Technol. B 25 (1), 130-139 (Jan/Feb 2007).

11:20am **TF-MoM11 Physical and Electrical Characteristics of $Zr_xHf_{1-x}O_y$ Films Deposited by Atomic Layer Deposition Method**, ***S. Bang***, *S. Lee, S. Jeon, S. Kwon, W. Jeong, I. Kim, H. Jeon*, Hanyang University, Korea

Zirconium and hafnium-based dielectric materials have been widely studied as a gate oxide for the next generation of CMOS technology due to high dielectric constant, a relatively wide band gap and thermodynamic stability on Si. However, ZrO_2 and HfO_2 films can be crystallized at the temperature below 500°C. For gate dielectrics, an amorphous structure is always preferred to a polycrystalline structure, because a crystalline film can induce high grain boundary leakage current and lead to non-uniformities in k value and in film thickness. Thus, efforts have been made to improve the properties of HfO_2 and ZrO_2 by adding different elements such as Si, Al, N, Ti, and Ta. Addition of Si, Al, or N allows for the increased crystallization temperature of HfO_2 and ZrO_2. However, there is a drawback of a lowered dielectric constant. Although the addition of Ti can increase dielectric constant of HfO_2 and/or ZrO_2 films, it can degrade the leakage current characteristics by decreasing a band offset. The addition of metal elements to improve the quality of high-k oxide film, without reducing dielectric constant and increasing leakage current, is important. ZrO_2 has similar chemical structure to HfO_2 and is completely miscible with HfO_2. Zr addition can yield stability to the higher dielectric constant tetragonal phase. In this study, we deposited $Zr_xHf_{1-x}O_y$ films varying with the content of Zr on Si substrates by adding Zr into HfO_2 film using atomic layer deposition (ALD) process and investigated its physical and electrical characteristics. Auger electron spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) were used to analyze the chemical composition and bonds. AES and RBS data indicated that the composition ratio of $Zr_xHf_{1-x}O_y$ films is varied as the Zr content change in those films. And X-ray diffraction (XRD) was used to analyze the structure properties of $Zr_xHf_{1-x}O_y$ films. The capacitance values of $Zr_xHf_{1-x}O_y$ films showed about 415 ~ 620pF/cm^2 on capacitance-voltage (C-V) measurement. For the analysis of other electrical properties, C-V and current-voltage (I-V) analyses were measured to evaluate the dielectric constant, EOT, and leakage current of $Zr_xHf_{1-x}O_y$ films, etc.

11:40am **TF-MoM12 An ALD Growth Study of ZrO_2 on Si(100)**, ***P.J. Evans***, *G. Traini, J. Murison, M.J.Y. Tayebjee, N. Loh, D.-H. Yu, A.P.J. Stampfl*, Australian Nuclear Science and Technology Organisation, *T.-W. Pi*, National Synchrotron Radiation Research Center, Taiwan

Zirconium and some of its alloys, oxides and nitrides are known for their anti-corrosive and excellent wear resistant character. For this reason the nuclear industry uses Zr-based materials due to their low neutron absorption character, mechanical strength, toughness and ability to withstand harsh environmental conditions such as high temperatures and intense radiation. ZrO_2 has also been singled-out as a candidate material for inert matrix fuels to be used in Generation IV nuclear reactors. The formation of ZrO_2 under different growth conditions leads to variations in electronic properties and crystal structure. Control of growth will enable tuning the electronic and structural properties of this material for specific applications. The current preliminary study investigates the effect of deposition conditions on the electronic and crystal structure of ALD grown ZrO_2 films on silicon, using synchrotron-based high resolution photoemission, TEM, SIMS and glancing angle x-ray diffraction. The precursors used in the deposition were $ZrCl_4$ and H_2O using two growth temperatures of 200°C and 300°C. In addition, ZrO_2 films were subjected to rapid thermal annealing at 600°C to investigate their valence electronic structure on crystallization.

Thin Film

Room: 613/614 - Session TF-MoA

Emerging Topics in Atomic Layer Deposition

Moderator: S.M. George, University of Colorado at Boulder

2:00pm **TF-MoA1 Atomic Layers in Nano(bio)technology**, ***M. Knez***, *L. Zhang, S.-M. Lee,* Max-Planck-Institute of Microstructure Physics, Germany, *A.J. Patil, S. Mann,* University of Bristol, UK, *K. Nielsch, U. Gösele*, Max-Planck-Institute of Microstructure Physics, Germany**INVITED**

In nanotechnology biological systems play an increasingly important role, since some of the naturally occurring biological macromolecules show perfect order on the nanoscale. The perfection of the natural organization of molecules is, in particular for the nanotechnology, often a target for imitation, but can almost never be obtained in a similar quality. An alternative way to obtain nano- or microstructures in close similarity to natural ones is their structural replication from inorganic materials or the modification of the chemical or physical properties of such systems by attachment of inorganic materials. Some of the methods applied recently rely on wet-chemistry which frequently leads to non-uniformity or bad quality of the attached materials. The ALD is one method-of-choice for performing such replication and modification experiments, since it offers the unique possibility to cover biological structures with inorganic films as thin as few Angstroms or nanometers. In this way a number of novel nanostructures with interesting properties can be synthesized, however, limited with the deposition processes which can be performed at temperatures below the stability limit of the biological or organic molecular units.

2:40pm **TF-MoA3 Al_2O_3 and W/Al_2O_3 Atomic Layer Deposition on Quantities of Multiwalled Carbon Nanotubes**, ***A.S. Cavanagh***, *C.A. Wilson, S.M. George*, University of Colorado at Boulder

Atomic layer deposition (ALD) can be employed to coat individual single-walled (SW) and multi-walled (MW) carbon nanotubes (CNTs). We have performed Al_2O_3 and W/Al_2O_3 ALD on quantities of multiwalled carbon nanotubes (MWCNTs) in a rotary reactor designed for ALD on high surface area nanoparticles. Al_2O_3 ALD was performed using trimethylaluminum (TMA) and H_2O. W ALD was performed using WF_6 and Si_2H_6. Al_2O_3 ALD on MWCNTs yielded nanospheres that grew with the number of trimethylaluminum and H_2O reaction cycles. Al_2O_3 ALD is believed to nucleate only at defect sites on the surface because the graphene surface of MWCNTs is unreactive. The NO_2/TMA nucleation procedure developed by Farmer and Gordon [Nano Letters 6, 699 (2006)] for ALD on SWCNTs was used to obtain very conformal Al_2O_3 ALD films on gram quantities of MWCNTs. The Al_2O_3 ALD films grew linearly with the number of TMA/H_2O reaction cycles. This Al_2O_3 ALD film is not covalently attached to the MWCNTs. Evidence for only a physisorption interaction was provided by ALD-coated MWCNTs where the Al_2O_3 ALD coating had broken to yield "ALD macaroni on a CNT string". W ALD also grew on the conformal Al_2O_3 ALD coating to create W/Al_2O_3 bilayers. X-ray photoelectron spectroscopy indicated that the surface of the metallic W was oxidized to form WO_3 upon exposure to atmosphere. The W ALD oxidization should be avoided by passivation with Al_2O_3 ALD. Calculations show that a metallic W ALD coating significantly enhances the CNT conductivity.

3:00pm **TF-MoA4 Molecular Layer Deposition of Alkyl-Aromatic Polyamide Films**, ***Q. Peng***, *R.M. VanGundy, G.K. Hyde, S.M. Stewart, G.N. Parsons*, North Carolina State University

Organic thin film materials with well controlled microstructure have significant applications in organic light-emitting devices, organic thin film transistors, organic photovoltaic cells, quantum devices, molecular electronics, biomaterial interfaces, and others. Molecular layer deposition (MLD) is a binary self-limited deposition process to form uniform and conformal polymer thin films with well controlled microstructure. We have recently investigated vapor-phase polymer MLD using (1, 4 butane diamine) and aromatic (terephthaloyl dichloride) polyamide. 1, 4 butane diamine and terephthaloyl dichloride were evaporated at room temperature and 70°C respectively. Growth on a variety of surfaces, including Au, Si-OH, Si-H, methyl-terminated Si, and amino-terminated Si, was investigated, with substrate temperature controlled between 70 and 150°C. An in-situ quartz crystal balance was used to monitor the adsorption and desorption behavior of the monomers. Generally, the deposition rate decreased as the reaction temperature increased. At 85°C, the thickness of the polyamide film measured using ellipsometry as a function of the number of deposition cycles results in a growth rate of 0.2 nm/cycle. Transmission infrared spectroscopy verified the characteristic polyamide peaks in the films. Contact angle measurements were carried out after each monomer dosing cycle resulting in expected changes in the surface energy with each half-cycle. The thermal stability, chemical inertness and capacitance properties of the deposited polymer thin film were also characterized. Results give insight into process requirements to achieve well controlled molecular layer deposition of organic films that include aromatic elements.

3:40pm **TF-MoA6 Fabrication of Hybrid Inorganic/Organic Multilayers Using Atomic and Molecular Layer Deposition**, ***D. Seghete***, *S.M. George*, University of Colorado at Boulder

Inorganic/organic multilayers occur in the nacreous layer of the mollusk shell and are among the strongest structures in nature. These "brick and mortar" composites are known for their high elasticity, toughness, and hardness. In this study, we report the fabrication of alternating inorganic and organic multilayers consisting of inorganic alumina (Al_2O_3) or tungsten (W) in combination with organic alucone polymer. Al_2O_3 atomic layer deposition (ALD) is performed using trimethylaluminum (TMA) and H_2O as the reactants. W ALD is accomplished using WF_6 and Si_2H_6 as the reactants. The organic alucone layer is grown using molecular layer deposition (MLD) with TMA and ethylene glycol as the reactants. The growth of the inorganic/organic multilayers was investigated using in situ quartz crystal microbalance studies. The nucleation of the inorganic Al_2O_3 or W ALD was explored on the alucone layer. The nucleation of the organic alucone MLD was also examined on the Al_2O_3 and W layers. The nucleation behavior provides information about the bonding between the inorganic and organic layers. The adhesion between the inorganic and organic layers is important for the mechanical properties of these multilayer structures. The structure and stability of the inorganic/organic multilayers were also explored using x-ray reflectivity measurements. Future mechanical property studies are planned using a nanoindenter.

4:00pm **TF-MoA7 Optimization of ALD Conformality in Ultra-High Aspect Ratio Nanopores Formed in Anodic Aluminum Oxide Templates**, ***E. Robertson***, *I. Perez, L. Henn-Lecordier, S.J. Son, S.B. Lee, G.W. Rubloff*, University of Maryland

The very high conformality for thin film deposition in high aspect ratio structures is a major driver for broad use and adoption of atomic layer deposition (ALD) processes. ALD is particularly promising for applications coupled to anodic aluminum oxide (AAO) membranes, in which cylindrical nanopores with uniform dimensions (15-300nm dia) and spacing are formed by self-assembly during anodization. In turn these structures form templates useful for creating energy and display devices within the AAO template, or released nanotube or nanowire systems after AAO dissolution, e.g. for nanoparticle-based targeted drug delivery. We have created high-K dielectric nanotubes by HfO_2 ALD in AAO templates to investigate the relationship between ALD process parameters and the conformality of the ALD films in the nanopores as a function of nanopore dimensions and aspect ratios. SEM was used to measure pore diameters (40-80nm) before and after the ALD deposition. The HfO_2 nanotubes were then released by dissolution of the AAO template and examined via TEM imaging of the nanotubes on standard grids. TEM profiles showed HfO_2 nanotubes with lengths 1-2 microns (determined by the AAO template) and having wall thicknesses in the range 3-10 nm which vary with position along the depth of the original AAO nanopores. The AAO templates are attractive both for the applications above and for the ease with which they generate very high aspect ratio nanopores to study ALD conformality, while the nanotube release through AAO template dissolution provides a very simple means to achieve TEM analysis of ALD conformality. These advantages are particularly striking in comparison to requirements for more conventional high aspect ratio devices such as DRAM trench structures, where challenging lithography, dry etching, etc. must be combined with difficult cross-sectional TEM sample preparation to understand and optimize ultrathin conformal device layers.

4:20pm **TF-MoA8 Molecular Layer Deposition of Alucone Polymer Films Using Trimethylaluminum and Various Glycols**, ***A.A. Dameron***, *S.D. Davidson, B.B. Burton, J.A. McCormick, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Conformal polymeric films can be grown by a sequential, self-limiting surface chemistry process known as molecular layer deposition (MLD) that is very similar to atomic layer deposition (ALD). The MLD reactants are typically monomers for step-wise condensation polymerization and can yield completely organic or organic-inorganic alloys. Our earlier work has demonstrated polyamide growth using diamines and diacid chlorides. Alucone MLD is performed using trimethylaluminum (TMA) and various glycols as the reactants. When the glycol is ethylene glycol (EG), the alucone is poly(aluminum ethylene glycol), $[Al-(OCH_2CH_2O)_x]_n$. Alucone films have been fabricated on silicon substrates at temperatures ranging from 85 °C to 175 °C. In situ quartz crystal microbalance and ex situ x-ray reflectivity experiments have confirmed linear growth of the alucone film versus number of TMA/EG reaction cycles at all temperatures. The MLD growth rates decreased at higher temperatures. Growth rates were 4 Å per cycle at 85 °C and 1.7 Å per cycle at 135 °C. In situ and ex situ Fourier transform infrared spectroscopy (FTIR) have also been used to monitor the surface reactions during alucone growth. Experiments with other glycols, such as benzene-1,4-diol (hydroquinone), demonstrate the general applicability of the alucone MLD surface chemistry to fabricate organic-inorganic films with tunable functionality.

4:40pm **TF-MoA9 Film Properties and In-Situ Optical Analysis of TiO_2 Layers Synthesized by Remote Plasma ALD**, ***W. Keuning***, *J.L. Van Hemmen, O. Muraza, E. Rebrov, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

TiO_2 is a widely studied material due to its optical and photocatalytic properties and its hydrophilic nature after prolonged UV exposure. When synthesized by atomic layer deposition (ALD) the TiO_2 can be deposited with ultimate growth control with a high conformality on demanding topologies and even at room temperature when e.g. using a plasma based process. We report on the deposition of TiO_2 films using remote plasma ALD with titanium (IV) isopropoxide as precursor and O_2 plasma as oxidant. Stochiometric TiO_2 films with carbon and hydrogen levels below the detection limit of Rutherford backscattering/elastic recoil detection (< 2 at.%) have been deposited within the temperature range of 25°C to 300°C. Depending on the ALD conditions and film thickness amorphous films turn anatase for temperatures higher than 200°C as revealed by X-ray diffraction. It is demonstrated that this change in crystal phase can also be observed by spectroscopic ellipsometry revealing an increase in growth rate per cycle (from typically 0.45 Å/cycle to 0.7 Å/cycle) and change in bandgap (from 3.4 eV to 3.7 eV) when the TiO_2 becomes anatase. An accompanying change in surface topology is clearly observed by atomic force microscopy. The hydrophilicity of low temperature TiO_2 films is studied by contact angle measurements for adhesion purposes revealing that the amorphous films are super-hydrophilic after UV exposure.

Plasma Science and Technology

Room: 606 - Session PS1+TF-TuM

Plasma Enhanced Atomic Layer Deposition and Plasma Deposition

Moderator: S. Agarwal, Colorado School of Mines

8:00am **PS1+TF-TuM1 Characteristics for HfO_2 Gate Dielectrics Deposited by Remote Plasma ALD Method**, *S. Kim, **H. Jeon***, Hanyang University, South Korea **INVITED**

Many high-k dielectric materials have been studied extensively to replace current gate dielectric materials such as SiO_2 and SiO_xN_y. Among the high-k dielectric materials, Hf-oxide is considered to be one of best choices for 45 nm technology and beyond. However, most of high-k oxides such as HfO_2, ZrO_2, Ta_2O_3, and TiO_2 are transition metal oxides with the ionic nature and have poor interface quality and poor thermal stability with Si substrate. In addition, they exhibits high oxide traps and interface state densities, and large amount of oxygen vacancies, and are easily crystallized compared to SiO_2. To overcome these drawbacks of high-k oxides, the technologies for growing high quality high-k oxides and improving the interface properties between high-k oxide and Si substrate are required. In this study, we chose HfO_2 as high-k gate dielectrics and atomic layer deposition (ALD) as a deposition method. Among many deposition methods, ALD method is studied by many researchers because of its thin film deposition superiority. In our lab we applied both direct plasma ALD (DPALD) and remote plasma ALD (RPALD) methods to grow HfO_2 thin films on Si substrates. These two different plasma methods exhibited the different thicknesses of silicate interlayer. We believe this interlayer is critical for the degradation of high-k dielectric materials. To investigate these interlayers we grew several different buffer layers before HfO_2 growth. These buffer layers were formed by remote plasma oxidation (RPO) and nitridation (RPN) on Si substrates to monitor this interlayer, to suppress the initial formation of Hf silicate or interlayer and to improve the interlayer quality. The buffer layers were thin SiO_2, SiO_xN_y, Al_2O_3, nitrided Al silicate and nitrided Hf silicate layers. The HfO_2 films with buffer layers suppressed silicate formation or growth of an interlayer more effectively than those without buffer layers. The HfO_2 films with buffer layers also showed lower effective oxide thickness (EOT), lower effective fixed oxide charge density ($Q_{f,eff.}$), and lower leakage current density compared to those without buffer layers. The physical and electrical properties of HfO_2 with buffer layers will be presented and discussed depending on the various buffer layers.

8:40am **PS1+TF-TuM3 Pulsed Plasma-Enhanced Pulsed CVD of Y_2O_3 in MIM Capacitors**, ***C, Vallee**, M. Kahn, E. Gourvest, M. Bonvalot, O. Joubert*, CNRS, France

The development of integrated metal-insulator-metal (MIM) capacitors for advanced analog and rf circuits aims at achieving development of capacitors with higher capacitance density, low leakage current, and good voltage linearity. High k materials are thus integrated and evaluated as MIM dielectrics. Moreover, system-on-chip (SOC) applications also require a deposition process with a low thermal budget which can be carried out with a plasma deposition process. In the past, we have shown interesting results on MIM capacitors based on Y_2O_3 materials deposited by a low temperature process, namely pulsed liquid injection MOCVD assisted or not by a capacitive RF plasma. With the plasma, depositions have been achieved at temperatures as low as 300°C, and for this reason, good results have been obtained with TiN as bottom electrode. Without plasma, the deposition takes place at 450°C and a non desirable TiO_x interface is formed, which degrades the MIM electrical properties. In this study, we compare Y_2O_3 MIM capacitors deposited on $WSi_{2.3}$ substrates when assisting the pulsed CVD process by a pulsed RF plasma instead of a continuous plasma. With $WSi_{2.3}$ substrates, the interfacial layer is SiO_2-like, which can be beneficial to the MIM electrical properties in terms of linearity behavior. The plasma is pulsed either in phase or out of phase with the pulsed liquid injection of precursors. Moreover, depending on the plasma pulse width and frequency, the plasma can play a role in precursor dissociation and CVD post-deposition in-situ annealing treatment. The electrical behavior C(V) and I(V) of the obtained structures will be presented and discussed in terms of capacitance density, capacitance linearity and leakage currents. They will be correlated to chemical analysis results (XPS and FUV-SE), with special attention devoted to carbon content as well as metal/oxide interface investigations. C(V) curves suggest the presence of positive charges in the oxide, some of which are mobile, when the plasma is continuously applied. In this study, we will show the impact of exposure time of the dielectric to the plasma on the amount of trapped positive charges in the oxide affecting the MIM linearity properties. Moreover, the nature and thickness of the interfacial dielectric layer originate from both oxygen and solvent which can be limited by pulsing the plasma.

9:00am **PS1+TF-TuM4 Engineering Plasma-Enhanced Chemical Vapor Deposition to Deliver Self-Limiting Deposition of Metal Oxide Thin Films**, ***M.T. Seman**, S. Agarwal,* Colorado School of Mines, *J.J. Robbins,* CMD Research, LLC, *C.A. Wolden*, Colorado School of Mines

In this presentation we describe how conventional plasma-enhanced chemical vapor deposition (PECVD) may be engineered to deliver self-limiting deposition of metal oxides using pulsed power modulation. Self-limiting growth is assured when no deposition occurs during continuous operation with either the plasma on or the plasma off. The requirements that must be met to achieve this behavior are described. The pulsed PECVD technique has the potential to combine the digital control over thickness and composition provided by atomic layer deposition with the high throughput and low temperature capability offered by PECVD. To date the process has been demonstrated for both tantalum[1] and aluminum oxides,[2] and in this paper we focus on the process-property relationships in the former system. Tantalum oxide films were deposited by pulsed PECVD using continuous delivery of oxygen and penta-ethoxy tantalum (PET, $Ta(OC_2H_5)_5$) in a capacitively-coupled reactor. Deposited films were characterized by spectroscopic ellipsometry, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and dielectric performance. The deposition rate per pulse may be readily adjusted over a broad range (1- 10 Å/pulse) using variables such as the PET concentration and the plasma off time. With these variables fixed digital control over film thickness is demonstrated. The process is insensitive to substrate temperature, with a constant deposition rate observed from 90 to 350 °C. Films contain impurities due to carbon and hydroxyl groups, however these signals attenuate as the rate is reduced and are not detectable by FTIR for rates < 3 Å/pulse. Films deposited under these conditions at 190 ºC displayed a high dielectric constant ($\kappa \sim 25$) while maintaining leakage current densities below 1 $\mu A/cm^2$ out to a field strength of 1 MV/cm.

[1] M. Seman, J. J. Robbins, S. Agarwal, and C. A. Wolden, Appl. Phys. Lett. 90, 131504 (2007).

[2] S. Szymanski, M. T. Seman, and C. A. Wolden, Surf. Coat. Technol. in press (2007).

9:20am **PS1+TF-TuM5 Peter Mark Memorial Award Lecture - Plasma-assisted Atomic Layer Deposition: Applications, Opportunities, and Mechanisms**, ***W.M.M. Kessels****, Eindhoven University of Technology, The Netherlands **INVITED**

Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin films with a high conformality and with submonolayer growth control. Recently, the extension of the technique with plasma processes is actively being researched. These so-called plasma-assisted ALD processes can provide several potential advantages over thermal ALD for selected applications such as an enhanced growth rate, improved material properties, and lower deposition temperature (down to room temperature). In this contribution, different plasma-assisted ALD configurations such as direct plasma, remote plasma and radical enhanced ALD will be discussed and an overview will be presented of oxide and nitride materials (Al_2O_3, HfO_2, TiO_2, TiN, TaN, etc.) deposited. In particular, remote plasma ALD processes based on halide and metalorganic precursors and plasmas of H_2, N_2, O_2, NH_3 and combinations thereof will be described and the resulting material properties will be presented for wide substrate temperature ranges. The versatility of the plasma-assisted ALD process will be illustrated by several applications ranging from the semiconductor industry (capacitor stacks) to emerging applications in the field of 3D-integration in microelectronics (Cu diffusion barriers), photovoltaics (Si surface passivation), energy storage (Li diffusion barriers) and flexible electronics (ultrahigh moisture barrier coatings). Generic insight into the plasma-assisted ALD surface reactions will be presented from mechanistic studies carried out by a variety of in situ techniques: spectroscopic ellipsometry for monitoring film thickness and film properties (including electrical resistivity and crystal phases), transmission infrared spectroscopy to probe reactive surface groups, quartz crystal microbalance measurements to measure surface mass uptake, and mass spectrometry and optical emission spectroscopy to detect reaction products. On the basis of the results, the paradigms for plasma-assisted ALD are reviewed and differences with thermal ALD processes are discussed.

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* Peter Mark Memorial Award Winner

10:40am **PS1+TF-TuM9 Silicon Based Coatings by Means of Glow and Townsend Dielectric Barrier Discharges**, ***F. Massines***, CNRS PROMES, France, *N. Gherardi*, LAPLACE CNRS-UPS-INP, France **INVITED**

The development of a PECVD process working at atmospheric pressure and allowing an easy on-line treatment of silicon wafer, glass plate or polymer film is a challenge of great interest. The successful solution will avoid batch treatments and significantly reduce the cost of the coating. The main questions to be solved are how to get a well controlled thin film in terms of chemical composition, structure and thickness? and how to get a high growth rate? Previous to the process development, the main difficulties concern the plasma homogeneity, the gas injection over large dimensions, the control of the atmosphere in the plasma area while the substrate is moving and the efficiency of the transfer of the reactive species to the surface taking into account the very low diffusion of the neutral radicals at atmospheric pressure. In case of two dimensional materials like, dielectric barrier discharge (DBD) appears like the more suitable discharge: it is cold, robust and not disturbed by the movement of the substrate. As example DBD generate the plasma of corona treaters useful for surface activation. However, making a thin film coating having well controlled and uniform properties is more delicate. Homogeneous DBD (HDBD) is a solution to reach that goal. Conditions to get such a HDBD are now widely known and easy to up-scale in one direction allowing to get a uniform plasma band of several meters in the direction perpendicular to that of the substrate movement. This solution is in competition with remote plasmas but knowing that the quenching of excited state drastically increases with the pressure, and as far as the substrate can be moved inside the discharge without inducing perturbation, remote plasma has to be avoid. At atmospheric pressure, the reactive gases leading to the coating formation are diluted in a main gas, which is usually helium, argon or nitrogen. The main gas determines the discharge regime and then the energetic species created during the plasma development. In nitrogen, the HDBD is a Townsend discharge while in noble gases the HDBD is a glow one. In this presentation results concerning SiOx coatings obtained from SiH4 or hexamethyldisiloxane mixed with N2O and diluted in N2 will be compared. The coating thickness, the refractive index and the chemical composition as a function of the gas residence time will be discussed and correlated to the main growth mechanism.

11:20am **PS1+TF-TuM11 Film Microstructure Control and Characterization of Ion Bombardment- Aided Remote Plasma Deposition of Silicon Dioxide Films**, ***M.A. Creatore***, *N.M. Terlinden, M.C.M. van de Sanden*, Eindhoven University of Technology, the Netherlands

The control on thin film growth and microstructure in plasma deposition is a challenging issue. For example, in the case of an inorganic layer on an organic substrate (e.g., SiO_2 on polymers), the organic/ inorganic interphase affects the bulk inorganic properties, such as adhesion and moisture permeation barrier performance. Within this framework, ion bombardment-aided remote plasma deposition of SiO_2 layers, deposited from a hexamethyldisiloxane/O_2 chemistry, is carried out: the purpose is to engineer an interphase allowing the growth of dense, yet adhesive barrier films. This control is achieved by coupling the use of ion bombardment with a graded growth flux, obtained by a gradient (e.g. a decrease) in the hexamethyldisiloxane flow rate during film growth. At constant substrate bias voltage, i.e. constant ion energy, this gradient allows to tune the ion-to-growth flux ratio and the film densification. Initially, an adhesive porous layer is deposited, gradually shifting towards a highly dense barrier layer, due to the increase in the ion-to-growth flux ratio. The role of ion bombardment on the film microstructure is investigated by means of ellipsometric porosimetry, which monitors the refractive index (n) change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the layer. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity and the pore volume distribution can be extracted. In the absence of ion bombardment porous (n= 1.35-1.38) layers are characterized by an isotherm shape mimicking the structure of disordered mesoporous films (pore diameter in the range of 2-50 nm), i.e. a very broad distribution in pore size and shape, resulting in 20% porosity. A progressive increase in substrate bias voltage leads towards film densification (n=1.46) and induces a change in the isotherm: the adsorption/desorption process becomes reversible since unrestricted ethanol multilayer adsorption occurs on the non- porous surface. When a mild ion bombardment (ion energy of 20 eV) is accompanied by an increasing ion-to-growth flux ratio, both the isotherm and the hysteresis behavior exhibit the transition from meso- to microporosity (pore diameter less than 2 nm). The implications in terms of porosity determination in barrier layers deposited on polymeric substrates will be also addressed.

11:40am **PS1+TF-TuM12 Self-Limiting Growth of Aluminum Oxide by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, ***S.F. Szymanski***, *M.T. Seman, D. Richards, C.A. Wolden*, Colorado School of Mines

In this presentation we describe the self-limiting deposition (~ Å/pulse) of aluminum oxide by pulsed plasma-enhanced chemical vapor deposition (PECVD). In this process the trimethyl aluminum (TMA, $Al(CH_3)_3$) and oxygen are mixed and delivered simultaneously in a remote PECVD configuration. Deposited films were characterized by spectroscopic ellipsometry, Fourier transform infrared spectroscopy, and dielectric performance. In addition, the plasma and gas-phase chemistry in this system were characterized using optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS), respectively. The chemistry and deposition kinetics were quantified as a function of TMA concentration, plasma power, substrate temperature, and pulse parameters. The deposition rate per pulse scaled with the degree of precursor exposure during the plasma off step. Through appropriate control of the TMA concentration and pulse duration, the depositing rate may be readily adjusted over a broad range (1 - 10 Å/pulse). The deposition rate also decreases with plasma power, and OES is used to highlight the role of atomic oxygen in this process. The chemistry was quantified under steady-state operation using the QMS. It is shown that O_2 and TMA are unreactive with the plasma off. In contrast, TMA is completely consumed during plasma operation. Combustion of the TMA precursor is complete, yielding a mixture of CO, CO_2, H_2O, and H_2. Transient experiments show how TMA adsorbed on the walls of the chamber can impact both deposition rate and quality. The deposition rate was found to be independent of temperature for $T_s > 100$ °C. At lower temperatures the deposition rate per pulse increased, but film quality was degraded. Using a combination of ex situ film characterization and in situ diagnostics it is suggested that this behavior may be attributed to thermal chemistry occurring between TMA supplied during the off step with H_2O produced during the plasma on step. This reaction adversely effects film quality, but its effects are mitigated when the both reactor walls and substrate are maintained at temperatures > 100 °C.

12:00pm **PS1+TF-TuM13 Correlation of Surface Reactivity and Gas Phase Properties of CN Active Species in the Plasma Deposition of Carbon Nitride**, ***J. Stillahn***, Colorado State University, *D. Liu*, Dalian Nationalities University, China, *E.R. Fisher*, Colorado State University

Amorphous carbon nitride materials have generated interest due to their potential for commercial applications. One of the possible precursors in the plasma enhanced chemical vapor deposition (PE-CVD) of carbon nitride is the CN radical, but its role in the deposition process is still unclear. In an effort to clarify the processes taking place during film formation, carbon nitride deposition systems have been studied in rf inductively coupled plasmas by utilizing acetonitrile (CH_3CN) as a film precursor to allow direct generation of CN active species. The imaging of radicals interacting with surfaces (IRIS) technique has been utilized in our lab to provide a measure of the surface reactivity of the CN radical, R(CN), in these systems. Preliminary results indicate that CN radicals formed in acetonitrile plasmas react with near unit probability during deposition of a-CN_x:H films. Results from IRIS studies using other CN precursors will also be discussed. Characterization of gas phase species in these deposition systems has also been performed using spectroscopic and mass spectrometric (MS) methods. MS measurements are consistent with the direct formation of CN active species, and mass spectra are dominated by ions formed by the loss of CN from the parent molecule. Measurement of the relative number density of gas phase CN radicals by laser-induced fluorescence (LIF) spectroscopy indicates that increases in CN radical production due to increases in the pressure of the precursor gas or applied rf power give way to plateau behavior at higher values for both pressure and power. LIF measurements of the rotational temperature of CN radicals yield values near 320 K, suggesting that the rotational energy of CN radicals is re-distributed to maintain near-equilibrium conditions in the plasma. These data, along with film formation and characterization studies, will be discussed with respect to the information that they provide about the deposition process and their implications for continuing work in this area.

Thin Film

Room: 613/614 - Session TF-TuM

Two-Dimensional Carbon Nanostructures

Moderator: B.C. Holloway, Luna Innovations Incorporated

8:00am **TF-TuM1 Study of Growth Process and Structures of Carbon Nanowalls Synthesized Using Radical Injection Plasma Enhanced CVD**, ***S. Kondo,*** Nagoya University, Japan*, K. Yamakawa,* Katagiri Engineering Co., Ltd., Japan*, M. Hiramatsu,* Meijo University, Japan*, M. Hori*, Nagoya University, Japan

Carbon nanostructures, such as fullerene, carbon nanotubes and carbon nanowalls (CNWs) have received great attention for several applications, due to their outstanding physical, chemical and mechanical properties. Among a variety of nanocarbons, CNWs are considered as two-dimensional carbon nanostructures. CNWs are the graphite nanostructure with edges, which comprise the stacks of plane graphene sheets standing almost vertically on the substrate, forming a unique nanostructure similar to a maze with high aspect ratio. The large surface area and sharp edges of CNWs are useful as templates for the fabrication of other types of nanostructured materials, which have potential various applications such as in energy storage and electrodes for fuel cell as well as an electron field emitter. We have successfully synthesized CNWs using the radical injection plasma enhanced chemical vapor deposition (RI-PECVD) employing C_2F_6 and H_2 gases. The system consists of a parallel-plate capacitively coupled plasma (CCP) region and a surface wave microwave excited H_2 plasma (H_2-SWP) region over the CCP. Using this system, the heated substrate was showered with fluorocarbon radicals as well as plenty of H atoms in a controlled manner. Considering the practical applications of CNWs, further investigations are required to clarify the growth mechanism and to control their structures and properties. Furthermore, it would be useful to investigate the etching characteristics of CNWs for the modification of CNWs structure or pattern transfer of CNWs to other materials. CNWs were evaluated by Raman spectroscopy, TEM, ellipsometry and XPS measurements. In the initial stage of CNWs growth on a Si substrate by RI-PECVD, we have confirmed that a thin layer of approximately 10 nm in thickness was deposited in the first 1 min, and subsequently CNWs grew in the vertical direction from a lot of nuclei on this thin film. This thin film was found to be amorphous carbon with a little amount of fluorine. The CNWs film with the bottom amorphous carbon layer was exfoliated from the Si substrate. Both sides of the detached CNWs film were etched by Ar/H_2 plasma. The etching rates of CNWs and amorphous carbon thin film were 140 and 15 nm/min, respectively. It is noted that after the removal of amorphous carbon thin film, the morphology of the CNWs was still maintained on the backside, resulting in the formation of free-standing CNWs filter or membrane.

8:20am **TF-TuM2 Evaluation and Control of Electric Conduction of Carbon Nanowalls Fabricated by Plasma-Enhanced CVD**, ***W. Takeuchi,*** *M. Ura,* Nagoya University, Japan*, Y. Tokuda,* Aichi Institute of Technology, Japan*, M. Hiramatsu,* Meijo University, Japan*, H. Kano,* NU Eco-Engineering Co.,Ltd., Japan*, M. Hori*, Nagoya University, Japan

Carbon nanowalls (CNWs), two-dimensional (2-D) carbon nanostructure, consisting of graphite sheets standing vertically on the substrate, have attracted much attention for several applications, including field emitter arrays, gas storage, and membranes for electrochemical energy storage. Recently, it was reported that 2-D multilayer graphene sheet offers high mobility and huge sustainable currents. Therefore, CNW films potentially would possess high mobility and huge sustainable current density, since the CNWs are basically graphene sheet. Considering the practical applications of CNWs, further investigations are required to clarify the growth mechanism and to control their structure and properties. In this study, we focused on the evaluation and control of electric properties of CNWs. CNWs were fabricated on the quartz substrate by the plasma enhanced CVD with H radical injection employing a mixture of C_2F_6/H_2. We investigated the influence of N_2 or O_2 addition to the process gas mixture on the morphology and electric properties of CNWs. Hall measurement and Raman spectroscopy were used to evaluate the electric properties and structure of CNWs. The Hall coefficient was positive for the CNW film grown without additives. When O_2 was added to the plasma, it was still positive. In the case of N_2 addition, it displayed negative value. The positive or negative value of the Hall coefficient implies p- or n-type, respectively. Therefore, it was found that the conduction type of CNW films was controllable by adding N_2 or O_2 to the C_2F_6/H_2 plasma. Morphology and crystallinity of CNWs were also changed by the addition of N_2 and O_2. In the Raman spectroscopy, all samples have a strong peak at 1590 cm^{-1} (G-band) indicating the formation of a graphitized structure, and another peak around at 1350 cm^{-1} corresponding to the disorder-induced phonon mode (D-band). The G-band width in the Raman spectrum increased when N_2 was added. In the case of O_2 addition, G-band width and peak intensity ratio of D band to G band of CNWs decreased. These results indicate that nitrogen would be included in CNWs and act as a donar, while accompanied by the slight degradation of graphite crystallinity. On the other hand, oxygen would play a role of etching of amorphous carbon content and contribute to the higher graphitization, while conduction type of CNW films would not change.

8:40am **TF-TuM3 Low Temperature Deposition of Carbon Nanosheets by C_2H_2/H_2 Plasma Enhanced Chemical Vapor Deposition**, ***M.Y. Zhu****, R.A. Outlaw, K. Hou, P. Miraldo, D. Manos*, College of William and Mary

Two-dimensional carbon nanosheets were previously deposited by radio frequency plasma enhanced chemical vapor deposition (PECVD) using CH_4/H_2 plasma on a variety of substrates. In this work, we report the deposition of the same nanostructure using C_2H_2/H_2 plasma at a substrate temperature more than 100 ºC lower than that for typical depositions using CH_4/H_2 plasma. The decrease of required substrate temperature is a great benefit to device fabrications. Carbon nanosheets were deposited on silicon substrates at temperatures ranging from 500 ºC to 600 ºC while other parameters were 100% C_2H_2 gas (5 sccm total gas flow rate), 35 mTorr gas pressure, 1000 W input RF power, and 10 minutes deposition duration. For substrate temperature from 550 ºC to 600 ºC, the carbon nanosheets deposited have sheet-like structures and flat surface morphologies, and are free-standing on substrate surfaces, as characterized by scanning electron microscope (SEM). High-resolution transmission electron microscopic (HR-TEM) results revealed that the edges of the nanosheets consist of about 3-8 atomic layers. Selected area electron diffraction pattern of carbon nanosheet samples matches that for polycrystalline graphitic structures. Raman spectra of carbon nanosheets have the characteristic D and G peaks for defective sp^2 graphitic structures. Detailed results showed faster growth rates and high Raman D/G peak ratios for samples deposited at higher substrate temperatures. Carbon nanosheets were also deposited using various (60-100%) C_2H_2 in H_2 concentrations while other parameters were fixed at 600 ºC substrate temperature, 5 sccm total gas flow rate, 1000 W input RF power, and 10 min deposition duration. With a decreasing C_2H_2 in H_2 concentration, both the nanosheet growth rate and the Raman D/G ratio were decreased, however, the basic nanosheet structures were maintained. Cross-sectional SEM images showed that carbon nanosheets deposited using C_2H_2/H_2 gas mixture have a straighter vertical orientation and a more uniform sheet height distribution than those deposited using CH_4/H_2 mixture, therefore are expected to have improved field emission properties. Field emission from C_2H_2/H_2 carbon nanosheets are measured under diode configuration and the results will also be presented.

9:00am **TF-TuM4 Field Emission Performance of Carbon Nanosheets**, ***K. Hou****, R.A. Outlaw,* College of William and Mary*, M.E. Kordesch,* Ohio University*, M.Y. Zhu, P. Miraldo,* College of William and Mary*, B.C. Holloway*, Luna Innovations Incorporated*, D. Manos*, The College of William and Mary

Carbon nanosheet, a novel two-dimensional carbon nanostructure consisting of vertically oriented ultra-thin graphitic sheets terminating with 1-3 graphene layers, are fabricated by inductively coupled radio frequency plasma enhanced chemical vapor deposition. Carbon nanosheet, with its atomic-scale edge structure, high purity, and uniform height distribution have been confirmed to be a promising candidate for the application as the cold cathode material in vacuum electronic devices. In this study, we present the latest field emission test results of carbon nanosheet thin film including total current, lifetime in a slow pulse mode, and lifetime in a dc mode. These tests were conducted using a diode configuration having an anode-cathode distance of 254 μm. Further, the emission uniformity of carbon nanosheet thin films was primarily studied by photoelectron emission microscopy. To date, we have routinely achieved total currents of more than 20 mA from ~30 mm^2 while maintaining a useful current density of ~0.1 A/cm^2. Among them, a maximum total current of 26 mA has been measured from a 32 mm^2 testing area at an applied electric field of 25.5 V/μm. The test result suggests that the field emission of nanosheet film is not saturated at this field level but is limited by the test apparatus. The lifetime in a slow pulse mode was conducted by applying a series of identical voltage ramps over a long time period with a duty factor of 21%. The maximum current on the order of 13 mA in each voltage ramp was recorded for 96 hours. The test result reveals that the standard deviation of the maximum is less than 2.1%. The lifetime in a dc mode was conducted by applying a constant negative bias to the sample. A stable ~1.5 mA emission current was obtained from the carbon nanosheet thin film for 200 hours. The standard deviation of the emission current is less than 3.6% during the test period. Photoelectron emission microscopy was used to investigate the field emission uniformity over the surface of carbon nanosheet thin films. In addition, field emission electron microscopy images, formed without photon illumination, were also captured. The analysis of these images show that a small number of nanosheet emission sites dominate the emission current.

9:20am **TF-TuM5 Enhanced Field Emission from Mo$_2$C Coated Carbon Nanosheets**, ***M. Bagge-Hansen***, *P. Miraldo, R.A. Outlaw, M.Y. Zhu, M. Hou, D. Manos*, College of William and Mary

Carbon nanosheets, a new morphology of graphite, have shown remarkable promise as field emission cathodes for applications such as microwave tubes and flat panel displays. The sharp emission edges of the sheets are typically 1-3 graphite sheets thick (~1 nm) and thus provide a superior geometry for field emission enhancement. Fowler-Nordheim theory suggests further field emission enhancement is possible by lowering the work function. The effective work function of carbon nanosheets, previously undetermined, was calculated and found to be analogous to that of graphite, 4.8 eV. By applying a thin film coating of Mo$_2$C (Φ = 3.5 eV), the field enhancement factor from the geometry, ß, was reduced by only a factor of two, yet field emission current substantially increased. A molybdenum coating was deposited on a carbon nanosheets sample by physical vapor deposition in very high vacuum (p ~1x10^{-8} Torr) and determined to be ~3 monolayers thick by Auger electron spectroscopy. The coated sample was radiatively heated to T~250°C to promote molybdenum reaction with adventitious carbon found in defects of the carbon nanosheets' emission edges and the underlying graphite structure. Auger electron spectroscopy and scanning electron microscopy were used to verify the composition and conformity of the coating, respectively. Field emission testing in an ultrahigh vacuum (p ~5x10^{-10} Torr) diode assembly with 250 µm spacing showed lowering of the effective work function after the coating procedure and consequently, increased emission current. At an applied field of 9 V/ µm, the emission current was found to be 100 µA compared ~0.1 µA for the carbon nanosheets. A comparison of linear (R^2 = .999) Fowler-Nordheim plots of coated and uncoated samples yielded values for the work function of uncoated CNS and the fractional emitting area of ~2% for carbon nanosheets. The experimental data of Mo$_2$C-coated CNS was significantly more repeatable and stable than the uncoated CNS.

9:40am **TF-TuM6 Production of Large Area Graphene Sheets by Si Desorption from SiC**, ***G.G. Jernigan***, *J.C. Culbertson, B.L. VanMil, K.K. Lew, R.L. Myers-Ward, D.K. Gaskill, P.M. Campbell, E.S. Snow*, U.S. Naval Research Laboratory

With DeHeer's[1] initial report of graphene formation by the thermal desorption of Si from SiC, efforts have been underway to use this method to make large area sheets of graphene for device fabrication purposes. Mobility measurements of graphene on SiC, however, have not approached the values obtained with graphene exfoliated from graphite, indicating that material issues and other factors may be affecting the quality of graphene from SiC. We will report on our efforts to produce large area graphene sheets using 2- and 3-, Si-face, 4H and 6H SiC wafers. Using x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), atomic force microscopy (AFM), Raman spectroscopy, and electrical characterization, we have studied graphene sheets and graphite films formed on SiC by Si desorption in ultra-high vacuum (UHV). The wafers were initially subjected to hydrogen etches at 1400 °C and 1580 °C to remove polishing damage and to produce smooth surfaces prior to entrance into UHV. XPS measurements show the hydrogen-etched surfaces are initially covered by an oxide, which can be desorbed at 1000 °C in UHV resulting in a surface containing excess Si. At ~1300 °C, the surface becomes stoichiometric in Si and C and a $\sqrt{3}$ x $\sqrt{3}$ R30 LEED pattern is observed. At ~1350 °C, we observe a $6\sqrt{3}$ x $6\sqrt{3}$ R30 LEED pattern develop when graphene has formed, and a 1x1 LEED pattern for graphite films formed at temperatures greater than 1400 °C. AFM images show that the process of Si desorption from the surface results in the formation of hexagonal pits and that the liberation of carbon onto the surface produces the graphene layer. As more Si is desorbed from the surface, the carbon forms into 3-dimensional islands with a hexagonal shape. Interestingly, the sheet conductance remains constant while the islands coalesce into a thick graphite layer. Raman spectroscopy of the graphene sheets is complicated by strong transitions from the underlying SiC substrate. Nonetheless, D, G, and D' lines can be distinguished, and their intensities are observed to increase with increasing sheet thickness. The frequency of the D' line can also be used to distinguish the formation of graphene and graphitic material. We will discuss how process parameters affect the graphene quality as judged by the multiple techniques.

[1] J. Phys. Chem. B 108, 19912-19916 (2004).

10:40am **TF-TuM9 Epitaxial Graphene - A New Paradigm for Nanoelectronics**, ***W.A. de Heer***, Georgia Institute of Technology **INVITED**

Multilayer graphene grown on single-crystal silicon carbide by vacuum decomposition is a promising material for nanoelectronics. The material can be patterned using standard nanolithography methods. The transport properties, which are closely related to those of carbon nanotubes, are dominated by a single graphene layer at the silicon carbide interface. This epitaxial layer reveals the Dirac nature of the charge carriers. Unlike graphite, multilayer graphene is electronically related to single layer graphene with an anomalous Berry's phase as evidenced from transport measurements, from infrared absorption measurements and from Raman scattering measurements. Patterned structures show quantum confinement of electrons and phase coherence lengths beyond one micrometer at 4K, with mobilities exceeding 25000 cm2/Vs. These parameters suggest that all-graphene electronically coherent devices may be possible. Recent developments will be discussed including epitaxial graphene FETs.

11:20am **TF-TuM11 Rotational Stacking of Graphene Films Grown on 4H-SiC(000-1)**, ***J. Hass***, *J.E. Millán-Otoya, M. Sprinkle, X. Li,* The Georgia Institute of Technology, *F. Varchon, L. Magáud,* LEPES-CNRS, France, *P.N. First, E.H. Conrad*, The Georgia Institute of Technology

The presence of Dirac electrons and micron scale coherence lengths have been demonstrated in multi-layer graphene grown on SiC, suggesting that an all-carbon paradigm for electronic circuits may be possible.[1] It is now critical to understand the source of these unique transport properties and explain their dependence on: 1) graphene stacking order and 2) graphene/SiC substrate interactions. We will present surface X-ray reflectivity data that suggest a new structural model for multilayer graphene grown on the SiC (000-1) (C-terminated) face.[2] Reflectivity modeling indicates a high density of stacking faults with distinct rotational alignments. These complex rotational phases will be discussed in the context of recent ab initio calculations which show that this type of stacking effectively decouples adjacent graphene layers. This provides a potential explanation for transport being confined to a single graphene layer.

[1] C. Berger, et al., Science 312, 1191 (2006).

[2] J. Hass, et al., Phys. Rev. B, in press (2007).

11:40am **TF-TuM12 Probing the Interface between Graphene and SiC at the Atomic-scale***, ***N.P. Guisinger***, National Institute of Standards and Technology, *G.M. Rutter,* Georgia Institute of Technology, *J.N. Crain, E.A.A. Jarvis, M.D. Stiles,* National Institute of Standards and Technology, *P.N. First,* Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology

Graphene films on SiC exhibit coherent transport properties that suggest the potential for novel carbon-based nanoelectronics applications. Through controlled processing of SiC graphitization, large domains of single layer graphene can be realized opening the possibility for large area fabrication of carbon structures. Recent studies suggest that the role of the interface between single layer graphene and silicon-terminated SiC can strongly influence the electronic properties of the graphene overlayer. In the present study we have investigated this interface at the atomic scale, utilizing scanning tunneling microscopy and spectroscopic measurements at 4 K. These techniques allow us to probe both the graphene adlayer and the underlying electronic states associated with the SiC surface reconstruction. A novel imaging of the underlying interface is demonstrated by exploiting the energy dependence of the density of states of the SiC substrate versus the graphene overlayer. The first layer of graphene becomes semi-transparent at energies of 1 eV above or below the Fermi-energy, yielding images of the SiC interface. Our analysis of calculations based on density functional theory shows how this transparency arises from the electronic structure of a graphene layer on the SiC substrate. * This work was supported in part by the Office of Naval Research, by Intel Research, and by NSF grant ECS-0404084.

12:00pm **TF-TuM13 Quasiparticle Interference in Epitaxial Graphene***, ***G.M. Rutter***, Georgia Institute of Technology, *J.N. Crain, N.P. Guisinger,* National Institute of Standards and Technology, *P.N. First,* Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology

Understanding the role that defects play in the transport properties of graphene is essential for realizing potential carbon-based electronics. In this study, scanning tunneling spectroscopy was used to measure scattering from defects in epitaxial graphene grown on SiC(0001). Energy-resolved maps of the differential conductance reveal standing-wave modulations of the local density of states on two different length scales, corresponding to two classes of allowed scattering vectors. While backscattering is normally suppressed due to the chiral symmetry of Dirac quasiparticles in graphene, the presence of atomic defects is shown to mix quasiparticle wavefunctions of different symmetries. From Fourier transforms of the spectroscopic conductance maps we determine the energy-momentum dispersion relation for both occupied and unoccupied states near the Fermi level of single-layer and bilayer epitaxial graphene. * This work was supported in part by the Office of Naval Research, by Intel Research, and by NSF grant ECS-0404084.

Nanomanufacturing Topical Conference

Room: 615 - Session NM+TF-TuA

Nanomanufacturing of Materials

Moderator: M. Tuominen, University of Massachusetts, Amherst

1:40pm **NM+TF-TuA1 Nanoscale Patterning with S-layer Proteins and Area Selective Atomic Layer Deposition**, ***J.R. Liu***, *C.M. Tanner, E. Lan, B.S. Dunn, J.P. Chang*, University of California at Los Angeles

Nano-sized crystalline bacterial cell surface layer (S-layer) proteins have the intrinsic property to reassemble into two-dimensional arrays with ordered pores of identical size onto solid supports,[1] ideal as a template for nanoscale patterning. In this work, we demonstrated that, when combined with area selective atomic layer deposition (ALD), the reassembled S-layer proteins can be effective nanotemplates to pattern nano-sized dielectrics. S-layer proteins were reassembled on Si wafer from the solution containing protein units and $CaCl_2$. Atomic force microscopy (AFM) and transition electron microscopy (TEM) images showed that the protein unit size and the pore diameter are about 10 nm and 5 nm, respectively. Octadecyltricholorosilane (ODTS) was used to modify the more hydrophilic protein surface since ODTS has been demonstrated to be an effective monolayer resist on a hydrophilic SiO_2 surface toward ALD of HfO_2.[2] High-k oxides were only deposited in the pores built by the protein units by an area selective ALD after the S-layer nano-template was modified by ODTS. Attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR), contact angle measurement, and x-ray photoelectron spectroscopy (XPS) were employed to analyze the reassembling, modification, and removing process of S-layer proteins. FTIR analysis of the reassembled S-layer proteins before and after ODTS treatment revealed NH (3297 cm^{-1}), CH_3 (2968 and 2866 cm^{-1}), CH_2 (2922 cm^{-1}), CO (1645 cm^{-1}), and CN (1525 cm^{-1}) from S-layer proteins, while the intensity of CH_2 increased after modified by ODTS, due to the 17 CH_2 groups in ODTS. The ODTS treated S-layer proteins surface became more hydrophobic, evident by a contact angle change from 59° to 84° for 2h and 101° for 40h. After cleaning, the peaks of NH (3297 cm^{-1}), CH_3 (2968 and 2866 cm^{-1}), CH_2 (2922 cm^{-1}), CO (1645 cm^{-1}), and CN (1525 cm^{-1}) from S-layer proteins disappeared, confirming that S-layer proteins have been removed completely. The current-voltage (I-V) of oxide nanopatterns is characterized by a conductive AFM.

[1] U. B. Sleytr, P. Messner, D. Pum, and M. Sara, Angew. Chem. Int. Ed., 1034-1054, 38, 1999.

[2] R. Chen, H. Kim, P. C. Mclntyre, and S. F. Bent, Appl. Phys. Lett., 4017-4019, 84, 2004.

2:00pm **NM+TF-TuA2 Plasmonic Nanoparticle Complexes for Diagnostics and Therapeutics**, ***N.J. Halas***, Rice University **INVITED**

The combination of metallic nanostructures and molecular adsorbates provides a broadly adaptable route to the development of optically addressible, functional nanocomplexes. In particular, nanostructures based on this approach can be designed to sample, and, via Raman scattered light, report on specific aspects of their chemical environment. Combining this sensing functionality with photothermal heating of the local environment of the nanocomplex provides an important strategy for functional therapeutics for cancer and beyond.

2:40pm **NM+TF-TuA4 Conduction Nature of Nanochannels of Track Etched Polymeric Membranes**, ***K. Awasthi***, University of Rajasthan, India

The nanopores are developed by using one side etching of swift heavy ion irradiated polymeric membrane. In an electrolytic cell, the chemical solution serves as well as etchant and as an electrolyte. In the moment breakthrough of a track the beginning and increasing electrical current supplies information of the birth and growing of the track. The membranes used can be seen as model systems acting as interconnects between two separate liquids. There is a significant difference in the electrical conduction behavior of the electrolytes having common anion. It is clear from the voltage current characteristics that electrical conduction through the etched membrane of polycarbonate is dependent on size of cation.

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3:00pm **NM+TF-TuA5 Laser Sintering of Nano-Silver coated Polyetheretherketone Powder**, ***D. Pohle***, *C. Damm*, University Erlangen-Nuremberg, Germany, *T. Rechtenwald*, BLZ, Bavarian Laser Center gGmbH, Germany, *A. Rösch, H. Münstedt*, University Erlangen-Nuremberg, Germany

The effectiveness of silver as oligodynamic bactericide is proven and well investigated. The silver ions inhibit vital activities of the bacteria, such as breathing and metabolism. Elemental silver particles provide a large reservoir of antimicrobial silver ions, as in contact with water and dissolved oxygen they release small amounts of silver ions, only. The oxidation occurs on the surface of the particles. Accordingly the ion concentration and the rate of silver ion release are dependent on the surface to volume ratio of the elemental silver particles. The polymer matrix used in this investigation is polyetheretherketone. PEEK is a high performance thermoplastic with melting temperature of 345°C, very good mechanical properties and outstanding stability against chemicals and radiation. Its water uptake is below 0.5%. Because of this an antimicrobial equipment of the bulk material by use of silver is difficult. Silver nanoparticles were generated. Polyvinyl alcohol was dissolved in distilled water and silver nitrate was added. Sodium borohydride was used as reduction agent. Formation of elemental silver nanoparticles occurred, which were stabilized by the PVA. PEEK powder (PEEK 150 PF, Victrex, UK) was coated with silver nanoparticles by giving the polymer powder into the silver dispersion for 24h. The coated PEEK powder was used in a laser sintering (LS) process to generate antimicrobially equipped polymer specimens. LS of PEEK is a challenge because of its very high melting temperature and the irregular shape of the polymer particles. A modified laser sintering machine (EOSINT P 380, EOS, Germany) was used to obtain powder bed temperatures up to 350°C. After a pre-treatment of the polymer powder, including sieving and adding a small amount of carbon black to increase the flow ability, it was possible to manufacture discs with a diameter of 10mm and a height of 3mm. By use of LS specimens with open porosity are generated, so water can easily infiltrate the polymer parts. Stripping voltammetry showed that the sintered specimens released much more silver ions than hot pressed dense PEEK specimens. The silver release as function of time plot indicates that the release is governed by diffusion. To investigate the antimicrobial efficacy of the polymer specimens Escherichia coli was used. The antimicrobial tests were made by use of a solid agar plate method. As expected by the silver ion release test the specimens are active against E. coli.

4:00pm **NM+TF-TuA8 TEM-Based Metrology and Structural Characterization of HfO_2 ALD Films Formed in Anodic Aluminum Oxide Templates**, ***I. Perez***, *E. Robertson, L. Henn-Lecordier, P. Banerjee, S.J. Son, S.B. Lee, G.W. Rubloff*, University of Maryland, College Park

A broad variety of nanotechnology applications are poised to exploit the self-assembly that occurs in forming anodic aluminum oxide (AAO) films, which can be structured to comprise cylindrical nanopores with uniform dimensions (15-300nm diameters) spaced closely and regularly in AAO films microns in thickness. Such AAO films comprise templates for manufacturing of energy devices (capacitors, batteries, solar cells), electrochromic displays, or – if released by AAO dissolution - nanoparticle systems for targeted, imageable drug delivery, in which ultrathin highly conformal layers are formed in the nanopores by atomic layer deposition (ALD) or electrochemical deposition (ECD). Nanomanufacturing of such structures relies on the availability of fairly rapid metrologies and material characterization techniques which are precise at the nanoscale. We have achieved this goal based on transmission electron microscopy (TEM) methods, demonstrated here for ALD HfO_2 nanotubes formed in AAO templates. The HfO_2 nanotubes are first released by dissolution of the surrounding AAO template, then captured on standard TEM grids for observation in the TEM, whose high spatial resolution readily allows determination of nanotube diameters and wall thicknesses as a function of distance along the nanotube. We have developed image analysis codes to extract this metrology information in semi-automated fashion, so that ALD deposition profiles can be readily compared with ALD and AAO process parameters to optimize nanostructure manufacturing and to validate further models for process conformality. Furthermore, we have used HRTEM to identify HfO_2 crystal phases at different locations along the nanotubes upon annealing, carried out on nanotubes either while embedded in the AAO template or after release. For annealing at 650°C for 30 minutes, we find the expected monoclinic phase of HfO_2 is formed. These results demonstrate that the ability to release nanotubes from the AAO template, coupled with rapid HRTEM characterization and metrology, comprises an effective means to support AAO-based nanodevice manufacturing.

4:20pm **NM+TF-TuA9 Nano-Manufacturing of Materials at Oak Ridge National Laboratory's NanoApplications Center, *S.M. Robinson***, Oak Ridge National Laboratory

The NanoApplications Center (http://nanotech.ornl.gov/) at Oak Ridge National Laboratory (ORNL) employs state-of-the-art facilities and multidisciplinary R&D capabilities to transition the discoveries of nanoscience to innovative technologies for energy environment, and economic competitiveness. It fosters innovation of new energy-related nanotechnologies and helps transform industry by enabling the responsible development of processes for mass production and application of nano-scale materials, structures, devices, and systems that provide unprecedented energy, cost, and productivity benefits. Capabilities within the NanoApplications Center include 1) materials processing and fabrication, 2) characterization, and 3) responsible nanomanufacturing, and 4) rapid prototyping for development and deployment. This paper describes example nano-manufacturing projects for materials processing and real-time measurements for process control. These include investigation of infrared-based processing for high temperature processing of metals to enhance metallurgical and mechanical properties by controlling grain size and development of coating processes that infuse alloys several hundred nanometers deep into the surface of a metal to create enhanced durability. To better enable nanomanufacturing, researchers at ORNL have developed and applied novel real-time characterization techniques to process monitoring and control. A commercial differential mobility analyzer is being used to sample and characterize nanoparticles in real time.

4:40pm **NM+TF-TuA10 Nanometrology: A Key Element for Successful Nanomanufacturing, *M.T. Postek***, National Institute of Standards and Technology **INVITED**

Nanomanufacturing is the essential bridge between the discoveries of nanoscience and real world nanotech products - it is the vehicle by which this Nation will realize the promise of major technological innovation across a spectrum of products that will affect virtually every industrial sector. For nanotech products to achieve the broad impacts envisioned, they must be manufactured in market-appropriate quantities using reliable, repeatable, and commercially viable manufacturing processes. In addition, they must be manufactured so that environmental and human health concerns are met, worker safety issues are appropriately assessed and handled, and liability issues are addressed. Critical to this realization of robust nanomanufacturing is the development of the necessary instrumentation, metrology, and standards. This will allow the physical dimensions, properties, functionality, and purity of the materials, processes, tools, systems, products, and emissions that will constitute nanomanufacturing to be measured and characterized. This will in turn enable production to be scaleable, controllable, predictable, and repeatable to meet market needs. If a product cannot be measured it cannot be manufactured. This presentation will discuss some of the challenges confronting the effective development of the nanometrology needed for the success of nanomanufacturing.

Thin Film

Room: 613/614 - Session TF-TuA

Surface Chemistry for Atomic Layer Deposition

Moderator: S. Rossnagel, IBM

1:40pm **TF-TuA1 Infrared Characterization of Atomic Layer Deposition and Post Annealing of Lanthanum Oxide Films, *J. Kwon*, *M. Dai,*** Rutgers University, *E. Langereis,* Eindhoven University of Technology, The Netherlands, *Y.J. Chabal,* Rutgers University, *K. Kim, R. Gordon*, Harvard University

La_2O_3 is a potential material for high-k gate dielectrics in microelectronics due to its relatively large permittivity, thermal stability in contact with Si, suitable band gap and conduction band offset. Uniform and conformal thin layers of metal oxides can be realized by a self-limiting atomic layer deposition (ALD) process. Surface nucleation and overall interface formation mechanisms are unfortunately not well understood since most of film characterization has been performed with ex-situ measurements. We report on in-situ Fourier transmission infrared (FTIR) studies of ALD growth and post-deposition annealing of La-oxide thin films on Si substrates using a metal-amidinate precursor[1] and D_2O. Film growth rates were determined from ex-situ RBS measurements. Atomically flat hydrogen-terminated Si(111) surfaces were used as substrates for La-oxide film growth. IR spectra were obtained at every half-cycle of the initial stages and post-deposition annealing was studied up to 800°C by performing IR measurements after 20 cycles of ALD process at 100°C increments. Between 200 and 300°C substrate temperatures, the first La-precursor exposure consumes approximately 30% of surface hydrogen, as measured by the intensity loss of the monohydride Si-H stretching mode (2083 cm^{-1}). A D_2O exposure is used each time to complete the cycle. More than 90 % hydrogen is consumed after the third metal-precursor dosing (2.5 cycle) at 300°C deposition temperature. La_2O_3 grown at 200°C shows higher concentration of carbonate species (modes in the 1390 ~ 1470 cm^{-1} region) incorporated into the film compared to 300°C grown films, probably due to incomplete elimination of the metal precursor by D_2O. The intensity of these modes decreases with increasing annealing temperature and almost completely disappears at 400 ~ 500°C annealing. Carbonate groups in the films grown at 300°C are lower, but profound ligand decomposition is observed around 2000 cm^{-1}. Si-O-Si modes (900 ~ 1200 cm^{-1}) are observed to increase from the very initial ALD cycle, consistent with interfacial SiO_x formation at 300°C. Films grown at 200°C show much slower interface oxide formation, but even a mild (400°C) post-deposition anneal triggers substantial interfacial SiO_x formation.

[1] B. S. Lim et al., Appl. Phys. Lett. 84, 3957 (2004).

2:00pm **TF-TuA2 Understanding the Long Nucleation Period for Pd ALD on Alumina Substrates, *D.N. Goldstein***, *S.M. George*, University of Colorado

Palladium (Pd) atomic layer deposition (ALD) can be performed on alumina substrates using $Pd(hfac)_2$ (hfac= hexafluoroacetylacetone) and formalin. However, this system requires a nucleation period of 50-100 cycles before Pd grows steadily at 0.2 Å/cycle. To understand the long nucleation period, this study explored the details of the surface reactions occurring during Pd ALD nucleation. This research utilizes in situ Fourier Transform Infrared (FTIR) spectroscopy on nanopowder substrates to observe the surface species. $Pd(hfac)_2$ dissociatively adsorbs on the Al_2O_3 substrate to yield surface Pd(hfac) and Al(hfac) during the initial $Pd(hfac)_2$ exposure. During the first formalin exposure, only the hfac ligands attached to Pd are removed and the Al(hfac) species remain on the substrate. In addition, the formalin exposure adds formate species to the available Lewis acid sites on Al_2O_3. After the first cycle, no more surface Pd(hfac) is observed and formalin exposures remove some of the Al(hfac) species. These Al(hfac) species are believed to be the cause for the long nucleation period. Surface Al(hfac) is continually produced from $Pd(hfac)_2$ exposures and competes with Pd metal for the same surface sites. The fate of Al(hfac) is either thermal decomposition to trifluoroacetate groups or removal from the surface as a volatile enol isomer. Formalin provides hydrogen to release the enol of hfac but cannot remove the trifluoroacetate groups. Trifluoroacetate groups may be a source of fluorine contamination in the films. The nucleation period ends when the volatile hfac products desorb and Pd can cover the original Al_2O_3 surface. At this point, only Pd(hfac) species are observed in the FTIR spectra. Transmission electron microscopy studies reveal Pd nanocrystallites that increase in number with increasing number of ALD cycles. These crystallites eventually coalesce to a conformal Pd film.

2:40pm **TF-TuA4 Simulations of the Surface Chemistry of HfO2 Atomic Layer Deposition, *C.B. Musgrave***, *A. Mukhopadhyay,* Stanford University, *J.F. Sanz*, Universidad de Sevilla, Spain **INVITED**

We have used a combination of theoretical techniques to explore the surface chemistry of atomic layer deposition of metal oxides and nitrides, including HfO2, HfN, HfOxNy and WN. Our main focus has been on the chemical mechanisms involved in the ALD of HfO2. Density functional theory has been employed using both the cluster and periodic supercell models of the reacting surface to determine detailed mechanisms of the surface chemistry of ALD. In addition to locating transition states and applying transition state theory to predict reaction rates, we also simulate ALD surface reactions using Born-Oppenheimer quantum molecular dynamics. These simulations provide a rich and complex picture of the atomistic detail of the ALD process which shows that the chemistry of ALD is much more complicated than initial descriptions suggested. In addition to finding various reaction pathways and predicting their relative rates, we also investigate processes such as dissociation of adsorbed precursors via microsolvation and the effect of surface hydration on the ALD mechanism.

4:00pm **TF-TuA8 Passivation and Atomic Layer Deposition on Halide-Terminated Ge Surfaces, *P. Ardalan***, *C.B. Musgrave, S.F. Bent*, Stanford University

Because of the poor oxide of germanium, alternative passivation methods are required for practical use of Ge in devices. We have studied the passivation of germanium surfaces by alkanethiolate self-assembled monolayers (SAMs) and by ALD-deposited titanium dioxide (TiO_2). We have also investigated the ability of the SAMs to block TiO_2 deposition for application to area selective ALD. Our studies started with halide-terminated (Cl- or Br-) Ge(100) and (111) surfaces, which have been shown to exhibit good stability and resistance to oxidation. The initial functionalization of Ge surfaces by HCl and HBr was investigated by various experimental and theoretical methods, including x-ray photoelectron spectroscopy and density functional theory. Next, these surfaces were exposed to 1-alkanethiols to form alkanethiolate self-assembled monolayers (SAMs), where the formation and bonding of such SAMs were studied by the same methods. We also investigated the ALD of TiO_2 on halide-terminated Ge surfaces, with the results showing a strong temperature dependence of the growth process. Finally, we have explored the area selective ALD of TiO_2 at the Ge surfaces. We observe that the 1-alkanethiolate SAMs protect the Ge surfaces from ALD, leaving TiO_2 to deposit only at regions of the Ge surfaces which are functionalized by halides but not protected by the SAMs. The results demonstrate a new route to Ge surface functionalization and passivation.

4:20pm **TF-TuA9 Step by step in-situ X-ray Photoelectron Spectroscopy Investigation on ALD Al_2O_3 Films using TMA and Water**, ***K.J. Choi,*** University of Texas at Dallas, *S.J. McDonnell,* Dublin City University, Ireland, *R.M. Wallace, J. Kim*, University of Texas at Dallas

In atomic layer deposition (ALD) of Al_2O_3 on H-terminated silicon substrates, it is often observed that the initial growth rate of Al_2O_3 films is much slower than that in the steady-state condition after several cycles. This phenomenon is frequently called an incubation period, which has been extensively investigated by using various in-situ surface characterization methods, such as quartz crystal microbalance, quadrupole mass spectroscopy, FT-IR etc. Although X-ray photoelectron spectroscopy (XPS) provides useful chemical binding information at the surface, a relatively few papers have been published regarding in-situ XPS investigations possibly due to a ultra-high vacuum (UHV) requirement which is not easily compatible to ALD system. In this study, in-situ XPS is used to investigate on chemical binding status during formation of Al_2O_3 thin films on an HF-last Si wafer. All experiments were carried out in an UHV system consisting of various deposition tools, including atomic layer deposition, sputter deposition, molecular beam epitaxy/deposition, and e-beam evaporation, as well as surface characterization methods including XPS, UPS, STM and AFM. The Al_2O_3 film was grown at 300°C on HF-last Si substrate using trimethylalumium [$Al(CH_3)_3$, TMA] as the aluminum precursor and H_2O as the oxidizing agent. A cycle of the deposition process consisted of 0.1 s of TMA pulse, 10 s of N_2 purge, 0.1 s of H_2O pulse and 10 s of N_2 purge. The growth rate is about 0.11nm/cycle. XPS analysis was conducted on Al_2O_3 thin films resulting from a 3-cycle deposition. The Al_2O_3 thin films were grown in half cycle steps (TMA pulse+N2 purge or H_2O pulse + N_2 purge) and analyzed in-situ so that the initial growth of Al_2O_3 could be observed. The $Al2_{P3/2}$ photoelectron emission peak appears after the 1 cycle + TMA pulse + N_2 purge. As the number of cycles is increased, the peak intensity of $Al2_{P3/2}$ increases in TMA pulse + N_2 purge step, and does not increase in H_2O pulse + N_2 purge step. In addition, we will also present in-situ vs. ex-situ XPS analysis of ALD Al_2O_3 in this presentation.

4:40pm **TF-TuA10 Multi-Scale Simulation of High-κ Gate Dielectrics Deposited by Atomic Layer Deposition**, ***Z. Hu***, *C.H. Turner*, The University of Alabama

Two of the most critical issues currently facing the semiconductor industry are the discovery of high-κ gate dielectric replacement materials for SiO_2 and the development of deposition processes that will afford high surface uniformity and controlled growth at the atomic scale. Atomic layer deposition (ALD) is an ideal candidate for meeting these challenges, enabling the deposition of a material through highly uniform and conformal growth, with thickness control at the atomic layer level. Our current work involves the use of a multi-scale modeling strategy to gain theoretical insights into the structure, properties and deposition process of high-κ dielectrics materials, which can provide a better understanding of experimental results and accurate predictions of specific properties of the thin films deposited by atomic layer deposition (ALD). In this work, we present results obtained from ab-initio quantum mechanical cluster calculations and periodic density functional theory (DFT) calculations based on tight-binding techniques. A series of calculations were carried out to study the initial ALD surface reactions. We present detailed chemical mechanisms and kinetic data at typical ALD temperatures range from 150°C to 450°C. This information can be used to understand experimental results and optimize operating conditions. The effects of surface functionalities and precursors on the thin film deposition process are discussed. Our DFT calculations show the complexity of the growth mechanisms during ALD processing. In addition, we predicted a new oxygen incorporation mechanism, which is relevant to the formation of the SiO_2 interfacial oxide layer during the ALD of Al_2O_3. As a replacement material for SiO_2, the potential high-κ oxide should form a high-quality interface with Si. We used molecular dynamics (MD) simulation to study the TiO_2/Si interface. A variable-charge inter-atomic potential was developed to describe the TiO_2/Si interface where the coordination environment may change. The TiO_2/Si interface structure was investigated by using MD with simulated annealing technique. The post-annealing oxidization process of the Si substrate was simulated by introducing external O atoms into the system to create concentration gradient. The atomic-scale mechanisms that govern the oxidation process can provide fundamental insight into the formation of the SiO_2 interfacial oxide and a better understanding of the TiO_2/Si interface structure.

5:00pm **TF-TuA11 Branched Interfacial Organic Layers: Controlling Nucleation and Growth of Thin Films**, ***M. Sharma***, *A. Dube, K.J. Hughes, J.R. Engstrom*, Cornell University

Organic layers hold great potential for use in modern electronic and optoelectronic devices, owing to both their unique material properties, and their processing properties, such as their tendency towards self-assembly. In the work we describe here we have investigated the use of self-assembled monolayers (SAMs), or more accurately interfacial organic layers (IOLs), that possess a branched backbone for use as nucleation site multipliers and amplifiers. Here we describe the synthesis and characterization of two branched IOLs, their reactivity with precursors for atomic layer deposition (ALD), and the subsequent nucleation and growth of ALD thin films of TiN on these layers. The first IOL we consider is a layer that possesses a regular branched backbone with terminal $-NH_2$ groups, based on a sequential chemical reactions and application of polyamidoamine (dendrimer) chemistry. Here, an appropriately chosen $-NH_2$ terminated SAM serves as the anchor, from which additional growth is seeded, forming an IOL with a "Y" backbone and $-NH_2$ termination. A second IOL we consider is a randomly branched organic film, possessing -OH groups both at terminal points and along the backbone, which have been grown using anionic ring-opening polymerization of glycidol. In both cases the IOLs themselves have been characterized using X-ray photoelectron spectroscopy (XPS), ellipsometry and contact angle measurements. Furthermore, the layers have been characterized concerning their reactivity with two precursors for ALD, $Ti[N(CH_3)_2]_4$ and $Ta[N(CH_3)_2]_5$, using XPS. For the dendrimer we find that the adsorptive capacity of the surface scales with the generation of the dendrimer, i.e., the branching step effectively doubles the reactivity of the surface. For the poly-G layer, however, we find that sufficiently thick layers can virtually strip the Ta complex of all of its ligands, forming a TaO_x core. These observations are borne out in the subsequent growth of ALD thin films of TiN on these layers. Nucleation on the dense $-NH_2$ terminated dendrimer is relatively facile, and STEM shows a highly conformal layer. Growth on poly-G depends sensitively on its thickness-thin layers behave in a manner similar to the dendrimer IOL, whereas thicker poly-G layers behave more akin to unreactive long-chain $-CH_3$ layers. We will conclude with a discussion of our results on porous low-κ materials.

Thin Film

Room: 4C - Session TF-TuP

Aspects of Thin Films Poster Session

TF-TuP1 A Polymer-Based Process for Substrate Transfer or Conformal Coating of Carbon Nanosheets*, **R.A. Quinlan**, B.C. Holloway, M.Y. Zhu, K. Hou*, The College of William and Mary

Carbon nanostructures such as chemically vapor deposited carbon nanotubes have shown remarkable thermal, mechanical and electrical properties, making them an area of intense scientific interest. However, their actual use in new technology has been limited by both the extreme nature of efficient growth conditions and the difficulty of conformally coating the structure while maintaining the original morphology. Carbon nanosheets - vertically oriented nanostructures of 1-5 graphene layers - have shown promise as a more robust alternative carbon nanostructure. Previous reports have detailed the synthesis of carbon nanosheets via RF PECVD on metallic, insulating and semiconducting substrates, their characterization via Raman, XRD, SEM, TEM, FTIR, PIXE, ERDA, and TDS. Of interest, previous BET measurements yielded an effective surface area of ~1,300 m^2/g, which is comparable to that of the theoretical limit for carbon nanotubes (1315 m^2/g) and much higher than that of activated charcoal. Here we report, that utilizing a customized polymer incorporation technique, nanosheets have been transferred to alternative substrates while maintaining their original morphology. The ability to transfer nanosheets to a substrate that need not take on the thermal budget of the carbon nanostructure synthesis combined with the ability to pattern nanosheets using standard photoresist techniques offers the potential for an enabling technology for more realistic nanosheet-based devices and sensors. In addition the conformal coatings of nanosheets with an industrial silicone, standard photo resist, and two photoactive polymers via a tailored spin-casting or drop-casting procedure of the polymers will also be discussed. SEM shows that, at low loadings, a conformal coating of polymer on the nanosheets is produced; thicker loadings cause intercalation of the polymer between the nanosheets and a complete incorporation of the nanosheets into a solid polymer film. Tuning the deposition conditions allows for air release and eliminates void formation and thereby minimizes undercutting when patterning the nanosheets via photoresist-based techniques.

TF-TuP2 Carbon Nanotube (CNT) Growth and Substrate Adhesion for CNT-based Materials, ***M.J. Bronikowski***, Jet Propulsion Laboratory

Growth of Carbon Nanotubes (CNTs) by chemical vapor deposition (CVD) on various substrates has been studied as various CVD process parameters are varied, and CNT up to several millimeters long have been grown in both continuous dense mats and as patterned CNT bundle arrays. The adhesion of these CNT mats to their substrate surfaces has also been investigated as a function of processing conditions, and various methods to improve CNT-substrate adhesion have been investigated. Recent results will be presented from these studies, which have as their long-term goal the incorporation of as-grown, aligned CNT mats into composite materials, so that CNTs' outstanding mechanical, thermal and electrical properties can be exhibited by the resulting materials.

TF-TuP3 Vacuum Phase Deposition of Thin Films of poly(2,6-dimethyl-1,4-phenylene oxide)/Polystyrene/Silver Nanostructured Composites and Their Electrical and Surface Adhesion Characteristics, ***I.S. Bayer**, A. Biswas, P.C. Karulkar*, University of Alaska, Fairbanks

Thin nanocomposite films comprising Poly(2,6-dimethyl-1,4-oxyphenylene)/Polystyrene and Poly(2,6-dimethyl-1,4-oxyphenylene)/Silver were fabricated using an electron beam assisted physical vapor co-deposition technique. The fabrication process is a one step novel vapor phase co-deposition of polymers and metal on substrates maintained at room temperature in a vacuum chamber. Glass, Polyethylene terephtalate, aluminum and gold were used as substrates during experiments. Nanocomposite film topologies were studied with various techniques including AFM, X-Ray diffraction, Raman Spectroscopy, Scanning Electron Microscopy and finally static contact angle measurements to estimate surface adhesion properties as a function of silver volume filling. Fabrication of the thin film structures involved evaporation and subsequent condensation of materials from specially designed tungsten crucibles. The crucibles were heated in a controlled manner by bombarding with electrons generated by applying high voltage to tungsten filaments. The deposition system had four crucibles allowing four different components to be co-deposited simultaneously. Before deposition of nanocomposites, preliminary and separate experiments were conducted in order to establish evaporation rates of Polystyrene and Poly(2,6-dimethyl-1,4-oxyphenylene) (a.k.a PPO). Different metal volume filling ratios in the thin film nanocomposites were achieved by adjusting relative evaporation rates of polymers and silver. AFM and electron micrographs of the deposited nanocomposites featured a nanoporous surface morphology. Using a multi-fluid contact angle technique (Kaeble plots) surface energy of the nanocomposites was estimated as a function of metal filling. Composite surface energy polarity increased as a function of increasing silver filling. Above a critical metal filling the composites were conductive, on the other hand particularly below this critical metal filling, based on forward bias I-V measurements, nanocomposite film-metal interfaces displayed Schottky barrier type characteristics. In addition, a number of thin film capacitors were also made by co-deposition of PPO and metal on Aluminum substrates. The thin film capacitors exhibited capacitance densities of about 4-7 nF/cm^2 up to 80 MHz frequency.

TF-TuP4 Influence of Glancing Angle Deposition (GLAD) Technique on Mechanical, Structural and Optical Properties of CuInS2 Thin Films, ***F. Chaffar Akkari***, Photovoltaics and Semiconductor Materials Laboratory, Tunisia

Porous films of CuInS2 nanostructures were grown on glass substrate by Glancing Angle Deposition (GLAD) technique and the substrate motion in order to sculpt a typical columnar microstructure into desired shapes. The deposition angle θ with respect to the surface normal was varied from 0 degree to 80degree in order to directly probe the effect of atomic shadowing on the surface morphological evolution. By changing the direction of the incident flux of the species impinging on the substrate surface, deposited films form columns that are tilted with respect to the substrate normal. The growth mechanisms and the morphology of such films were studied by scanning electron microscopy and X-ray diffraction. The influence of the flux angle was investigated. Optical properties of these coatings were also measured and discussed.

TF-TuP5 Role of Carbon Nanotube and Water in Photoconductivity of Polythiophne Based Water Soluble Polymer, *J. Choi, **D.Y. Kim***, Wayne State Univ.

Polythiophene based water soluble polymer, Sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate)] (PTEBS) is attractive as a strong candidate for photovoltaic devices and humidity sensor. PTBS is water soluble, processable using conventional solvents, and shows high response to visible light. However, the higher energy band gap and the low conductivity of the polymer are obstacles for the full utilization of full visible light spectrum range and efficient charge separation, which are critical to the efficiency of photovoltaic devices. In order to develop an efficient solar cell, understanding conduction mechanism of polymer is essential. To overcome the obstacles related to the intrinsic properties of PTEBS, we studied the photo-response as a function of voltage, polymer concentration, carbon nanotube, phase and wavelength of light. In result, we found out the photo-response depends on the applied bias voltages, carbon nanotube incorporation, wavelength of light, phase of polymer and humidity. These results can be directly applicable to design efficient photovoltaic devices for the practical applications.

TF-TuP6 Study of Point Defects in Uranium Oxide by Ab-Initio and Semi-Empirical Calculations, ***P.V. Nerikar**, S.B. Sinnott*, University of Florida

Uranium oxide is used as the standard nuclear fuel in pressurized water reactors. Point defects have an important effect on the physical properties of the fuel as they can cause swelling of the material and change the crystal structure thereby reducing the fuel performance. The aim is to understand the stability of these defects while including their correct electronic structure. Here, density functional theory calculations using the local spin density approximation with the Hubbard U correction term, or the L(S)DA+U method, is used in combination with thermodynamic approaches to calculate the formation energy of point defects present in UO_2. The nudged elastic band method is used to calculate the migration energies. These calculations are supported by semi-empirical simulations using two different potentials and larger supercells. We have been able to predict the correct electronic structure of UO_2 which allows us to consider charged defects. We predict the defect formation energies of neutral uranium vacancy and interstitial to be 4.2 eV and 7.29 eV respectively. For the oxygen vacancy and interstitial, we predict the values to be 6.33 eV and -2.71 eV respectively. The calculations thus predict that the oxygen Frenkel pair complex is the dominant defect in UO_2, which is also what is observed experimentally. We observe a similar trend with our semi-empirical calculations. We will discuss the effect of temperature, pressure and microstructural features, such as grain boundaries, on the defect formation energies.

TF-TuP7 Chemical, Optical and Electrical Properties and Radiation Effects of ZrO2/Si and HfO2/Si, ***J.M. Burst**, B.W. Schmidt, N.D. Vora, R.D. Geil, S.K. Dixit, R. Schrimpf, B.R. Rogers*, Vanderbilt University

HfO2 and ZrO2 ceramics find use in many diverse applications. Hafnia has broad usefulness in protective coatings, optical thin films, and the technologically important MOS gate dielectric. Zirconia is studied for its thermal barrier, catalytic, optical and electronic applications. Much previous work has either focused on measuring a specific material property as a function of processing, or measured radiation-induced effects without much accountability given towards material processing. Here we report on the chemical, physical, optical and electrical properties of MOCVD-grown thin hafnia and zirconia films and relate their performance to their surface, interfacial and processing conditions. We combine fundamental and application-specific analyses such as in situ Spectroscopic Ellipsometry, X-Ray Photoelectron Spectroscopy (XPS), Medium Energy Backscattering Spectrometry (MEBS) and electron microscopy with surface roughness and Capacitance-Voltage measurements both before and after radiation exposure.

TF-TuP8 PL and EL from Eu-Activated $CaAl_2O_4$-Based Multicomponent Oxide Thin-Film Phosphors, ***H. Fukada**, S. Matsui, T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

In this paper, we describe the photoluminescent (PL) and electroluminescent (EL) characteristics from Eu-activated $CaAl_2O_4$-based multicomponent oxide thin-film phosphors. Various Eu-activated $CaAl_2O_4$-based thin-film phosphors were developed using multicomponent oxides composed of $CaAl_2O_4$ with $CaGa_2O_4$ or $CaIn_2O_4$ as the host material. The phosphor thin films were prepared on thick $BaTiO_3$ ceramic sheets by either a conventional or a combinatorial r.f. magnetron sputtering deposition (rf-MSD) using a powder target. In $((CaAl_2O_4)_{1-X}$-$(CaGa_2O_4)_X)$:Eu phosphor thin film preparation, a powder mixture of CaO, Al_2O_3 and Eu_2O_3 and/or CaO, Ga_2O_3 and Eu_2O_3 calcined at a temperature range of 1000-1300°C in either a pure Ar gas or air was used as the target. The sputter depositions were carried out under the following conditions: atmosphere, either a pure Ar or an Ar+O_2 (2%), pressure, 6 Pa; r.f. power, 140 W; and substrate temperature, 100-350°C. Some deposited thin films were postannealed in either air or an Ar+H_2 (5%) gas atmosphere for 30-300 minutes at 500-1000°C. It was found that PL characteristics of $CaAl_2O_4$:Eu phosphor thin films were significantly affected by the deposition and postannealing conditions. Intense yellow-green (Y-GL) PL emission was observed from as-deposited $CaAl_2O_4$:Eu thin films prepared in a pure Ar sputter gas atmosphere using a powder target calcined at 1000°C in air. In addition, blue (B) PL emission was observed in $CaAl_2O_4$:Eu thin films postannealed in an Ar+H_2(5%) gas atmosphere at a temperature above approximately 800°C, and the intensity of the B emission increased as postannealing temperature was increased. The EL device fabricated using a postannealed $CaAl_2O_4$:Eu thin film as the emitting layer exhibited red EL emission. In addition, in the $((CaAl_2O_4)_{1-X}$-$(CaGa_2O_4)_X)$:Eu multicomponent oxide phosphor thin films were prepared by the combinatorial rf-MSD method. The obtained PL and EL characteristics from these multi-component oxide phosphor thin films were considerably affected by the postannealing conditions as well as the chemical composition ($CaGa_2O_4$ content or Ga/(Al+Ga) atomic ratio; X

TF-TuP9 Macroscale Surface Morphology in KMC Simulations of Growth on Surfaces with Negative Ehrlich-Schwoebel Barriers, ***A.K. Jones**, A. Ballestad, S. Cheng,* University of British Columbia, Canada, *T. Li,* University of Illinois, Urbana, *J. Rottler, T. Tiedje*, University of British Columbia, Canada

In order to understand which atom scale processes are important in controlling macroscopic shapes in epitaxial crystal growth, we have simulated the epitaxial growth process numerically, using a kinetic Monte Carlo (kMC) simulation of a restricted solid-on-solid model. Step edge potential barriers (Ehrlich-Schwoebel or ES barriers) are a well-known example of an atomistic property which has an important effect on macroscopic surface morphology. Most theoretical work has concentrated on the effects of positive ES barriers, which are commonly found in metals, and which lead to spontaneous mound formation. In the case of GaAs and probably other III-V semiconductors, epitaxial growth is found to be stable, suggesting a negative ES barrier. In this paper we consider epitaxial growth dynamics for vicinal surfaces with negative ES barriers. In kMC simulations as a function of surface slope we find a "magic slope" with a step density minimum. The step density minimum is caused by the fact that linear arrays of steps are more efficient at capturing adatoms than step edges in the form of loops, thereby reducing island nucleation and step density for small vicinal angles. We show that the step density minimum produces a preferred macroscopic slope similar to a crystal facet but with a different physical origin, in the smoothing of patterned substrates during epitaxial growth. Conventional wisdom[1] suggests that in the absence of nucleation, negative ES barriers lead to unstable step edges (step bunching) for 1D vicinal 'surfaces' and positive ES barriers lead to stable step edges (equally spaced steps). In kMC simulations on 2D vicinal surfaces we find a contrary result. In the case of negative ES barriers the steps become evenly spaced and the growth is stable, with or without nucleation. For 2D vicinal surfaces with positive ES barriers, at low temperatures nucleation on top of monolayer islands eventually leads to mounds and unstable growth. If nucleation is turned off, above a critical value of the ES barrier, step edge wandering eventually produces enclosed regions (pits) which do not fill in, which also leads to unstable growth.

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TF-TuP10 Detection of H_2 at High Temperature by Nickel Oxide (NiO) Based Gas Sensors, ***H. Steinebach**, L.W. Rieth, F. Solzbacher*, University of Utah

Stricter restrictions in exhaust gas emissions are creating a need for gas sensors that can operate in harsh environments and high temperatures (> 500 °C). NiO is one of the few stable p-type oxide-based gas sensitive semiconductors. Being exposed to reducing gases like H_2 or NH_3 decreases the charge carrier concentration. The sensitivity of ~50 nm thick NiO films with and without 5 nm thick gold, platinum or titanium promoter layers were compared to each other. Promoters are used to increase the gas sensitivity of metal oxides. H_2 sensitivities between 3 and 7.5 were measured from NiO films with Ti promoter layers at an operating temperature of 600 °C. NiO thin film were deposited by radio frequency (RF) sputtering with an 8" ceramic NiO target in a pure argon atmosphere (10 mTorr, 500 W, 2.48 nm/min). The films were deposited on inter-digitated electrodes (IDE) with 100 µm finger spacing to measure the change in resistance during test gas exposure. Promoter layers were deposited in a separate sputtering system. The gas sensing films were annealed for 5 hours at 900 °C in synthetic air (80% N_2, 20% O_2), nitrogen or oxygen in order to achieve stable films. As deposited and annealed films were characterized by Atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to measure the surface morphology, composition and grain size. The grain size was calculated by the Scherrer equation to be ~22 nm for the (200) NiO, Bunsenite peak, for all annealing conditions. Particle size measured from AFM micrograph were consistently near 100 nm from all annealing conditions. The gas sensitivity of these films was investigated using H_2 in synthetic air (80% N_2, 20 % O_2) or nitrogen as a carrier gas. The carrier gas composition has a strong effect on sensitivity of NiO gas sensors, with higher sensitivity in synthetic air. Pure NiO films without promoters showed gas sensitivity (S) ~1 to 4700 ppm H_2 at an operating temperature of 600 °C in synthetic air (80% N_2, 20 % O_2) carrier gas. Using the same testing conditions, promoted NiO sensitive layers with Pt and Au promoter layers showed reduction in sensitivity (S<1). Using Ti promoter layers increased the sensitivity up to 7.5 at these conditions.

TF-TuP11 Effects of Annealing Gas on Characteristics of High-k Oxide Films (HfO2) Deposited by ALD for MIM Capacitors, ***S.W. Jeong**, B.K. Kim, E.T. Lee, Y.H. Roh*, Sungkyunkwan University, Korea

Research on the insulating films in metal-insulator-metal (MIM) capacitors has focused on ways to increase the dielectric constant of insulator to improve the packing density of integrated RF capacitors. High-k oxide (e.g., Ta_2O_5) has been suggested as an alternative material to replace SiO_2 and Si_3N_4. However, reliability problem caused by leakage current may limit the application of Ta_2O_5. Properties of HfO_2 grown on the Si substrate shows a dielectric constant which is comparable to that of Ta_2O_5. Further, the characteristics of HfO_2 more stable than those obtained from Ta_2O_5, suggesting that we may use HfO_2 film as insulator in MIM capacitor. In this work, we report the physical and electrical properties of ALD-deposited HfO_2 film (11-12 nm) annealed at various gases (N_2, O_2, N_2O). HfO_2 films were annealed at 400, 600, 800°C using a rapid thermal processor for 1 min. Top and bottom metal electrodes were Pt and Pd, respectively. The electrical characterization indicates that HfO_2 MIM capacitors fabricated at 800 °C under O_2 ambient show the most desirable electrical properties, such as a high capacitance density of ~16.9 fF/µm^2, a low leakage current of 2.7×10-4 A/cm^2 at -5 V, low-voltage coefficients of capacitance, and good-frequency dispersion properties. In addition, better properties were obtained from the samples annealed using N_2O than those of samples treated using N_2. These results indicate that oxygen content has certain role(s) on the electrical properties of ALD-deposited HfO_2 film. These results, as well as further investigation of physical properties of the samples using XPS, will be presented at the conference.

TF-TuP12 Transparent Multi-Layer Diffusion Barrier Coating on PES Substrate by Low-Temperature PECVD

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Recently, transparent barrier coatings on polymer substrate have received much attention for liquid crystal displays, organic light-emitting-diode (OLEDs) displays, solar modules, and food packing applications. In this work, SiO$_x$N$_y$ and methylcyclohexane (MCH) plasma polymer films as transparent diffusion barrier coating were deposited by a low temperature plasma enhanced chemical vapor deposition (PECVD) on polyether sulfone (PES) substrate using hexamethyldisilazane (HMDSN)/N$_2$O/O$_2$/Ar gas and methylcyclohexane/Ar gas mixtures, respectively. Effects of source flow rates, plasma power and chamber pressure were investigated. The deposition rate, chemical bonding states, transparency, surface morphology and WVTR were characterized by FE-SEM, fourier transform-infrared (FT-IR) spectroscopy, UV-visible, atomic force microscope (AFM) and permeability measurement system. Multilayer structures were also fabricated in one PECVD system. Transparent multilayer of SiO$_x$N$_y$/plasma polymer with the optical transparency larger than 90%.

TF-TuP13 Fabrication of Silver Oxide Films using Reactive Bias Sputter-Deposition

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Silver suboxide (Ag$_2$O) is known to be a p-type semiconductor with a narrow band gap (1.2 eV). Lower temperature processes are needed to form the oxide films because the oxide is reduced by heat-treatment over 200 ^{o}C by dissociating the oxygen. This report describes fabrication of silver oxide films at lower temperatures using a reactive sputtering system by applying a substrate bias voltage (V$_s$). According to XRD analyses, silver films have been deposited by bias free sputtering with a lower oxygen partial pressure while AgO films have been fabricated with a high oxygen partial pressure. In the lower oxygen partial pressure environment, applying a substrate bias made silver react to oxidize such that Ag$_2$O$_3$ and Ag$_2$O films were fabricated by applying a $V_s = 20$ V, and Ag$_2$O$_3$ being formed at $V_s = 40$ V. Ag$_2$O$_3$ films showed very high resistivity. Ag$_2$O films showing p-type characteristics and lower resistivity were fabricated at $V_s = 40$ V after bias free sputter-deposition, that is, combining with and without substrate bias resulted in the fabrication of Ag$_2$O. The negative oxygen ions accelerated by the substrate bias can contribute to fabricate silver oxide in the lower oxygen partial pressure environment.

TF-TuP14 Photoluminescence Excitation Spectroscopy of Cu(In,Ga)Se$_2$ Thin Films

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Cu(In,Ga)Se$_2$ (CIGS) and related materials yield the highest performance thin film solar cells and show excellent promise for very high efficiency multijunction devices if adequate single junction devices can be produced. However, intrinsic defect chemistry and the origin of band edge fluctuations are not understood and are likely responsible for limited device performance. Low-temperature, long-wavelength photoluminescence excitation (PLE) spectra of films with varying composition, growth temperature, substrate orientation and crystallinity are presented. Despite low excitation power, low-temperature, long-wavelength PLE measurements allow for the detection of luminescence by selective wavelength excitation and reveal sub-gap absorption bands. Position-dependent photoluminescence spectra acquired from epitaxial bicrystals and apertured photoluminescence spectra on device-grade polycrystals are also presented. Local area scanning tunneling microscopy band edge measurements on in situ cleaved and sputtered CIGS are used to interpret PL results.

TF-TuP15 Phase Formation Control of Sputtered Ta(N) Films

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High quality Ta(N) barrier is required for the 65 nm node and beyond. Not only must this Ta(N) barrier be dense and conformal, it must have the correct phase and orientation in order to minimize electromigration (EM) and stress migration (SM) of dual damascene Cu structures. Two phases of Ta barrier can be observed after sputter deposition: a-Ta, which is body centered cubic (bcc), and beta-Ta which is distorted tetragonal. These two phases have different properties: alpha-Ta has lower bulk resistivity (15 - 30 µW cm vs. 150 - 200 µW cm) higher temperature coefficient of resistivity, and slightly higher density. Furthermore, a-Ta has a higher potential for driving <111> Cu orientation for better EM reliability. The formation of alpha-Ta by sputter deposition processes can occur through several methods. i) Small additives, such as N or O, into the Ta film can lead to a change in the crystalline structure from tetragonal beta-Ta to distorted a-Ta. ii) deposition temperature exceeding 400 °C. iii) using a base layer of TaN between the dielectric and deposited Ta film can drive the formation of alpha-Ta. More recently it has been observed that phase of deposited Ta(N) grown films largely depends on the combination of ion kinetic energy and ion-to-neutral flux ratio. Previous work has shown that low kinetic energy (< 20 eV) and high ion-to-neutral ratio (> 15) are essential to synthesizing low resistivity alpha-Ta. In this study, it was observed using selective area diffraction (SAED), that, under normal sputter deposition conditions, beta-Ta tends to form preferentially on the field, while weak alpha-Ta tends to form along feature sidewalls. Several studies various TaN underlayers to promote alpha-Ta formation throughout the feature have been conducted. Experimental and modeling studies to characterize process regimes necessary to synthesizing low resistivity alpha-Ta film will be discussed. Overall, the ability to deposit a TaN/Ta barrier and seed layer with the correct phase and orientation throughout the feature is essential in order to improve reliability of dual damascene Cu structures. Although, a TaN underlayer does promote alpha-Ta phase, as the TaN barrier size shrinks, the ability to deposit sputtered alpha-Ta throughout the feature is critical. It was demonstrated that the high ionization efficiency of the Inova HCM allows for the deposition of alpha-Ta at the feature sidewall.

TF-TuP16 An EIES Flux Sensor for Monitoring Deposition Rate at High Background Gas Pressure with Improved Accuracy

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Electron impact emission spectroscopy (EIES) has been proven to be a critical tool for film composition control during co-deposition processes for the fabrication of multi-component thin film materials including the high-efficiency CIGS (copper-indium-gallium-diselenide) photovoltaic cells. This technique is highly specific to atomic species because the emission spectrum of each element is unique, and the typical width of atomic emission lines is very narrow. Non-interfering emission lines can generally be allocated to different atomic species. However, the electron impact emission spectra of many molecular species are often broadband in nature. When the optical emission from an EIES sensor is measured by using a wavelength selection device with a modest resolution, such as an optical filter or monochromator, the emissions from common residual gases may interfere with that from the vapor flux and cause erroneous flux measurement. The interference is most pronounced when measuring low flux density with the presence of gases such as in reactive deposition processes. This problem is solved by using a novel EIES sensor that has two electron impact excitation sources in separate compartments but with one common port for optical output. The vapor flux is allowed to pass through one compartment only. Using a tri-state excitation scheme and appropriate signal processing technique, the interfering signals from residual gases can be completerly eliminated from the output signal of the EIES monitor for process control. Data obtained from Cu and Ga evaporations with the presence of common residual gases such as CO$_2$ and H$_2$O are shown to demonstrate the improvement in sensor performance. The new EIES sensor is capable of eliminating the effect of interfering residual gases with pressure as high as in the upper 10^{-5} Torr range.

TF-TuP17 Top-emitting Organic Light-emitting Diodes with Ba/Ag/ITO Cathode and Built-in potential Analyses in these Devices

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The top-emitting organic light-emitting diodes (TEOLEDs) have generated considerable interest in recent years, owing to their use in active matrix displays. Significant progress has been made in the development of thin semitransparent conducting cathodes (STCCs), semi-transparent conducting cathode (STCC) thin film composed of Ba (x nm)/Ag (10 nm)/ITO (100 nm) (x: 0,, 1, 2 and 3 nm) were fabricated by thermal evaporation. The optical properties of STCCs at the wavelength of 535 nm showed the transmittance of about 77 % and the reflectance of about 13 %, respectively. The TEOLED which is consisted of glass/Ag (100 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, 15 nm)/tris(8-quinolinolato) aluminum (III) (Alq3, 55 nm)/Ba (x nm)/Ag (20 nm)/ITO (100 nm) showed the highest driving performance when the deposition thickness of Ba is 1 nm. The effect reducing the barrier height for an electron-injection from Ba to Alq3 can explain a driving performance of these devices. We proved these results by measuring a built-in potential in the devices. Meanwhile, in the case of the top-emitting device with the Ba (1 nm)/Ag (20 nm)/ITO (100 nm) cathode, the maximum luminance was about 80,000 cd/m2 and an external quantum efficiency at about 100 cd/m2 was 1.5 %.

TF-TuP18 Novel Method to Fabricate BLT/CeO2/Si MFIS Structure by One-Step Chemical Mechanical Polishing Process

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Metal-ferroelectric-insulator-silicon field-effect-transistors (MFISFETs) have attracted much attention as promising non-volatile memory devices due to their nondestructive read operation possible. Both the ferroelectric and insulator materials are generally known not to be etched well with plasma etching system. Plasma damage on sloped sidewall of the ferroelectric materials and integration problem by the sloped sidewall were also reported in plasma etching process. In this study, BLT/CeO2/silicon structure was fabricated by damascene process of chemical mechanical polishing (CMP) with one-step polishing process. The process parameters of CMP were optimized for one-step CMP process for BLT/CeO2 films. This novel method to fabricate the MFIS structure could reduce the many process steps. Vertical sidewall of the BLT/CeO2 structure was also obtained, which led to densify the devices without the plasma damage. The C-V and I-V characteristics of the BLT/CeO2/Si structures were measured for MFISFET devices. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2006-005-J00902).

TF-TuP19 Dielectric and Piezoelectric Properties of Polished PZT Ceramics for MEMS Applications, ***P.-J. Ko****, P.-G. Jung, Y.-K. Jun,* Chosun University, Korea*, N.-H. Kim,* Sungkyunkwan University, Korea*, W.-S. Lee*, Chosun University, Korea

Piezoelectric actuators and sensors are main applications of micro-electro-mechanical system (MEMS). The perovskite lead zirconate titanate (PZT) piezoelectric ceramic is one of the most commonly used piezoelectric materials due to its high dielectric constant and piezoelectric coupling coefficient. The piezoelectric PZT films have been successfully fabricated and processed by using various semiconductor technologies in manufacture of MEMS applications. Some investigations on PZT-chemical mechanical polishing (CMP) process were also carried out for the patterning and the improvement of surface morphology. In this study, dielectric and piezoelectric properties of the polished PZT films were investigated for the application of CMP process to the piezoelectric MEMS applications. The crystal structure and the microstructure of PZT films were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively before and after CMP process. The P-E hysteresis loops of the polished PZT films were analyzed and compared to the as-deposited samples. Consequently, the CMP process parameters were optimized for the sufficient piezoelectric coefficient of PZT films. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2006-005-J00902).

TF-TuP20 Nitrogen-dope Effect for Photofunctional Properties of Titanium Dioxide Films Prepared by Magnetron Sputtering, ***J. Hamaguchi****, I. Takano, M. Sato*, Kogakuin University, Japan

Titanium dioxide is anticipated as one of materials which are alternative for existing solar cell technology based on silicon. Silicon has a wide wavelength range including visible light, while titanium dioxide has a shorter wavelength range under ultraviolet light, according to each band gap. Hence, many researchers have studied about improvement of absorbance band in titanium dioxide, such as doping of nitrogen using plasma,[1] doping of chromium using ion implantation,[2] or dye sensitization of titanium dioxide. In this study, photofunctional properties of nitrogen-doped titanium dioxide were investigated about the films prepared by each method of ion implantation to titanium dioxide and reactive magnetron sputtering. In the former, nitrogen ion implantation was performed after preparing titanium dioxide by reactive magnetron sputtering. In the latter, nitrogen doping was performed during formation of titanium dioxide by reactive magnetron sputtering in nitrogen gas atmosphere. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic change of methylene blue solution was applied to photocatalytic property. Light irradiation to titanium dioxide 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 titanium dioxide and platinum electrode were measured in a potassium hydrogencarbonate solution using an unresisted ammeter. In the case of nitrogen doping during film formation, photofunctional property using a fluorescent lamp showed lower photocatalytic effect and photocurrent as compared with the case of a sterilization lamp. The higher photocatalytic effect and photocurrent using a sterilization lamp were obtained at N_2 gas flow rate of 0.6 sccm and 0.4-0.5 sccm respectively, while both properties using a fluorescent lamp also showed the same behavior as a sterilization lamp.

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TF-TuP21 Formation of Nitrogen-doped Diamond like Carbon Films in a C_7H_8 Gas Atmosphere by the Ion Beam Assist 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 representative mechanical properties 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 field emission source. In this study, mechanical properties were investigated about the DLC films prepared by the ion beam assist method. The ion beam assist method of present study was applied for formation of nitrogen-doped DLC films using irradiation of nitrogen ion in a C_7H_8 gas atmosphere. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and Raman spectroscopy. The mechanical properties were evaluated by the hardness and a friction coefficient. The hardness was measured from size of an indentation with a Knoop indenter. The friction coefficient was measured for a SUJ2 ball with a constant load 0.98N until the sliding distance reaches a length of 10m. On mechanical properties, the film prepared at an acceleration voltage of 12 kV obtained the highest hardness in spite of very thin carbon layer, while the friction coefficient of this film showed the high value close to that of stainless steel. Conversely, the hardness of the film prepared at a voltage of 1 kV showed the low value, while the friction coefficient of this film obtained the lowest value. The ware track of the film prepared at a voltage of 1 kV had a small thrust in a depth as the film showed the low friction coefficient compared with the film of 12 kV. The concentration of nitrogen was around 7% at an acceleration voltage of 1 kV and was not an enough value for leading the drastic change of physical matters.

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TF-TuP22 Effects of Annealing on the Characteristics of SnO2:Sb Films Prepared by RF Magnetron Sputtering Method for Transparent Electrodes, ***S.U. Lee****, W.S. Choi, B. Hong*, Sungkyunkwan University, Korea

Tin oxide (SnO2) have been widely used as transparent conducting thin film material for application in various fields such as liquid crystal displays, optoelectronic devices, solar cells, heat mirrors and gas sensors, etc.[1] Recently the increased utilization of many transparent electrodes has accelerated the development of inexpensive transparent conducting oxide (TCO) materials. Antimony-doped tin oxide films (ATO) show the best thermal and chemical stability than other TCO films such as Al-doped zinc oxide (ZnO) and tin-doped In2O3 (ITO). Moreover, the production cost of ATO films is cheaper than other TCO materials. However its resistivity is still unsatisfactory. So, in this work, we investigated the effect of annealing treatment on the resistivity variation of the ATO films. Tin oxide films doped with antimony (Sb) of 6 wt% were deposited on 7059 corning glass by RF magnetron sputtering methods for the application to transparent electrodes. The synthesized ATO films were annealed at temperatures ranging from 300 to 600 oC in steps of 100 oC using RTA equipment in oxygen and nitrogen ambient, respectively. We measured and compared the properties of the post annealed ATO films using structural, electrical and optical methods as a function of the annealing temperature.

[1] A.V. Tadeev, G. Delabouglise, M. Labeau, Thin Solid Films 337 (1999) 163.

TF-TuP23 Self-Assembly of Organic Thiocyanates on Gold: An Alternative to Thiols?, ***C. Shen****, M. Buck,* University of St Andrews, UK*, T. Weidner, M. Zharnikov*, Universität Heidelberg, Germany

Adsorption of organothiols is a standard way to form self-assembled monolayers (SAM) on coinage metals, in particular on gold and it is the ease of preparation and flexibility in the design of the molecular structure which enables the tailoring of surface properties for a diversity of applications in (bio)sensors, electronics, or electrochemistry. However, thiols are prone to oxidation to disulfides which can seriously impede the formation of SAMs. This becomes particularly apparent in the case of dithiols where poorly ordered multilayers can form rather than well-defined monolayers with one thiol binding to the substrate and the other thiol moiety forming the SAM surface. A viable alternative to protected or unprotected thiols has recently been reported by Ciszek et al.[1] who demonstrated that thiocyanates form thiolate SAMs through cleavage of the S-CN bond. While SAMs formed from thiocyanates are, therefore, chemically identical to thiol SAMs, there are structural differences between the respective SAMs with organothiocyanates resulting in layers of inferior quality.[1,2] Since the structural quality of SAMs is a decisive factor in some applications such as those related to electrochemistry we have investigated possibilities of how to improve the quality of thiocyanate based SAMs. Applying spectroscopic and electrochemical characterisation and scanning tunneling microscopy it is shown that high quality films from isocyanate precursors can be formed. However, the quality is critically dependent on the preparation parameters such as temperature, concentration, or exposure time.

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[2] Dreesen, L.; Volcke, C.; Sartenaer, Y.; Peremans, A.; Thiry, P. A.; Humbert, C.; Grugier, J.; Marchand-Brynaert, J. Surf. Sci. 2006, 600, 4052.

TF-TuP24 Effect of Substrate Temperatures on Amorphous Carbon Nitride Films Prepared by Reactive Sputtering, *M. Aono, H. Akiyoshi, N. Kitazawa,* ***Y. Watanabe***, National Defense Academy, Japan

Amorphous carbon nitride (a-CNx) thin films were deposited on silicon single crystal and fused silica substrates by rf-reactive sputtering method using a graphite target and the effect of the substrate temperatures on film properties has been studied. The substrate temperature was varied from room temperature to 873 K. Film composition and their chemical bonding states were analyzed by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR). Film hardness was measured by nano-indentation method using a Berkovich diamond tip and the maximum load was kept at 1 mN. XPS studies show that the decreasing tendency in the composition ratio of carbon to nitrogen in a-CNx films with the substrate temperature is observed, but the bonding fraction of nitrogen and sp3-carbon increases with the substrate temperature. The D-peak position obtained from Raman spectroscopy shifts to high wave number with the substrate temperature. The nano-indentation tests reveal that the film hardness increases from 2 to 12 GPa as the substrate temperature increases from RT to 823 K. These results suggest that the film hardness is closely related to the bonding states between carbon and nitrogen. The effect of the substrate temperature on other properties will be discussed.

TF-TuP25 Investigating the Surface Morphology of Polymer Thin Films Grown by Matrix-Assisted Pulsed Laser Evaporation, ***J.M Fitz-Gerald***, *A.T. Sellinger, E.M. Leveugle, L.V. Zhigilei*, University of Virginia

The ability to achieve controlled growth of polymer and polymer nanocomposite thin films in a dry-processing environment is of significant interest to both the microelectronics and biomedical communities. While matrix-assisted pulsed laser evaporation (MAPLE) has been successfully utilized to deposit thin films spanning several classes of polymer, films often possess excessive surface roughness due to the ejection of matrix-polymer clusters from the irradiated target. Research has shown that as an ejected cluster travels through the laser-generated plume, internal polymer molecules are pushed towards the boundaries of the cluster, forming a balloon-like structure that is subsequently deposited onto the substrate surface. The deposition of these clusters results in numerous surface features exhibiting a range of geometries. In order to investigate the structural origin of these features in greater detail, coarse-grained molecular dynamics simulations were conducted to model the behavior of these clusters upon deposition onto the substrate at incident velocities of 100, 500, and 1000 m/s. The results of these simulations suggest that the structural range of surface formations observed experimentally can be partially attributed to the velocities of incident clusters prior to deposition. Previous experimental work has shown that the presence of these features can be reduced in pure polymer films by either decreasing the polymer concentration in the targets, or through substrate heating. Similar experiments were therefore performed for polymer/carbon-nanotube (CNT) composite thin film growth in an effort to both alleviate surface roughness, and enhance the dispersion of CNTs in deposited films. Characterization included the use of high-resolution electron microscopy, high-speed imaging, and infrared spectroscopy.

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+SS+TF-WeM

Catalysis for Hydrogen Storage and the Hydrogen Economy

Moderator: G. Fisher, Delphi

8:00am **EN+SS+TF-WeM1 Catalysts for Hydrogen Production by Sulfur-Iodine Thermochemical Water Splitting Cycle*,* *L.M. Petkovic*,** *D.M. Ginosar, K.C. Burch, H.W. Rollins, S.N. Rashkeev, H.H. Farrell*, Idaho National Laboratory

Thermochemical cycles can be used to split water through a series of chemical reactions where the net result is the production of hydrogen and oxygen at much lower temperatures than direct thermal decomposition. When the primary energy source to drive the cycle is nuclear or solar heat, hydrogen can be produced without the need of fossil fuels and without generating gasses considered to be responsible for global warming. The sulfur-iodine (S-I) thermochemical cycle appears promising for producing hydrogen from water. The S-I cycle consists of three simultaneous reactions: the decomposition of hydroiodic acid (HI) to produce hydrogen and generate iodine for recycle, the decomposition of sulfuric acid to produce oxygen and generate sulfur dioxide for recycle, and a main reaction where incoming water and the recycle chemicals react to regenerate HI and sulfuric acid. Both HI and sulfuric acid decomposition reactions are facilitated by heterogeneous catalysts. The high-temperature, harsh chemical reaction conditions of the sulfuric acid decomposition reaction present a significantly challenging environment for catalytic materials. In this work a number of titania (rutile)-supported platinum-group metal (i.e., Pt, Ir, Pd, Ru, and Rh) catalysts were investigated for this reaction. To develop an understanding of the factors that cause catalyst deactivation, density-functional theory-based first-principles calculations and computer simulations for transition metal particles positioned on titania (rutile) were performed. In addition, experimental determination of the activity and stability of activated carbon catalysts for the HI decomposition reaction will also be presented. Results of activated carbon characterization analyses, including surface area, temperature programmed desorption, Boehm's titration results, and contact pH of the activated carbons will be discussed.

8:20am **EN+SS+TF-WeM2 Trends in Hydrogen Splitting on Transition Metals at 1 Bar*,* *M. Johansson*,** *O. Lytken, I. Chorkendorff*, Technical University of Denmark

Despite the fact that the interaction of hydrogen with various metal surfaces has been studied extensively under ultra-high vacuum conditions, there is very little data available for the hydrogen dissociation rate on clean surfaces at pressures on the order of 1 bar. Here we investigate the hydrogen splitting rate for a number of transition metals by measuring the rate of the H-D exchange reaction. Experiments are also carried out in the presence of CO, in order to investigate the mechanism behind CO poisoning of the anode catalyst in proton-exchange membrane fuel cells. The experiments are performed in an apparatus which combines an ultra-high vacuum chamber for sample preparation and surface analysis with a high-pressure cell.[1] Model catalysts are prepared by electron-beam evaporation of metal spots onto a highly ordered pyrolytic graphite (HOPG) substrate. Typically, the spots are 1 mm in diameter and 50 Å thick. The rate of the H-D exchange reaction for each catalyst spot is measured in the high-pressure cell with the help of a combined gas dispenser and gas sampling device. The gas is sampled 0.2 mm from the center of the spot, and the sampled gas is analyzed with mass spectrometry. Measurements were carried out at 1 bar with a gas mixture containing 1 percent D_2 in H_2, with or without the addition of 10 ppm CO. The temperature was varied in the range 40 - 200 °C. The model catalysts were characterized with Auger Electron Spectroscopy (AES) before and after exposure to gases in the high-pressure cell. In order to take the back-reaction (HD splitting) into account, a simple model for the H-D exchange reaction is used. It is assumed that the sticking probability, S, is the same for H_2, HD and D_2. Under the conditions of interest here, S is mainly dependent on the coverage of adsorbed species on the catalyst surface. Once S has been extracted from the experimental data, the dissociative adsorption/desorption rate for pure H_2 at 1 bar can be calculated. So far, the metals Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt have been investigated. The measured values for S are reasonably consistent with data obtained with high hydrogen coverage under vacuum conditions. Metals which bind hydrogen strongly are expected to give lower values for S. However, S is found not to correlate with the heat of adsorption for hydrogen as determined at low coverage under vacuum conditions. The most active metal for hydrogen splitting is Ru, closely followed by Rh. For these metals, S is close to being independent of temperature. Pt and Pd give comparable values for S in the temperature range investigated, but the temperature dependence is stronger for Pd than for Pt. The activity then decreases in the order Ir, Co and Ni. No measurable activity is found for Cu. The addition of 10 ppm CO lowers the splitting rate significantly on all the metals, also at 200 °C. Among the investigated metals, Pt and Ir are the ones most sensitive to CO poisoning.

[1] M. Johansson, J. Hoffmann Jørgensen, I. Chorkendorff, Rev. Sci. Instrum., 75 (2004) 2082.

8:40am **EN+SS+TF-WeM3 Catalytic Autothermal Reforming of Renewable Fuels at Millisecond Times*,* *L. Schmidt***, University of Minnesota **INVITED**

We compare the reforming of different types of biofuels by autothermal reforming at millisecond contact times to produce synthesis gas, hydrogen, and chemicals. Fuels examined are alcohols, esters, carbohydrates, biodiesel, vegetable oil, and solid biomass. Biofuels generally have higher conversions than fossil fuels because the hydroxyl and ester linkages in these fuels produce higher sticking coefficients than for saturated alkanes. Consequently, conversions of all biofuels in these processes are nearly 100%. Highly oxygenated feedstocks tend to produce mostly syngas with little olefins or oxygenated products because surface reactions dominate, and these larger products are formed predominantly by homogeneous reaction processes after all oxygen is consumed. Recent results on production of syngas by reactive flash volatilization of nonvolatile liquids and solids will also be described. We show that, by impinging cold liquid drops or small solid particles onto the hot catalyst surface, the process can be operated in steady state with no carbon formation for many hours. This occurs because, while pyrolysis of vegetable oils and carbohydrates at low temperatures produces carbon, above ~600oC the equilibrium shifts to produce syngas rather than solid carbon.

9:20am **EN+SS+TF-WeM5 Transient Kinetic Analysis of Intermediates in Steam Reforming on Oxide Supported Cu Catalysts*,* *Y. Yang***, *R. Disselkamp*, Pacific Northwest National Laboratory*, C.T. Campbell*, University of Washington*, C. Mims*, University of Toronto, Canada, *D. Mei, J.H. Kwak, J. Szanyi, C.H.F. Peden*, Pacific Northwest National Laboratory

Formate hydrogenation was proposed to be the surface reaction channel forming methanol through reverse water gas shift by previous investigators [Chorkendorff et al., J. Vac. Sci. Technol. A, 10(4), 2277 (1992)]. The interconversion and decay of copper formates on a Cu/Gamma-Al2O3 catalyst are studied here using an apparatus that combines in-situ transmission-FTIR of adsorbed species and mass spectrometric detection of reactor effluent during transient kinetic analyses (transmission-FTIR/MS/TKA). At 573 K, ~ 2% CO and 0.07% methanol conversions were obtained by sending 2.5 bar H2:CO2 3:1 flow at 10 sccm through the reactor. It is also observed that at lower temperature, 353 K - 433 K, surface formate species are formed with the input feed stream as observed by IR. The kinetics of their transient reactivity (e.g., titration) are examined after switching to either a reducing (H2), oxidizing (2% N2O in He), or inert gas (He, Ar) feed stream. The kinetics of total formate decay at 306, 363, and 433 K under H2, He, or Ar gas exposure are observed to be comparable, suggesting that a thermal unimolecular desorption and not hydrogenation alone, is operative. However upon hydrogen exposure it is observed that within the broad formate IR band(s) there is internal species exchange which indicates two types of different formates are formed. Similar studies are presented for a SiO2 supported polycrystalline Cu sample to help identify the formate species. Methanol steam reforming on both samples were also studied for further understanding of the reverse reaction processes.

9:40am **EN+SS+TF-WeM6 Model Catalysts for Water-Gas Shift Reaction**, *S. Ma, X. Zhao, J.A. Rodriguez, P. Liu, **J. Hrbek***, Brookhaven National Laboratory

Gold supported on ceria was shown to be very active catalyst for water-gas shift reaction and low temperature CO oxidation. Both reactions are used to purify hydrogen by removing CO, a poison of fuel cell catalysts, and are therefore of importance in the hydrogen economy. In this presentation we will discribe the preparation, characterization and reactivity of an â?oinverseâ? model catalyst, i.e. CeOx nanoparticles supported on the Au(111) surface. Using STM and XPS we found that physical vapor deposition of Ce metal leads to formation of surface intermetallic compounds after annealing. The Ce-Au surface alloys have low reactivity toward oxygen, however, we were able to prepare CeOx by vapor-deposition of Ce in a moderate oxygen pressure (10-7 torr). Elongated flat ceria nanoparticles are 0.5 nm thick, several nanometers long and anchored mostly to steps. Atomically resolved images of the ceria island show well-ordered CeO2 (111) surfaces with few defects. Ce 3d photoelectron spectra were used to identify the oxidation state of Ce in oxides prepared by different methods. In general, oxidation at temperatures below 400 K leads to formation of poorly ordered nanoparticles of Ce2O3 and higher temperature annealing in background oxygen is needed to form CeO2. Individually, neither Au(111) nor CeO2(111) have any activity in the WGS reaction, while both the Au/CeO2(111) model catalyst and the CeOx/Au(111) inverse model catalyst show significant activity in high pressure experiments. Our photoemission data indicate that Ce2O3 nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the CeO2 nanoparticles are inactive. As the water dissociation could be the rate limiting step in the WGS reaction, our ability to identify dissociation products under vacuum conditions and to link them with the structural characterization at the atomic level reinforces reaction models in which the oxide support is not a simple spectator and plays an essential role in the WGS process. Acknowledgement: This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

10:40am **EN+SS+TF-WeM9 Double Role of Water in Fuel Cell Oxygen Reduction Reaction**, ***H. Ogasawara***, *L.-Å Näslund, J.B. MacNaughton, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

A management of appropriate humidity level is necessary for the fuel cell to operate. The oxygen reduction reaction (ORR) occurs at the triple phase boundary where gas, electrolyte containing water and catalytic metal particle contact forms humid and dry region on the surface of the catalyst. Using XPS and XAS, we have demonstrated active site poisoning by water, where the activation of oxygen to the adsorbed atomic phase occurs rapidly in the dry region, but not in the humid region. On the contrary, there is a promoter effect of water on the reduction of adsorbed atomic oxygen in the formation of a water-hydroxyl surface complex.

11:20am **EN+SS+TF-WeM11 Adsorption and Dehydrogenation of Carborane on Pt(111)**, ***A. Tillekaratne***, *M. Trenary*, University of Illinois at Chicago

The techniques of reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to explore the dehydrogenation on a Pt(111) surface of 1,2-dicarba-closo-dodecaborane, $C_2B_{10}H_{12}$, also known simply as carborane. Complex hydrides, such as the boranes and carboranes, are of interest as possible hydrogen storage materials because of their high hydrogen content. Many hydrides are quite stable and catalysts are needed to promote the release of hydrogen at low temperatures. The carbon and boron atoms of the $C_2B_{10}H_{12}$ carboranes occupy the vertices of a slightly distorted icosahedron and have a hydrogen weight percentage of 8.3. There are three isomers of these icosahedral carboranes, of which the ortho form (the 1,2 isomer) is the most readily available. The icosahedral structure of the boron-carbon cage structure of carborane is also adopted by the boron-rich solid boron carbide. The similarity in the structures of carborane and boron carbide has led to the successful use of carborane as a precursor gas for the growth of boron carbide thin films. However, the detailed mechanism by which carborane dehydrogenates to form boron carbide has not been previously investigated. At submonolayer coverages at 85 K the RAIRS spectrum of carborane displays strong B-H stretching vibrations near 2600 cm^{-1}, and a weak C-H stretch at 3090 cm^{-1} that indicate molecular adsorption at low temperature. The molecule is stable on the surface up to 250 K, where it is transformed into a new intermediate with a strongly red-shifted B-H stretch vibration at 2507 cm^{-1}. This intermediate is stable up to 400 K, above which no B-H stretch vibrations are observed. Hydrogen is released in stages as the carborane monolayer is heated from 85 to 800 K, which is also indicative of the formation of partially hydrogenated surface intermediates. Further analysis of the data may permit definitive identification of the surface intermediates formed during the course of carborane dehydrogenation on the Pt(111) surface.

11:40am **EN+SS+TF-WeM12 Short Range Order of Ti Dopants in Al(111): Implications for Hydrogen Storage**, ***E.M. Muller***, Brookhaven National Laboratory, *C.V. Ciobanu*, Colorado School of Mines, *P. Zahl, P. Sutter*, Brookhaven National Laboratory

Complex metal hydrides can potentially satisfy the need for lightweight, high-capacity hydrogen storage materials, a key requirement for the Hydrogen Economy. However, for most known complex hydrides the solid-state reactions involved in hydrogen release are not reversible, and their rates are low under moderate ambient conditions. The discovery that small amounts of Ti make the decomposition of sodium alanate ($NaAlH_4$) to NaH and Al reversible at moderate temperatures and pressures[1] has demonstrated doping with catalysts as a promising route to induce reversible hydrogen storage and fast reaction kinetics. A fundamental understanding of the catalytic effect of Ti in $NaAlH_4$ could form the basis for rational strategies to optimize a broader class of complex hydride hydrogen storage materials. We combine experiments on single crystal model surfaces and density-functional theory (DFT) to establish the role of near-surface Ti in the re-hydrogenation of NaH and Al to $NaAlH_4$. A likely primary effect of Ti is the formation of catalytically active surface sites enabling the facile dissociative chemisorption of H_2 on Al, which itself has very low affinity to H_2. Using chemically specific scanning tunneling microscopy and DFT we identify the stable configurations of Ti atoms incorporated into Al(111) surfaces as a first step to identifying potential catalytically active sites. Surprisingly, despite a higher surface energy of Ti (i.e., a driving force for diffusion into sub-surface sites), our observations show a pronounced stabilization of Ti at the Al surface where its catalytic effects are maximized. STM shows a large population of a specific Ti-atom pair complex, which has been predicted to catalyze H_2 dissociation.[2] We discuss the origin of this pairing, and the interaction of atomic and molecular hydrogen interactions with these surface Ti complexes.

[1] B. Bogdanovic and M. Schwickardi. J. Alloys Comp. 253-254, 1 (1997).

[2] E. Muller, E. Sutter, P. Zahl, C.V. Ciobanu and P. Sutter., Appl. Phys. Lett. 90, 151917 (2007).

12:00pm **EN+SS+TF-WeM13 Alane Formation on Al(111) and Ti-doped Al(111)**, ***S.C. Chaudhuri***, Washington State University, *J.-F. Veyan, S.C. Schaäfer*, Rutgers, The State University of New Jersey, *J.T. Muckerman*, Brookhaven National Laboratory, *Y.J. Chabal*, Rutgers, The State University of New Jersey

Complex metal hydrides, such as $NaAlH_4$, are candidates for hydrogen storage because they can reversibly release and recapture hydrogen under near ambient conditions. Surface processes in the hydrogen storage reaction in $NaAlH_4$, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na_3AlH_6 to the hydrogen-rich $NaAlH_4$, are considered as the basis for understanding reversible hydrogen storage in the chosen prototype system. Since metallic Al, particularly when doped with other metals, appear key to H_2 dissociation, we have undertaken a comprehensive study of H interaction with Al(111) and Ti-doped Al(111) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. We have combined in-situ infrared absorption spectroscopy with first principles calculations to investigate the reaction of atomic hydrogen reacts with Al surfaces. As previously observed,[1] IR spectra show that alanes are formed upon H exposure. Alanes are highly mobile species at or near room temperature and desorb from Al(111) surfaces at higher temperatures mainly as AlH, AlH_3 and Al_2H_6.[2] Using FT-IR we show that the size of the alanes formed on Al(111) depend on the temperature of the sample. For low temperatures (Ã90K), small alanes such as AlH_3 and Al_2H_6 are predominant. At higher temperatures (Ã250K), bigger alanes are formed. When the Al(111) surfaces are doped with 5% Ti, the Ti containing sites are reactive, dissociating molecular hydrogen, and thus act as a pump to generate hydride species on Al surfaces that subsequently convert into alanes. LEED is used to test the validity of first principles c alculations predicting that Ti atoms occupy hollow sites on the Al(111) surface. Using TPD, the nature of desorbed species from Al(111) and Ti-doped Al(111) surfaces have been analyzed as a function of the sample temperature after either atomic H or H_2 exposures. This presentation summarizes hydrogen dissociation on Ti/Al(111), and alane formation and mobility on both Al(111) and Ti/Al(111) surfaces.

[1] Eden P. Go, Konrad Thuermer, Janice E. Reutt-Robey, Surf. Sci. 437 (1999) 377

[2] Hara, M.; Domen, K.; Onishi, T.; Nozoye, H., J. Phys. Chem., 95, (1), (1991) 6-7

Surface Science

Room: 611 - Session SS2+EM+TF-WeM

SAMs and Organic Films I

Moderator: H. Fairbrother, Johns Hopkins University

8:00am **SS2+EM+TF-WeM1 Scanning Tunneling Microscopy Growth Study of a Columnar Liquid Crystalline Hexaazatriphenylene Derivative on Au(111)**, ***S.D. Ha***, Princeton University, *Q. Zhang, S. Barlow, S.R. Marder*, Georgia Institute of Technology, *A. Kahn*, Princeton University

The growth of a discotic liquid crystal derivative of tris(thieno)hexaazatriphenylene (THAP) is studied with scanning tunneling microscopy (STM). An electron transport material with relatively high electron affinity (4.59eV), THAP is expected to form columnar stacks in a thick bulk film. It is shown with STM that on Au(111), the first four monolayers of THAP molecules order in such columnar mesophases. The first monolayer forms a square 10.1Å x 10.1Å unit cell with one molecule per cell. However, this is much smaller than expected, and it may be due to buckling caused by the substrate interaction or in-plane molecule-molecule interaction. The second monolayer, at partial coverage, grows commensurate to the first monolayer in a rectangular herringbone with two molecules per 15.7Å x 14.0Å unit cell. The molecules tilt in order to conform to the packing of the first layer and the interlayer interaction controls the molecular orientation. Yet upon full coverage of the second monolayer, the intralayer interaction prevails and the molecules reorganize into a hexagonal close-packed (HCP) structure without obvious tilt. The unit cell is rhomboidal with dimensions 21.0Å x 22.2Å and one molecule per cell. Moreover, the rotational orientation of the molecules forms a herringbone pattern, with alternating rows of the HCP structure switching between two opposite orientations. As for the third and fourth monolayers, STM images indicate that they have HCP geometry with the same dimensions as the second layer. Given the tendency of molecules similar to THAP to stack into columns, it is likely that because the third and fourth layers have the same in-plane structure as the second layer, they are commensurate to the latter. Thus, on Au(111), THAP readily grows in the expected columnar liquid crystal fashion directly from the interface layer, and the columns are hexagonal close-packed with negligible molecular tilt.

8:20am **SS2+EM+TF-WeM2 UHV-STM Studies of DNA Bases on Au(111)**, ***W. Xu***, *R. Otero, M. Schock,* Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark, *R. Kelly, L. Kantorovich,* King's College London, UK, *F. Besenbacher*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

The self-assembly of Nucleic Acid (NA) base molecules on solid surfaces has recently attracted much attention as on one hand, such studies provide invaluable insight into fundamental interactions between these molecules. On the other hand, NA base molecules and DNA molecules are particularly interesting as promising building blocks for the bottom-up fabrication of functional supramolecular nanostructures on surfaces within the emerging area of nanotechnology. From a biological point of view, the self-assembly processes in DNA and RNA molecules are controlled by i) cross-strand interactions between NA base molecules, which are dominated by hydrogen bonds (H-bonds), ii) stacking interactions between NA base molecules along the strand, and iii) the interactions of NA base molecules with water molecules and metal ions, such as Na+, K+. Among these interactions, the hydrogen bonding between NA base molecules plays a crucial role in determining the conformation and biochemical properties of DNA and RNA molecules. Hence, it is important and interesting to study the fundamental interactions between NA base molecules at the single molecule level to reveal the exact physicochemical nature of the biological systems. Here we will show our recent experimental progress on four individual NA base molecules (guanine, adenine, cytosine, thymine) that are adsorbed on Au(111) surface under Ultrahigh Vacuum (UHV) conditions. We demonstrate by variable-temperature scanning tunnelling microscopy (VT-STM) experiments that guanine and adenine form 2D island with well-ordered structures through hydrogen bonds, and the so-called guanine quartet structure is found to be stabilized by the cooperative hydrogen bonds. Interestingly, cytosine only forms disordered 1D filamentary structure by fast cooling the sample, whose behavior could be described as a 2D organic glass. Thymine in the first stage (low surface coverage) also forms 1D filamentary structure steered by hydrogen bonds. However, when the surface coverage is increased, the filaments could merge into 2D well-ordered islands by van der Waals (vdW) interactions. Moreover, we have also investigated that the thymine 2D island can be broken back into the 1D hydrogen bonded filaments by STM manipulation, which further confirm that we are able to directly probe the hierarchy of bond-strengths involved in the surface self-assembly of multifunctional organic molecules with highly anisotropic interactions.

8:40am **SS2+EM+TF-WeM3 Understanding Molecular Exchange on Surfaces: Controlling and Elucidating the Mechanism of 1-Adamantathiolate Monolayer Displacement**, ***H.M. Saavedra***, *T.J. Mullen, C.M. Barbu,* The Pennsylvania State University, *A.A. Dameron,* University of Colorado, *V.H. Crespi, P.S. Weiss*, The Pennsylvania State University

We have investigated the solution-phase displacement kinetics of 1-adamantanethiolate self-assembled monolayers on Au{111} by n-dodecanethiol molecules using infrared spectroscopy, scanning tunneling microscopy, x-ray photoelectron spectroscopy and electrochemical desorption. The displacement reaction can be described by the fast insertion of n-dodecanethiolate at defects in the original 1-adamantanethiolate monolayer, which nucleates island growth and is followed by eventual slow ordering of the n-dodecanethiolate domains. Langmuir-based kinetics, which describe alkanethiolate adsorption on bare Au{111}, fail to describe this displacement reaction. Instead, a Johnson-Mehl-Avrami-Kolmogorov model of perimeter-dependent island growth yields good agreement with kinetic data obtained over a hundred-fold variation in n-dodecanethiol concentration. Analysis on a model-free basis suggests that displacement is a scale-free process within this concentration regime. The crucial role of the adsorbate lattice, along with the thermodynamic driving forces, rationalizes the rapid and complete displacement of 1-adamantanethiolate monolayers and explains why other monolayers reach kinetic traps that result in slow and incomplete displacement.

9:00am **SS2+EM+TF-WeM4 Thermal Treatment of Glutamic Acid Etched Ni Nanoclusters on Au{111} Leads to the Formation of 1-D Metal Organic Co-Ordination Networks**, *A.G. Trant, T.E. Jones,* ***C.J. Baddeley***, University of St Andrews, UK

The adsorption of glutamic acid onto 2-D Ni clusters on Au{111} has been investigated using reflection absorption infrared spectroscopy (RAIRS) and scanning tunnelling microscopy (STM). Adsorption at 300 K leads to two distinct adsorbate species which we conclude are zwitterionic species adsorbed either at Ni-like sites in the centre of the clusters or at interfacial sites at the edges of clusters. Adsorption of (S)-glutamic acid causes the complete destruction of clusters of initial diameter <3 nm. We conclude that the Ni islands have been corroded resulting in the formation of a Ni salt - presumably nickel (II) glutamate. On annealing to 350 K, chains of 1-D molecular features are observed in STM experiments. We discuss the possible composition and structure of this salt and conclude that the chains most likely consist of nickel (II) pyroglutamate. Metal pyroglutamate salts are known to be produced by heating glutamate salts. The intermolecular bonding and azimuthal alignment of the 1-D chains are discussed. We also report the formation of analogous networks from Ni + (R)-glutamic acid and discuss the influence of stereochemistry on the structure of the networks.

9:20am **SS2+EM+TF-WeM5 Crossover from Site-Sensitive to Site-Insensitive Adsorption of the Fullerene Derivative PCBM on Au(111) due to Hydrogen-Bond Formation**, ***D. Ecija***, *R. Otero,* Univ. Autonoma de Madrid, Spain, *L. Sanchez,* Univ. Complutense de Madrid, Spain, *J.M. Gallego,* Inst. de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, *Y. Wang, M. Alcami, F. Martin,* Univ. Autonoma de Madrid, Spain, *N. Martin*, Univ. Complutense de Madrid, Spain, *R. Miranda*, Univ. Autonoma de Madrid, Spain

The 2D arrangement of organic adsorbates at solid surfaces results from a combination of non-covalent intermolecular forces with molecule-substrate interactions. It is generally thought that molecule-substrate interactions determine adsorption geometry and conformation in first place, while intermolecular interactions affect the subsequent self-assembly of the adsorbates. Only when the molecules can form strong directional bonds, like hydrogen bonds or coordination bonds, and the corrugation of the adsorption potential energy is small, the supramolecular structure is dominated by intermolecular interactions. On the other end of the spectrum, vicinal or heterogeneous surfaces show a strong selectivity in the adsorption site of the adsorbates, leading to a final morphology which is almost exclusively substrate-controlled (templated growth). Usually, the role of molecule-substrate interactions on self-assembly is discussed at the single-molecule level, but this is strictly speaking just an approximation, since the formation of intermolecular bonds might modify the adsorption geometry and thus molecule-substrate interactions. For systems showing site-selective adsorption, the modification of the adsorption geometry upon intermolecular bond formation might result in the removal of the site-selectivity. By means of variable-temperature Scanning Tunneling Microscopy (STM) experiments and Density Functional Theory (DFT) calculations, here we investigate the crossover from site-selective to site-insensitive adsorption of PCBM, a C60 derivative, on the herringbone-reconstructed Au(111) surface as a function of the coverage. Whereas at low coverages PCBM self-assembly is dictated almost exclusively by the substrate-related preference for nucleating at the fcc sites of the reconstruction, with a selectivity close to 100%, at higher coverages intermolecular interactions take over the substrate influence, giving rise to PCBM islands that extend through fcc, hcp and dislocations of the herringbone reconstruction. Comparison with theoretical calculations offers the following picture of this crossover: at high-enough coverages hydrogen bonds between double rows are formed that modify the adsorption geometry of PCBM molecules, which in turn removes site-selectivity. The phenomenon of intermolecular interaction-driven modification of the adsorption geometry might thus be crucial to optimize the templating effect of surface nano-scale patterns on adsorbed organic overlayers.

9:40am **SS2+EM+TF-WeM6 Nanostructured Binary Molecular Films: Lessons from ACA:C_{60} Mixtures**, ***J.E. Reutt-Robey***, University of Maryland, *B. Xu,* Yanshan University, China, *C.G. Tao,* University of Maryland, *D.B. Dougherty,* National Institute of Standards and Technology, *W. Jin*, University of Maryland

Multi-component aromatic molecular films are of increasing interest in photovoltaic technologies and other organic electronic applications. Binary organic films offer the potential to tailor film structure on the nanoscale to optimize device performance through phase selection, domain size, distribution and orientation. A basic understanding of the factors that control structure in binary molecular films is thus important to advance these materials technologies. We report STM-studies of structure evolution in model donor-acceptor systems, such as ACA:C_{60} and Pentacene:C_{60}. Films prepared by sequential physical vapor deposition onto Ag(111) substrates under UHV are monitored directly with an integrated UHV-STM. We demonstrate how ACA:C_{60} film growth conditions can be adjusted to selectively fabricate films that range from phase-separated hexagonal -C_{60} and chain-phase [4 0, 2]-ACA domains to intermixed co-crystalline chiral domains comprised of C_{60}-terminated ACA pinwheels. Films produced with arbitrary composition generally lead to complex multi-phase structures. Predeposited ACA films with single phase structures provide the most effective pathway to single phases of intermixed structures. For example, the intermixed chiral phase is only accessible from the 2-D ACA molecular gas, whereas extended C_{60} chain structures may be accessed only from the dimer-phase [12 2, 6 5]-ACA domains. We apply lessons from the ACA:C_{60} system to Pentacene:C_{60}, mixtures, utilizing the 2-D pentacene gas to access an intermixed honeycomb Pentacene:C_{60} phase.

10:40am **SS2+EM+TF-WeM9 Detection of Gaseous Nitric Oxide Using X-ray Photoelectron Spectroscopy**, ***M. Dubey***, *J. Schwartz*, *S.L. Bernasek*, Princeton University

Detection of gaseous nitric oxide (NO) in biological systems has attracted significant attention since the identification of NO as the endothelial-derived relaxing factor (EDRF).[1] NO also acts as a signal molecule in the nervous system, and is associated with the presence of infection and Alzheimer's and other diseases. Apart from biological systems, NO is a main product released on the pyrolysis of nitro-organic explosives. For these reasons, much work has been done in the field of NO detection, and the need for a sensitive detector is evident. In this study, we report a direct and a highly sensitive technique to detect gaseous NO using X-ray Photoelectron Spectroscopy (XPS). The binding of NO by heme proteins is well understood,[2] and we have utilized it for detection. We have developed a reliable method to grow Self-Assembled Monolayers (SAMs) of alkylphosphonic acids on oxide surfaces.[3] This platform is used to covalently attach a uniform layer of an iron heme-like molecule, which was synthesized separately. Differential charging in XPS has been used to ascertain the uniformity of the organic film.[4] The N1s signal from the heme ligand was measured by XPS before and after exposure to NO. Before NO binds to the iron, a single nitrogen peak is present, attributed to the nitrogens of the porphyrin ring. After reaction with NO, a new, distinct peak was observed in the high resolution N1s spectrum. This peak is at a higher binding energy (approx 5.5 eV), and is attributed to the NO bound to the iron. An estimate of the bound NO was calculated using XPS and QCM to be about 40 picomoles.

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11:00am **SS2+EM+TF-WeM10 An In Situ EC-STM Study of the Restructuring of Self-Assembled Monolayers upon Metal Deposition**, ***C. Silien***, *M. Buck*, University of St Andrews, UK

The combination of electrochemistry and self-assembled monolayers offers interesting opportunities for nanotechnology due to high resolution defined by patterned SAMs and simplicity and scalability afforded by electrochemistry. However, control of processes such as electrochemical metal deposition on the nanometer length scale requires exact knowledge of the mutual influence of a SAM structure and electrochemical processes. Aiming for an understanding at the molecular level we report an investigation of the underpotential deposition of copper on Au(111) electrodes modified by ω-(4'-methyl-biphenyl-4-yl)-alkanethiols (H_3C-(C_6H_4)-(C_6H_4)-$(CH_2)_nSH$, BPn). As reported recently, this class of molecules gives rise to pronounced structural variations with length n of the alkane spacer and, for n = even, exhibits polymorphism.[1,2] Furthermore they can be prepared to an exceptionally high structural perfection. These properties make SAMs of BPn thiols an attractive basis for further tailoring of properties of functionalized electrodes and the electrochemical generation of nanometer-scaled structures. A decisive step in SAM controlled electrometallisation is the deposition of the first layer of metal which takes place in the underpotential region. Its understanding is of crucial importance as this layer forms at the SAM-substrate interface and, therefore, affects the properties of the system. Our in situ STM investigations of the underpotential deposition reveal, firstly, pronounced differences between BPn SAMs and alkane thiols and, secondly, a pronounced influence of the length of the alkane spacer in the BPn SAMs, i.e., whether n = odd or even. The molecular resolution achieved in this study combined with time resolved monitoring of the events occurring in the course of the copper deposition allows us to highlight the relationship between the SAM structure and its influence on the generation of nanometer scaled structures by electrochemical metal deposition.

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11:20am **SS2+EM+TF-WeM11 Irradiation-Promoted Exchange Reaction: A New Approach to the Fabrication of Heterogeneous Self-Assembled Monolayers and Chemical Lithography**, ***N. Ballav***, *T. Weidner, M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) can undergo an exchange reaction with the molecules capable of building a SAM on the same substrate upon the immersion into the respective solution. However, for most systems, the exchange reaction is very slow and incomplete at normal conditions, taking from days to weeks and occurring to a limited extent only. Using several different model systems, we show that the rate and extent of the exchange reaction can be significantly enhanced and even precisely tuned by either electron irradiation with a small dose or exposure to UV light. We assume that both electron and UV irradiation result in the appearance of structural and chemical defects in the target SAM, which promote the molecular exchange. The effect of irradiation and the parameters of the exchange reaction were monitored in detail and correlated with each other using several complementary experimental techniques. The developed approach, irradiation-promoted exchange reaction, can be considered as a platform for the preparation of heterogeneous mixed SAMs. Also, in combination with e-beam or UV-lithography, this method can be used for the fabrication of chemical patterns, including gradient ones. In this regard, the approach is similar to conventional photography: a desired pattern is initially written by electron or UV beam and later "developed" upon its immersion into the solution of a molecular substituent. There are no principal limitations for the form of the fabricated features while the characteristic length scale can be varied in a broad range from centimetres to several tens of nanometers.

11:40am **SS2+EM+TF-WeM12 Calcium Adsorption on Regioregular Poly(3-hexylthiophene): Synchrotron Radiation Photoemission and Microcalorimetric Studies**, ***J.F. Zhu***, *W. Zhao, W.H. Zhang,* University of Science and Techonology of China, *J. Farmer, C.T. Campbell*, University of Washington

The adsorption of Ca on the regioregular poly(3-hexylthiophene) (rr-P3HT) thin film surfaces at 300 K has been studied using synchrotron radiation photoemission spectroscopy, adsorption microcalorimetry and atomic beam/surface scattering. The polymer films were spin-coated on the Si wafers with typical thickness of > 100 nm and were free of oxygen contamination as clarified by both X-ray photoelectron spectroscopy and Auger electron spectroscopy. Synchrotron radiation photoemission spectroscopy provides precise experimental information on the alteration of the Ca/polymer interfacial energy level line-up and the chemical nature at this interface. The deposition of calcium on the rr-P3HT film at room temperature induced a decrease of the work function, indicating Ca donates electron density to the polymer substrate. Moreover, Ca adsorption led to the depression of the bands of the rr-P3HT. The strength of interaction between Ca and the rr-P3HT is probed by both microcalorimetric heats of adsorption and sticking probability measurements.

12:00pm **SS2+EM+TF-WeM13 Supramolecular Coordination Networks at Surfaces: Self-selection and Error Correction in Multi-ligand Nanopore Arrays**, ***S.L. Tait***, *A. Langner, N. Lin,* Max Planck Institute for Solid State Research, Germany, *C. Rajadurai, M. Ruben,* Research Center Karlsruhe, Germany, *K. Kern*, Max Planck Institute for Solid State Research, Germany and Ecole Polytechnique Fédérale de Lausanne, Switzerland

Supramolecular self-assembly of organic ligands and metal centers is a topic of growing interest for efficient molecular-scale patterning of surfaces. Molecular networks can be designed to self-organize in regular, 2D nanopore lattices, whose dimensions and properties can be controlled by selection of the organic ligands. This approach offers a natural alternative to current nano-fabrication methods, allowing atomic and molecular building blocks to organize themselves into useful nanostructures, and is a model system for supramolecular and biomolecular assembly in general. We present recent results of self-assembled supramolecular networks on the Cu(100) surface, which demonstrate multi-ligand construction of 2D arrays of compartments with tunable shape and size. These binary combinations of complementary ligands represent a significant step in complexity over previous studies. Of technological interest is the capability for modular replacement of either of the two ligands to produce a range of nanopore lattice sizes and shapes in a very predictable and programmable way. Of more fundamental interest in these systems is molecular level resolution imaging using scanning tunneling microscopy, which allows an unprecented perspective of fundamental steps to supramolecular assembly, such as structural error correction achieved by efficient molecule self-selection. Non-covalent metal—organic coordination provides room temperature stability and high structural ordering through directional and selective interactions, but also allows for bonding reversibility, enabling error correction during assembly. By selection of molecular building blocks with specific properties, we can "program" these systems to pattern a surface with homogenous networks of specific size, structure, and physical and chemical properties. The ability to tailor the size and functionality of nanometer-scale arrays produced by molecular self-assembly represents a unique opportunity for molecular recognition, heterogeneous catalysis, thin film growth, and other fields.

Thin Film

Room: 613/614 - Session TF-WeM

Thin Film and Nanoparticle Growth and Characterization

Moderator: J.M Fitz-Gerald, University of Virginia

8:00am **TF-WeM1 Dependence of Fiber Texture on Connectivity in Composite Thin Films**, ***J.M.E. Harper***, *D. Carlson, A.M. Brown, D.I. Filoti*, University of New Hampshire

The connectivity of metal-insulator composite thin films varies with composition from a continuous metal phase surrounding insulating islands, through a variety of interconnected networks, to disconnected metal islands within a continuous insulating phase. We show that the strength of the metal fiber texture correlates with the degree of metal connectivity. Composite thin films of Au-SiO$_2$ and Ag-Si were deposited using dual-source magnetron sputtering and the crystallographic texture was determined using x-ray pole figure measurements. For metal-rich compositions, we observe strong 111 Au or Ag fiber texture perpendicular to the substrate plane, similar to the fiber texture of pure fcc metal films. As the volume fraction of SiO$_2$ or Si is increased, the strength of the 111 fiber texture decreases monotonically until a random texture is observed. The composition at which the fiber texture is lost correlates well with the composition at which the metal component becomes discontinuous, as determined by resistivity and transmission electron microscopy measurements. We conclude that x-ray pole figure measurements of fiber texture can be used for non-contact determination of the connectivity of phases in composite thin films.

8:20am **TF-WeM2 Morphology Evolution during Growth of Epitaxial Ti$_{1-x}$Al$_x$N and Cr$_{1-x}$Al$_x$N Films onto MgO(100) and MgO(111)**, ***M. Beckers***, *H. Willmann, J. Birch,* Linköping University, Sweden, *J. v. Borany,* ROBL-CRG at ESRF, France, *P.H. Mayrhofer, C. Mitterer,* University of Leoben, Austria, *L. Hultman*, Linköping University, Sweden

Metastable Ti$_{1-x}$Al$_x$N has found widespread industrial use as hard coating for cutting and forming applications, while the knowledge base for Cr$_{1-x}$Al$_x$N on structure-property relations still evolves. Here, we report on growth studies of epitaxial Ti$_{1-x}$Al$_x$N and Cr$_{1-x}$Al$_x$N films deposited onto MgO(100) and MgO(111) substrates by reactive magnetron sputter epitaxy. Both orientations promote cube-on-cube epitaxial growth. However, transmission electron microscopy reveals a smooth single-crystal morphology for the MgO(100) and a facetted columnar morphology for the MgO(111) substrate. This can be ascribed to the highly anisotropic step energies for the corresponding nitride growth surfaces, resulting in a switch between layer-by-layer and island growth mode as characterized by in-situ x-ray diffraction experiments. High-resolution x-ray reciprocal space maps display that films deposited onto MgO(111) grow fully relaxed with lattice parameters that correspond well to literature values at the given compositions. The growth mode on MgO(100) substrates depends on the Al fraction. Ti$_{1-x}$Al$_x$N films at low Al fractions that are well lattice-matched to MgO show pseudomorphic strained growth with a small percentage of in-plane strain relaxation due to interfacial misfit dislocations, and exhibit almost defect-free single-crystal morphology. On the contrary, less lattice-matched (Ti,Cr)$_{1-x}$Al$_x$N films with x close to the AlN precipitation threshold show an initial pseudomorphic strained layer that relaxes for increasing film thickness. The relaxation starts with interfacial misfit dislocations that gradually evolve into a dislocation network along the {111}<110> slip system. For Cr$_{1-x}$Al$_x$N films with an Al fraction of 0.6, this dislocation network is superimposed by crystals of first-order twins about [111] with the orientation relationship Cr$_{1-x}$Al$_x$N (122) // MgO (100). The twins overgrow the primary (100) orientated film, likely due to the angular vicinity of fast growing (111) planes. These diverse relaxation mechanisms might be attributed to changed stacking fault energies for different Al fractions. Since polycrystalline Ti$_{1-x}$Al$_x$N and Cr$_{1-x}$Al$_x$N show AlN precipitation at grain boundaries during annealing, the observed morphology changes for different substrate orientation and stoichiometries have impact for the understanding of age hardening in these systems.

8:40am **TF-WeM3 A Mesoscopic View on Complex, Stress-Governed Phenomena in Submonolayer Ag-films on Pt(111) at High Temperature**, ***B. Poelsema***, *E. Van Vroonhoven*, University of Twente, The Netherlands

The growth of ultrathin silver films at 750 K on Pt(111) has been studied with LEEM. The STM-based previous reports on surface confined alloying in this bulk immiscible system are confirmed. This information is inferred from the evolution of the electron reflectivity as well as indirectly from the distribution of adatom islands indicative of highly unconventional nucleation behavior extending to extremely high coverages. De-alloying as previously reported is also confirmed basically. The in-situ mesoscopic data, however, reveal a number of previously unnoticed features. For instance de-alloying is accompanied by strong segregation effects. Platinum-rich disks evolve during de-alloying, showing up as persistent "dark spots" in a bright field measurement, irrespective of the energy of the probing electrons. Also no additional diffraction features spots are observed, indicative of the Pt-disks being highly disordered, amorphous or possibly liquid. In a very narrow coverage window around 85% of a monolayer μ-LEED measurements demonstrate a sudden stress relieve. At this point the de-alloying reaches a summit and the film temporarily releases stress by expansion. This goes together with enhanced segregation. Further along the route to monolayer completion we observe reentrant alloying which actually persists during the growth of a few more layers. Also the film quickly resumes its pseudomorphic structure.

9:00am **TF-WeM4 Field Emission Suppression from Stainless Steel Using Silicon Oxynitride Coatings**, ***N.D. Theodore***, *B.C. Holloway,* The College of William and Mary, *C. Hernandez-Garcia, H.F. Dylla,* Jefferson Lab, *D. Manos*, The College of William and Mary

We have developed a new RF inductively-coupled, plasma-based, reactive sputtering procedure to deposit high-purity silicon oxynitride (SiO$_X$N$_Y$) films. Oxynitride formation was verified using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Using profilometry, we determined that increasing the nitrogen plasma pressure or the RF power raises the deposition rate. However, FTIR results show that adjusting the plasma pressure also altered the amount of bound nitrogen in the silicon oxynitride layer. The resulting silicon oxynitride coatings have also been characterized with Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS), and elastic recoil detection analysis (ERDA) to determine their elemental composition and density. This silicon oxynitride coating drastically reduced field emission from large area, stainless steel electrodes. High voltage tests showed that a polished, 180 cm^2, stainless steel electrode exhibited 27 μA of field-emitted current at 15 MV/m; however, by applying a silicon oxynitride coating to a similarly polished electrode, emission current was drastically reduced to less than 300 pA at 30 MV/m. The field emission from these silicon oxynitride coatings seems to follow the electron emission mechanisms proposed by Schottky and Poole-Frenkel. Both of their emission equations predict that increasing the band gap, dielectric constant, and electron affinity of the silicon oxynitride coatings could further reduce field emission. Our most recent high voltage tests of two polished electrodes coated with a 'graded' silicon oxynitride layer supports these predictions; at 30 MV/m, the field emitted current was below 4 pA, the detection limit of our high voltage test system.

9:20am **TF-WeM5 A Study of Tungsten Silicon Nitride Films Used for Thermal Inkjet Printheads**, ***J. Wonnacott***, *E. Whittaker, G.S. Long, B. Risch*, Hewlett-Packard Company

Thin ternary films of tungsten and silicon nitride (WSiN) have been studied for use as heater resistors in thermal inkjet printheads. Product applications require films with the appropriate bulk resistivity and thermal stability at process and performance temperatures. A typical resistor may be required to heat and eject several billion ink drops over the lifetime of the printhead. The heating of the WSiN causes changes in film properties that adversely effect ink drop ejection and the subsequent print quality. Specific electrical annealing procedures have been used to stabilize the as deposited WSiN film for resistor firing conditions during printing. Various analytical techniques including X-Ray Diffraction (XRD), X-Ray Reflectance (XRR), X-Ray Fluorescence (XRF), X-Ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM) have been used to study the WSiN film characteristics after the initial Physical Vapor Deposition (PVD), after actual use in printheads, and after simulated use by rapid thermal processing on blanket deposited films. The PVD processing parameters and WSiN target composition have been varied to study the impact the resulting performance of the resistor film. Employing these analytical techniques optimized resistor films have been explored for high temperature stability characteristics.

9:40am **TF-WeM6 Ti as an Interface Stabilizer for Fe-Al Interfaces*,** ***W. Priyantha**, A. Comouth, A. Kayani, M. Finsterbusch, H. Chen, M. Kopczyk, D. Tonn, R.J. Smith,* Montana State University*, D.E. McCready, P. Nachimuthu*, Pacific Northwest National Laboratory

The use of ultra-thin metal interlayers to stabilize metal-metal interfaces and to limit interdiffusion has drawn much attention over the past few years, driven by a variety of technological applications. Earlier, we reported using a Ti monolayer as an interlayer to promote epitaxial growth and to minimize diffusion at the Fe/Al(001) interface. These findings encouraged us to explore the use of interlayer structures for thin films of technological interest deposited on Si wafers using RF sputtering. AlFe and FeAl metal bi-layers, with and without a Ti stabilizing interlayer, were studied using Rutherford backscattering (RBS) and X-ray reflectivity (XRR). Analysis revealed that FeAl and AlFe films without a Ti interlayer on SiO2/Si wafers showed considerable Fe-Al intermixing, especially when the Fe layer was deposited on top of the Al layer. With a Ti interlayer present the interfaces exhibited less interdiffusion.

* This work was supported by the National Science Foundation, NSF Grant DMR 0516603.

10:40am **TF-WeM9 Size-Selected Clusters: From 3D Atomic Structure to Applications in Biochips*, R.E. Palmer***, The University of Birmingham, UK **INVITED**

In this talk I will address both atomic-scale characterisation and biological applications of size-selected atomic clusters. Today's advancements in nanotechnology present new challenges for the quality, speed and precision of nanostructure characterization. Here we show that the new generation of aberration-corrected scanning transmission electron microscopes (STEM), coupled with simple imaging simulation, is capable of providing three-dimensional structural information[1] with atomic resolution in a single shot, revealing not only the size but also the shape, orientation and atomic arrangement, for size-selected gold nanoclusters that are preformed in the gas phase and soft-landed on an amorphous carbon substrate. The structures of gold nanoclusters containing 309 (@+=@5%) atoms can be identified with either decahedral, cuboctahedral or icosahedral geometries. The work illustrates a new and efficient means to study the atomic structure and the stability of supported, ultra-small metal clusters in the nanometre range, e.g. catalyst and extracellular particles, with single atom sensitivity. The controlled deposition of such size-selected Au clusters, of size 1-10nm, also provides a route to the fabrication of novel surface binding sites for individual biological molecules, notably proteins. We report the pinning[2,3] of size-selected Au_N clusters (N = 1-100) to the (hydrophobic) graphite surface to create films of arbitrary, sub-monolayer density. Gold presents an attractive binding site for sulphur and thus for cysteine residues in protein molecules. AFM measurements in buffer solution[4,5] show that GroEL chaperonin molecules (15 nm rings), which contain free cysteines, bind to the clusters and are immobilised.[5]. Peroxidase[6] and oncostatin molecules behave similarly. By contrast, green fluorescent protein (GFP) does not bind, consistent with detailed analysis of the protein surface; the cysteine residues lie in the interior of the folded protein. The results provide "ground rules" for residue-specific protein immobilisation by clusters. The extension of the approach to optical surfaces is enabling the production of prototype biochips (microrarrays) for protein analysis, e.g., early stage cancer-marker detection.

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11:20am **TF-WeM11 Formation of Robust, Freestanding Tantalum Oxide Films with Controlled Morphology*, P. Kruse**, S. Singh*, McMaster University, Canada

We have previously shown that electropolishing of tantalum in concentrated acid mixtures can reproducibly lead to very flat surfaces with dimples tens of nanometers in diameter, regular in shape, monodispersed in size and arranged in highly ordered arrays which even transverse grain boundaries. In this work, we are demonstrating the anodic growth of nanometer thick, detachable, amorphous tantalum oxide films with tuneable morphology (porosity) on these surfaces. Large (sqcm) sections of these flexible tantalum oxide films can be separated as sheets from the base tantalum surface by a Lift- Off-Float-On technique. The sheets can then be transferred to a wide variety of substrates, like Si wafers, glass slides, TEM grids etc. We have thoroughly characterised the films and are studying their growth conditions with the intention of gaining even better control over their morphology. Potential applications include nanotechnology, photonics and catalysis.

11:40am **TF-WeM12 Fabrication of Poly-Crystalline Silicon Thin Film by Using a Neutral Beam Deposition Method at a Low Temperature*, S.-K. Kang***, SKKU Advanvced Institute of Nano Technology (SAINT), Korea, *B.J. Park, S.W. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Poly-crystalline silicon (p-Si) thin films are generally applied to electronic and optoelectronic devices because of its higher carrier mobility than that of amorphous silicon (a-Si) film and excellent potential in fabricating higher speed, higher resolution and brighter TFT-LCD. Currently, p-Si film is fabricated by re-crystallizing an a-Si film with post-treatment method such as excimer laser annealing (ELA), solid phase crystallization (SPC), metal-induced crystallization (MIC), etc. However, these troublesome post-treatment requires high processing temperature (500~600 °C) which is higher than glass transition temperature. Furthermore, throughput and cost issues will become more critical as the substrate size is increased. Therefore, to simplify process steps and increase production throughput, direct p-Si deposition at a low temperature is definitely required. Chemical assisted neutral beam deposition (CANBD) is investigated as a new approach to fabricate and develop p-Si which has more excellent properties in this study. The difference of CANBD to the conventional PECVD is that the p-Si thin film formation energy of CANBD is supplied by controlled neutral beam energies. Decomposition of source gas (SiH_4) is enhanced by assisted neutral beam which is generated by low energy Ar neutral beam, resulting in the formation of low temperature p-Si. The p-Si made by the neutral beam deposition method shows better electrical property compared to silicon deposited by other processes at low temperature. Resistivity of grown silicon film is measured by 4-point probe measurement. Carrier concentration and carrier mobility are evaluated by Hall measurement. Film crystallinity is investigated by HRTEM, Raman spectroscopy, and X-ray diffraction analysis.

12:00pm **TF-WeM13 Properties of Nano-Crystalline Silicon Grown by Internal Linear Antenna-Inductively Coupled Plasma-type Plasma-Enhanced Chemical Vapor Deposition*, H.C. Lee**, H.B. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Considerable attentions have been paid to hydrogenated nano-crystalline silicon film deposited a low temperature because of its promising application to stable high efficient solar cell, thin film transistors, and color sensors. In particular, the development of nano-crystalline silicon film is one of the key issues in developing active matrix liquid crystal displays (AMLCD) and active matrix organic light emitting displays (AMOLED). For this purpose, good field effect mobility in the range of 2~5cm^2/Vs is required to have high quality resolution displays along with higher stability than amorphous silicon thin films due to the less hydrogen bonded to silicon in the film. In this study, nano-crystalline silicon was deposited using an internal-type inductively coupled plasma (ICP) source, and the properties of the nano-crystalline silicon were investigated as a function of operating pressure, SiH_4/H_2 gas mixture, additive gas, etc. Especially, the effect of initial nucleation condition by controlling gas combination on the crystalline size and crystalline percentage was investigated. The crystallinity and orientation of the deposited hydrogenated silicon thin film was estimated by using micro-Raman spectroscopy (Invia Basic Renisaw) and a high-resolution X-ray diffraction (HRXRD, D8 Discover Bruker). The dark conductivity was calculated by using the I-V characteristics of the films. Field effect mobilities were measured by the fabricated thin film trasnsistors. At the temperature lower than 200°C, nano-crystalline having the size of 30nm could be deposited and the volume fraction of the crystalline calculated by the Raman spectroscopy was higher than 40%. In the presentation, more detailed characteristics of nano-crystalline film deposited by the internal linear ICP film will be discussed.

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+TF+SS-WeA

Photovoltaics, Fuel Cells, and Alternative Energy Materials and Applications

Moderator: J.S. Lewis, RTI International

1:40pm **EN+TF+SS-WeA1 ENABLE-based Low Temperature Growth of In-rich InGaN Films**, ***T.L. Williamson***, *M.A. Hoffbauer,* Los Alamos National Laboratory, *N. Miller, R.E. Jones, K.M. Yu,* Lawrence Berkeley National Laboratory, *P. Flanigan, J. Wu,* University of California, Berkeley, *J.W. Ager, Z. Liliental-Weber, E.E. Haller, W. Walukiewicz*, Lawrence Berkeley National Laboratory

The different optimum growth temperatures for the group III-nitride compounds (e.g. GaN >900C and InN ~550C) make the growth of In-rich and fully compositionally graded InGaN films by MOCVD or MBE a considerable technological challenge. Recently, energetic neutral atomic-beam lithography & epitaxy (ENABLE) has been developed at LANL that makes possible isothermal low-temperature growth of high-quality GaN and $In_xGa_{1-x}N$ alloys over the entire composition range $(0<x<1)$. ENABLE uses a large flux of neutral nitrogen atoms to activate surface chemical reactions, thereby mitigating the need for high substrate temperatures and allowing the growth of high quality III-nitrides at substrate temperatures far below those of other conventional techniques (<600C) at rates exceeding 2 microns/hr. We will present recent results for ENABLE-grown InN and In-rich InGaN showing spectroscopic, X-ray diffraction, Rutherford backscattering spectrometry (RBS), transmission electron microscopy, and Hall effect measurements to assess the thickness, composition, crystalline quality, and optical and electrical properties of the films. InN films show intense luminescence at the bandgap of ~0.7 eV with electron mobilities exceeding 700 cm^2/ V·sec. We will also present characterization results for compositionally graded films grown from pure GaN and grading to InN and from pure InN and grading to GaN. These results establish ENABLE as a new technique uniquely capable of growing InGaN films of widely varying composition including compositionally graded InGaN films and InN/GaN heterostructures.

2:00pm **EN+TF+SS-WeA2 Tandem-Junction Solar Cells using BeTe Buffer Layers for AlGaAs Molecular Beam Epitaxy on Silicon Substrates**, ***K.P. Clark***, *E. Maldonado, F. Amir, W.P. Kirk*, University of Texas at Arlington

Monolithically-stacked tandem-junctions allow solar cells with conversion efficiencies above the single-junction limit. An optimal bandgap combination of 1.7 eV and 1.1 eV has a theoretical efficiency above 30% for a series-connected cell. Aluminum gallium arsenide epitaxially grown on silicon is a natural implementation, but has long-standing crystal-quality challenges due to lattice mismatch, thermal expansion mismatch, and island growth of AlGaAs. We report investigations of AlGaAs molecular beam epitaxy on prelayers of the wide-bandgap II-VI compound beryllium telluride BeTe on arsenic-passivated silicon. AlGaAs is nearly lattice matched to BeTe but has a strong tendency for island formation, which is suppressed by low-temperature growth initiation. $Al_{0.15}Ga_{0.85}As$-GaAs multiple quantum-well p-i-n junction structures were processed and characterized electrically under illumination. The short-circuit photocurrent J_{SC} and open-circuit voltage V_{OC} for the Si/BeTe based junction approach within 15% and 30% respectively of those for a similar junction grown on a GaAs substrate. We report techniques for initial AlGaAs growth including solid-phase epitaxy, BeTe termination, and germanium adlayers studied using RHEED diffraction, X-ray diffraction, and transmission electron microscopy.

Supported in part by NASA.

2:20pm **EN+TF+SS-WeA3 Gaseous Deposition of Lead Sulfide Nanoparticle/Ti-Phthalocyanine Composite Films**, *I.L. Bolotin, D.J. Asunskis, A.M. Zachary,* ***A.T. Wroble,*** *L. Hanley,* University of Illinois at Chicago

Composite materials composed of inorganic semiconductor nanoparticles (NPs) dispersed in organic matrices may find use in photovoltaics, photodiodes, nonlinear optical devices, and other applications. This interest arises from the possibility of tuning the optoelectronic properties of the composite by varying the NP size and concentration within the organic matrix. Bulk PbS is a group IV–VI semiconductor with a narrow band gap of 0.41 eV at room temperature. Strong quantum size effects occur for <20 nm PbS NPs. Among the other potential advantages of PbS NPs is their high electron affinity, which will enhance charge transfer from an intermingled organic phase. Most of the lead salt NP photovoltaics devices produced to date have been prepared from the solution phase using colloidal techniques. However, gaseous deposition techniques possess certain advantages for the synthesis of nanocomposites: it is inherently suited to film deposition, is compatible with traditional methods of fabricating semiconductor devices, allows control of oxidation during deposition, and it can reduce the agglomeration of NPs. This work demonstrates that gaseous deposition can synthesize a composite film with <5 nm diameter PbS NPs of narrow size distribution embedded within a titanyl phthalocyanine (TiPc) organic matrix. Composite film samples were fabricated here using a cluster beam deposition source combining magnetron DC-sputtering and gas-agglomeration techniques in a fashion similar to that originally developed by Haberland and coworkers. X-ray photoelectron spectroscopy showed that PbS was successfully incorporated into the TiPc matrix during co-deposition. Transmission electron microscopy (TEM) was used measure the size, shape, distribution, and crystallinity of the NPs in these composite films. Soft-landing of PbS clusters into the TiiPc organic matrix allowed the clusters to maintain their three-dimensional structure upon deposition. In the absence of the TiPc matrix, PbS showed the aggregation into much larger, irregularly-shaped particles. PbS NPs appeared homogeneously distributed in the TiPc matrix, with particle spacings of several times the particle diameter. TEM also showed that at least some NPs deposited into TiPc were crystalline. This method also allows for deposition of composite films composed of any evaporable organic and inorganic nanoparticles that can formed by sputtering and reaction within the cluster source.

2:40pm **EN+TF+SS-WeA4 Plastic Bulk-Heterojunction Solar Cells and Near-Infrared Photodetectors**, *G. Li, Y. Yao,* University of California, Los Angeles, *L. Yu, Y. Liang, S. Xiao,* University of Chicago, ***Y. Yang***, University of California, Los Angeles **INVITED**

Polymer based solar cells and photodetectors have tremendous application in harnessing solar energy and photodetection in a cost-effective way. Here we studied the self-organization effect in polymer solar cells and first demonstrated plastic near-infrared photodetectors using low band-gap polymer. The self-organization effect in polymer solar cells based on regioregular poly(3-hexylthiophene) (RR-P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is studied in an evolutional way, with the difference being spin-coating time ts (20 to 80 sec) which controls solvent annealing time (ta) by the solvent residue. Photoluminescence (PL), ultraviolet-visible (UV-vis) absorption spectroscopy, scanning atomic force microscopy (AFM), and grazing-incidence X-ray diffraction (GIXD) were conducted on these blend films and linked to the device performance. In addition to the high performance polymer solar cells, we also demonstrated a fast response near-infrared detector using a new low band gap material. With promising results shown in this presentation, we believe the low band gap materials will open up a new perspective in near-infrared detection.

4:00pm **EN+TF+SS-WeA8 Defect Characterization of CdTe and CdMgTe Solar Cells and Their Correlation to the Device Properties**, ***R.G. Dhere***, *D. Young, J. Scharf, A. Duda, B. To, R. Noufi*, National Renewable Energy Laboratory

CdTe solar cells are at the forefront of commercial thin-film solar cells because of the high laboratory efficiencies and relative ease of fabrication. The current losses for these devices are well understood, with very small room for improvement. On the other hand, open-circuit voltage (V_{oc}) of champion devices is much lower than its potential and presents the only path to improve device performance. In this paper, we present our work on the CdTe and CdMgTe devices fabricated by close-spaced sublimation and physical vapor deposition on glass/SnO_2/CdS substrates. The devices are heat-treated in chloride vapor after deposition, in a controlled ambient, in temperature range of 390°-440°C. The treatment results in recrystallization of the samples deposited at low temperature (~400° C) and selective recrystallization at the CdS/CdTe interface in samples deposited at higher temperatures. The post-deposition treatment also improves the electronic properties of the absorber due to reduced defect density and results in improved device performance. Our investigation studies the effect of bandgap variation and defect density within the space-charge region in the absorber on the device properties, particularly V_{oc}. The bandgap of the alloy is varied by changing the alloy composition of CdSTe alloy formed at the CdS/CdTe interface and CdMgTe alloy composition. We examine the bandgap range of 1.45-1.65 eV for the absorber layer. We have varied defect density in the absorber layer by adjusting the substrate temperature and degree of post-deposition chloride treatment. The structural properties of the samples are studied by atomic force microscopy. The devices have been characterized using drive-level capacitance profiling in combination with capacitance-voltage analysis, in addition to conventional photovoltaic analysis. We will present the data on the devices with a wide range of performance and investigate the correlation between device parameters and the material properties such as bandgap and defect density. This abstract is subject to government rights.

4:20pm **EN+TF+SS-WeA9 Electron Backscatter Diffraction of CdTe Thin Films - Effects of CdCl2 Treatment**, ***H.R. Moutinho***, *R.G. Dhere, C.-S. Jiang, B. To, M.M. Al-Jassim*, National Renewable Energy Laboratory

Electron backscatter diffraction (EBSD) utilizes the electron beam of a scanning electron microscope (SEM) to investigate the crystallographic orientation of materials with high spatial resolution. In EBSD, some of the electrons of the SEM beam are diffracted by the crystalline planes of the sample and collected by a detector, where they form a pattern of Kikuchi lines. These patterns are characteristic of the crystal structure and orientation, and they are collected while the electron beam is being scanned, forming maps of crystallographic orientation. In contrast to X-ray diffraction, which gives the crystallographic orientation of a macroscopic volume of the bulk sample, EBSD provides the individual orientation of volumes with nanometer dimensions. To optimize the EBSD signal, the sample must be inclined by about 70° in relation to the electron beam. Consequently, in rough samples, topographic features shadow some of the diffracted electrons from reaching the detector; thus surface preparation is a common requirement. In this work, we describe the surface processing of CdTe thin films deposited by close-spaced sublimation and physical vapor deposition (PVD). Most of the films studied were too rough to produce good EBSD data. Polishing flattened the sample, but created an amorphous layer on the surface, resulting in no diffraction patterns. Ion-beam milling was not as effective in flattening the surface, but removed rough surface features, resulting in high-quality EBSD data. Etching and light ion milling after polishing also produced good results. After optimizing the sample preparation process, we studied PVD CdTe samples after $CdCl_2$ treatment using dipping or vapor processes, with different parameters. We observed a striking difference in the sample microstructure depending on the $CdCl_2$ process and parameters–with grain sizes varying from a few to several dozen micrometers. Our results showed that maintaining a steady source of $CdCl_2$ during the treatment, compared to a fixed amount, results in completely different recrystallization dynamics. We also studied the grain structure from the substrate to the surface by doing EBSD in cross sections of the samples, as well as analyzing samples after different degrees of polishing.

4:40pm **EN+TF+SS-WeA10 Effect of Selenization Temperature on the Grain Growth of Absorber Layer in Ultra Thin CIGS/CdS Solar Cells**, ***S.A. Pethe***, *N.G. Dhere*, Florida Solar Energy Center

Solar cells based on $CuIn_xGa_{1-x}Se_2$(CIGS) have achieved efficiencies of 19.5% and therefore are promising candidates for economic, large-scale production. CIGS thin film solar cells having absorber thickness of 2.5 µm have shown good performance. However, CIGS being a direct bandgap material, theoretically efficient cells could be prepared with absorber thickness as low as 0.5 µm. The rationale behind decreasing the CIGS thickness is to reduce consumption of the scarce and costly resource, indium. It has been observed that the performance of the solar cells degrades as the thickness goes below 0.75 µm. 0.9 µm thick absorber layer are prepared at PV Mat Lab facility at Florida Solar Energy Center (FSEC) with device conversion efficiency of 6.26% as measured at FSEC. The reason for this degradation can be attributed to the defects in the bulk of the absorber material. We know from the Movchan&Demchishin zone model that the rate of grain growth becomes almost negligible once the grains with favored texture and orientation have consumed all the unfavorable grains. This results in columnar grain structure with parallel boundaries. Similar grain structure was observed for the CIGS absorber layers with thickness of about 2.5 µm. It was observed that the grains were finer towards the back contact and larger at the surface and as the thickness goes on reducing there is not enough material for the grains to grow and coalesce. This results in smaller grains and so larger grain boundaries. Another factor affecting the grain size is the mobility of the deposited species which can be increased by increasing the annealing temperatures during selenization. But in case of ultra thin film absorber layer the higher temperatures adversely affect the molybdenum back contact layer thus introducing higher series resistance issues. Hence, in case of ultra thin CIGS absorber layer the selenization time - temperature profile needs to be optimized to obtain a favorable columnar grain structure. The material characterization of the different absorber layers will be carried out using scanning electron microscopy and transmission electron microscopy. The absorber layers would be further fabricated on to complete the device and current-voltage characteristics would be carried out to understand the effect of different temperature-time profiles on the device parameters such as open circuit voltage, short circuit current, fill factor and finally the conversion efficiency.

5:00pm **EN+TF+SS-WeA11 Thin Film Epitaxial Growth of $CuInSe_2$ Bicrystals for Grain-Boundary Studies**, ***A.J. Hall***, *D.N. Hebert, A. Rockett*, University of Illinois at Urbana-Champaign

Photovoltaics based on $CuInSe_2$ and related materials have the highest performance of any thin film devices. The nature and role of grain-boundaries in $CuInSe_2$ devices is currently poorly understood. Previous studies on the influence of grain-boundaries in $Cu(In,Ga)Se_2$ devices have shown that they exhibit little to no detrimental effect on photovoltaic device performance. Polycrystalline $CuInSe_2$ devices currently outperform single crystal $CuInSe_2$ devices. Past studies have been focused on average electrical properties or local surface electrical measurements for observation of the influence of boundaries on film properties. Since polycrystal devices have crystal sizes on the order of 1 micron, optoelectrical measurements are difficult. In order to alleviate these difficulties, a single high-angle grain-boundary in epitaxial $CuInSe_2$ has been grown on a GaAs bicrystal substrate using a hybrid sputtering and evaporation technique. Electron backscatter diffraction and x-ray diffraction show that film growth is epitaxial across all boundaries (high-angle and twin) in the bicrystal substrates. Atomic force microscopy, profilometry, and focused ion beam cross-sectioning results indicate that surface polarity and termination have a strong influence on film thickness and morphology. Near grain boundary morphology suggests mass transport leading to boundary migration is occurring. It is proposed that high surface energy anisotropy (on the opposing $\{111\}_{A,B}$ surface facets) motivates mass transport during the growth of $CuInSe_2$ at crystal boundaries.

Thin Film

Room: 613/614 - Session TF-WeA

Oblique Angle Deposition

Moderator: M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

1:40pm **TF-WeA1 Fabrication of 3D Heterostructured Nanorod/Nanospring Arrays by Dynamic Shadowing Growth**, ***Y.P. He***, *Y.P. Zhao*, University of Georgia

One-dimensional (1D) heterogeneous nanostructures are important building blocks for nanodevice applications. Four basic methods have been employed thus far to fabricate heterogeneous 1D nanostructures: nanolithography, direct chemical reaction, template-directed electroplating, and vapor-based methods. A practical nanofabrication technique to produce heterogeneous nanostructures with arbitrary materials must meet the following criteria: (1) The ability to fabricate heterogeneous nanostructures with arbitrarily selected materials; (2) The ability to control the dimensions and uniformity of the heterogeneous nanostructures; (3) The ability to control the alignment of the heterogeneous nanostructures; (4) The ability to control the interfacial properties of the heterogeneous nanostructures. Here, we demonstrate a simple but versatile method to fabricate three-dimensional heterogeneous nanorod structures by multilayer dynamic shadowing growth (DSG). DSG is based on geometric shadowing effect and substrate rotation in a physical vapor deposition system. By programming the azimuthal rotation of the substrate, aligned nanorod arrays with different shapes can be fabricated. By changing the source materials during the deposition, we demonstrate that complicated heterostructured nanorod arrays, such as Si/Ni multilayer nanosprings,[1] can be easily produced, and they exhibit particular magnetic anisotropic behavior. We also use the DSG technique to design catalytic nanomotors[2] with different geometries that are capable of performing different and desired motions in a fuel solution. Using the shadowing effect, a thin catalyst layer can be coated asymmetrically on the side of a nanorod backbone. Catalytic nanomotors such as rotary Si/Pt nanorods, rotary L-shaped Si/Pt and Si/Ag nanorods, and rolling Si/Ag nanosprings, have been fabricated, and their autonomous motions have been demonstrated in a diluted H_2O_2 solution. We observed that the catalytic decomposition of H_2O_2 on the surface of catalyst generated a propelling force to push the nanorod from the catalyst side with an estimated driving force on the order of 10^{-13} - 10^{-14} N. This fabrication method reveals an optimistic step toward designing integrated nanomachines.

[1] Y.-P. He, J.-X. Fu, Y. Zhang, Y.-P. Zhao, L.-J. Zhang, A.-L. Xia, and J.-W. Cai, Multilayered Si/Ni Nanosprings and Their Magnetic Properties, small 2007, 3(1), 153-160.

[2] Y.-P. He, J.-S. Wu, and Y.-P Zhao, Designing Catalytic Nanomotors by Dynamic Shadowing Growth, Nano Lett. 2007, 7(5), 1369-1375.

2:00pm **TF-WeA2 Effects of Steering and Shadowing in Epitaxial Growth**, ***J.G. Amar***, University of Toledo **INVITED**

While a variety of surface relaxation processes are usually assumed to determine the surface morphology in epitaxial growth, the deposition process can also play an important role. For example, in the case of unstable metal epitaxial growth, the steering of depositing atoms due to short-range (SR) and long-range (LR) attraction can significantly enhance the surface roughness and mound angle,[1] while for large angles of incidence shadowing can also play an important role. In particular, in recent experiments on grazing incidence Cu/Cu(100) growth,[2] a series of morphological transitions was observed as the angle between the beam and substrate normal was increased, from symmetric to asymmetric mounds at moderate deposition angles, to asymmetric ripples oriented perpendicular to the beam at larger deposition angles, and finally to symmetric pyramids with (111) facets at very large angles. Here we discuss the roles of steering and shadowing in determining the observed surface morphology.[3] We first present results obtained using a simplified model which includes the effects of shadowing but not SR and LR attraction. Our results indicate that many of the features observed in Cu(100) growth, including the existence of a transition from asymmetric mounds to ripples, can be explained primarily by geometrical effects. We also show that the formation of (111) facets is crucial to the development of ripples at large angles of incidence. A second transition to 'rods' with (111) facets oriented parallel to the beam is also found at high deposition angles and film thicknesses. When steering due to SR and LR attraction is included, we find two main effects. In the multilayer regime 'flux-focusing' due to attraction tends to enhance the anisotropy and reduce the critical thickness for the ripple transition. In contrast, near the transition from ripples to rods, sideways attraction tends to stabilize the formation of symmetric pyramids as is observed experimentally. The scaling of the surface roughness and anisotropy as a function of film thickness and deposition angle and the effects of growth temperature and surface relaxation processes such as edge-diffusion on the surface morphology will also be discussed.

[1] J. Yu and J. G. Amar, Phys. Rev. Lett. 89, 286103 (2002).

[2] S. van Dijken et al, Phys. Rev. B 61, 14047 (2000).

[3] Y. Shim and J.G. Amar, Phys. Rev. Lett. 98, 046103 (2007).

2:40pm **TF-WeA4 Mechanisms of Thin Film Growth under Shadowing and Re-Emission Effects**, ***T. Karabacak***, University of Arkansas at Little Rock **INVITED**

Over the last decades, there has been a continuing interest on the mechanisms of the dynamic growth front morphology of thin films. Several competing mechanisms such as noise, surface diffusion, and shadowing have been well known to play roles in the evolution of surface roughness. Based on these effects, various growth models have been developed within the frame work of dynamic scaling theory in order to predict the evolution of thin film morphology. However, many experimentally obtained surfaces have been realized to be much rougher or smoother than the predictions of these models. Especially in processes where the shadowing effect is important due to the existence of obliquely incident particles (such as in sputter deposition, chemical vapor deposition, and plasma etching), the morphological evolution was smoother for deposition, while it was rougher for etched surfaces compared to the expected effect of shadowing. A recently recognized "re-emission" effect that originates from the non-unity sticking probability of incident particles offers a better understanding of morphological growth process. Non-sticking re-emitted particles can lead to a rough surface during etching and a smooth surface during deposition. It is shown that competing effects of shadowing and re-emission can predict many of the experimental results reported in the literature. It is also proposed that shadowing and re-emission effects can lead to a novel "universality class" of dynamic scaling behavior of the surface roughness.

4:00pm **TF-WeA8 Ripple Growth and - Orientation during Grazing Incidence Deposition**, ***H. Wormeester***, *F.L.W. Rabbering, F.G. Stoian, R. Gastel, B. Poelsema*, University of Twente, The Netherlands

Oblique incidence deposition is widely used for the preparation of anisotropic structures in thin films with interesting magnetic or optical properties. We have studied the consequences of oblique incidence deposition for the morphology of the growth-front for a "prototypical" system Cu/Cu(001). According to previous electron diffraction measurements, deposition at grazing incidence leads to the evolution of ripples, oriented perpendicular to the plane of incidence of the atom beam. Here we present new experimental results, obtained with high resolution low energy electron diffraction and STM, for various stages in the formation of the ripples. At grazing incidence, experiments indeed show that initially the ripples are oriented perpendicular to the plane of incidence of the atom beam. At more progressed stages of growth and at very grazing incidence deposition experiments show a deviation from the ripple formation. The ripple formation has also been studied with kMC simulations, which support (or actually predicted) experimentally observed changes in ripple formation at later stages in growth. The relevant activation barriers for intra- and interlayer diffusion processes in these simulations have been tuned to describe quantitatively(!) experimentally observed morphologies in a wide range of temperatures (150-300 K) and coverages (up to 40 ML). An essential role is played by both long and short range attractive interactions between the incoming particle and the substrate. The kMC simulations show a change in ripple orientation from perpendicular to the plane of incidence to parallel to this plane around a coverage of 40 ML at a temperature of 250 K for a deposition angle of 80°. At 230K this orientation transition has been found to occur at a much earlier stage in growth. At more grazing incidence deposition only ripples parallel to the plane of incidence have been found to develop and no change in orientation has been seen for smaller deposition angles. This orientation change is related to the very strong roughening of the growth front for grazing incidence growth and the corresponding heterogeneity of incident flux.

4:20pm **TF-WeA9 Biaxial Texture of Titanium Nitride Thin Films Deposited by Off-normal Incidence Magnetron Sputtering**, ***D. Deniz***, *J.M.E. Harper*, University of New Hampshire

We studied the development of crystallographic texture in titanium nitride films deposited by off-normal incidence reactive magnetron sputtering at room temperature. For a deposition angle of 40 degrees from normal, we obtained strongly oriented biaxial textures for a range of deposition conditions using both direct current (DC) and radio frequency (RF) sputtering. Texture measurements were performed by x-ray pole figure analysis of the 111 and the 002 orientations. Typically, we find that the 111 orientation is close to the substrate normal and the 002 orientation is close to the direction of the deposition source, showing substantial in-plane alignment. For example, TiN deposited by DC sputtering at 5% $N_2/(Ar+N_2)$ flow ratio and 2.2 mTorr total pressure showed 111 planes perpendicular to the substrate and 002 planes tilted 55 degrees from the substrate normal and facing the source. However, TiN deposited by DC sputtering at 2% $N_2/(Ar+N_2)$ flow ratio and 1 mTorr total pressure showed 111 planes tilted 18 degrees from the substrate normal but away from the source and 200 planes tilted 35 degrees from the substrate normal towards the source. The strength of biaxial texture decreases as the $N_2/(Ar+N_2)$ flow ratio is increased up to 20%. These results suggest a competition between texture mechanisms related to the substrate normal and related to the deposition direction.

4:40pm **TF-WeA10 Zeno Effect and Step Edge Barrier in Organic Thin Films**, ***C. Teichert***, *G. Hlawacek*, University of Leoben, Austria, *P. Frank, A. Winkler*, Graz University of Technology, Austria

Organic Semiconductors start to enter the market of consumer products as light emitting diodes, solar cells and thin film transistors. For the growth of reliable high quality devices a profound understanding of the processes related to formation of organic thin films is necessary. Here, we present an AFM study on the growth of para-sexiphenyl on a sputtered mica(001) surface. Para-sexiphenyl is a member of the group of small conjugated molecules with a high mobility[1] and the ability to emit blue light.[2] The morphology is characterized by the formation of mounds formed by upright standing molecules. Needle growth competes with the formation of the mounds. However, the characteristic layer distribution of the mounds can be fitted by a Poisson distribution. This shape is related to the Zeno effect known from inorganic epitaxy.[3] The mound shape for different film thicknesses has been analysed. Furthermore, statistical roughness parameters such as rms roughness σ, hurst parameter α and mound separation λ have been evaluated. Growth exponent β and dynamic exponent $1/z$ can be calculated and agree with the predictions made by the Zeno model. The mound separation λ and the size of the top terrace allow estimating the size of the Ehrlich Schwoebel barrier responsible for the cross-sectional shape of the mounds. Work has been supported by Austrian Science Fund (FWF) National Research Network "Interface controlled and Functionalised Organic Films" (S9707-N08).

[1] T. Birendra Singh, G. Hernandez-Sosa, H. Neugebauer, A. Andreev, H. Sitter, N.S. Sariciftci, Phys. Status Solidi B, 243, (2006) 3329.

[2] A. Kadashchuk, A. Andreev, H. Sitter, N.S. Sariciftci, Y. Skryshevski, Y. Piryatinski, I. Blonsky, D. Meissner, Adv. Funct. Mater. 14 (2004) 970.

[3] T. Michely and J. Krug; Islands, Mounds and Atoms (Springer, Berlin 2004).

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+SS+TF-ThM

Surface Science Challenges for Solar Energy Conversion

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

8:00am **EN+SS+TF-ThM1 Thermal and Photoreactions of Catechol on TiO_2**, ***P. Jacobson***, Tulane University, *X.-Q. Gong, M. Connors, A. Selloni,* Princeton University, *U. Diebold*, Tulane University

The wide band gap of titanium dioxide limits its use as a photocatalytic and photovoltaic material with solar radiation as its source. One method to increase the absorption of light at visible wavelengths is by attaching metallo-organic dye complexes. These dyes frequently use catechol and phosphonic or carboxylic acids to link the dye to the titanium dioxide surface. In an attempt to better understand the adsorption of these complex dyes, we have studied the adsorption of catechol (1,2-benzenediol) on the (110) and (011) faces of rutile titanium dioxide. Catechol was preferred over 'real' dye complexes for its ease of deposition under high vacuum conditions and simple chemical makeup. Ultraviolet photoemission spectroscopy shows a gap state introduced to the TiO_2 upon catechol adsorption. Increases in the Oxygen 1s shoulder in XPS indicate dissociative adsorption of catechol and formation of surface hydroxyls. For catechol adsorption on the rutile (110) surface a 3x1 overlayer results. Similarly, adsorption on the (011) surface forms a 2x1 overlayer. Formation of surface hydroxyls upon adsorption is believed to play a role in the formation of these ordered structures. To further study the catechol - titanium dioxide complex, temperature dependent measurements using STM, XPS, and UPS were made in the presence and absence of molecular oxygen. The difference in decomposition and intermediates formed will be discussed. These techniques were also used to study UV induced photoreactions of catechol on TiO_2.

8:20am **EN+SS+TF-ThM2 N Incorporation and Electronic Structure in High-Quality Epitaxial N-doped TiO_2 Anatase Grown by Molecular Beam Epitaxy**, ***S.H. Cheung***, *P. Nachimuthu, M.H. Engelhard,* Pacific Northwest National Laboratory, *M.K. Bowman,* The University of Alabama, *S.A. Chambers*, Pacific Northwest National Laboratory

N doping in TiO_2 is of potential interest for bandgap reduction and enhanced visible light absorption for water splitting. We have previously investigated high-quality N-doped TiO_2 rutile grown homoepitaxially by molecular beam epitaxy (MBE) on TiO_2(110) and α-Al_2O_3(0001).[1] To gain broader understanding of N-doped TiO_2, we now report a detailed study of N incorporation and the associated electronic structure in high-quality TiO_2 anastase grown by MBE on $LaAlO_3$(001). A mixed beam of atomic N and O was prepared in an electron cyclotron resonance plasma source while Ti was supplied from an effusion cell. The much higher thermodynamic stability of Ti-O bonds compared to Ti-N bonds resulted in N incorporation being limited to less than 1 at. %. The high degree of structural quality was evidenced by the observation of finite thickness fringes in the vicinity of the (004) Bragg peak in high-resolution X-ray diffraction. A formal charge of -3 on substitutional N was deduced from high-resolution XPS. Photoconductivity measurement capability is being set up at the time of abstract preparation and experimental results elucidating the role of substitutional N in reducing the bandgap will be presented at the meeting.

[1] S.H. Cheung, P. Nachimuthu, A.G. Joly, M.H. Engelhard, M.K. Bowman, S.A. Chambers, Surf. Sci. 601 (2007) 1754.

8:40am **EN+SS+TF-ThM3 Lattice Site Location for N in Homoepitaxial N-doped TiO_2 (110)**, ***V. Shutthanandan***, *S.H. Cheung, S. Thevuthasan, P. Nachimuthu, S.A. Chambers*, Pacific Northwest National Laboratory

TiO_2 is one of the most heavily studied materials for photocatalytic water splitting even though the optical absorption spectrum of TiO_2 has poor overlap with the solar spectrum, and the e^-/h^+ pair recombination rate is high. Bandgap reduction is one approach to enhancing visible light absorption. N doping causes a redshift of the bandgap into the visible and visible-light-induced photochemistry has been observed in this material. We have grown $TiO_{2-x}N_x$ rutile epitaxial films on rutile TiO_2 (110) single crystal substrates using oxygen plasma assisted molecular beam epitaxy. The N concentration (x) was varied by careful control of the atomic fluxes. The N dopant site location was studied using nuclear reaction analysis (NRA) and Rutherford backscattering spectrometry (RBS) in channeling and random geometries. $^{14}N(d,\alpha)^{12}C$ and $^{16}O(d,p)^{17}O$ nuclear reactions were used to identify the locations of N and O, respectively. NRA measurements in a channeling geometry for x = 0.04 and 0.05 clearly show that N substitutes for O in this concentration range. The x = 0.04 film shows a higher degree of N substitution (~98%) than the x = 0.05 film (~75%). Angular scans obtained around <110> for the x = 0.04 film exhibit a N angular half width that is slightly narrower (~0.05°) than that of host O. This narrowing is an indication that the N atoms are slightly displaced from the idealized anion lattice sites. The angular yield scan obtained for the x = 0.05 film exhibits a slightly larger angular half width for O, indicating that O positions are perturbed by N incorporation. In contrast, NRA and RBS measurements performed on the x = 0.12 film reveal that most of the N occupies random positions within the film, and glancing incidence XRD reveals limited Ti_2N secondary phase formation. These results clearly demonstrate that the upper limit of N solid solubility in crystalline TiO_2 rutile is ~3 at. % of the anions. Higher N concentrations can be incorporated by varying the growth conditions to facilitate defect formation, but the quality of the materials drops considerably and secondary phase formation occurs.

9:00am **EN+SS+TF-ThM4 Photochemically Activated Tethering of Molecular Monolayers to Anatase and Rutile TiO_2 Surfaces**, ***H.J. Kim***, *E.C. Landis,* University of Wisconsin-Madison, *S.H. Cheung, S.A. Chambers,* Pacific Northwest National Laboratory, *T.F. Kuech, R.J. Hamers*, University of Wisconsin-Madison

Molecular interfaces to TiO_2 are an important component of dye-sensitized solar cells and other emerging systems for solar-to-electrical and solar-to-fuel conversion. Using X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy,we demonstrate that organic alkenes will link to the surfaces of titanium dioxide in both anatase and rutile forms when illuminated with ultraviolet light. This provides a versatile way to covalently link functional organic molecules directly to oxide semiconductors. Measurements have been performed on epitaxial thin films of anatase (001), bulk crystals of anatase(101), rutile (001), rutile (110), and nanocrystalline anatase. Quantitative XPS measurements have been used to investigate the kinetics of functionalization and its dependence on the structure of the bulk samples and the dependence on exposed crystal face. We will compare the functionalization of these surfaces and discuss the mechanism of the modification. Implications for tethering of photochemically active molecules to these surfaces will be discussed.

9:20am **EN+SS+TF-ThM5 Progress and Challenges in Solar Energy Conversion Using Semiconductor/Liquid Junctions**, ***N.S. Lewis***, California Institute of Technology **INVITED**

Semiconductor/liquid contacts are useful in photoelectrochemical cells as well as for probing the fundamental surface chemistry and surface physics of semiconductors. In this talk, we will discuss the thermodynamics and dynamics of charge flow across semiconductor/liquid interfaces with an emphasis on comparison of theory and experiment for charge transfer in 1-electron outer-sphere redox systems. In addition, we will discuss the principles of surface modification to control the electrical, electronic, and chemical properties of Si surfaces. Finally, we will discuss the use of photoelectrochemistry in transport, localization, and movement of charge molecules in three dimensions in solution in real time.

10:00am **EN+SS+TF-ThM7 An Organic Donor/Acceptor Lateral Superlattice at the Nanoscale: Towards an Optimum Morphology for Photovoltaic Devices**, ***R. Otero***, *D. Ecija,* Universidad Autonoma de Madrid, Spain, *G. Fernandez,* Universidad Complutense de Madrid, Spain, *J.M. Gallego,* ICMM-CSIC, Spain, *L. Sanchez, N. Martin,* Universidad Complutense de Madrid, Spain, *R. Miranda*, Universidad Autonoma de Madrid, Spain

One of the major factors limiting the efficiency of organic photovoltaic devices is the fact that, instead of free electron-hole pairs, photon absorption usually leads to the formation of tightly bound excitons (bound states of an electron-hole pair) which can diffuse only for a characteristic length of about 10 nm before radiative recombination occurs. The hitherto most successful approach to promote the dissociation of the photogenerated excitons is to use blends of phase-segregated electron-donor/electron-acceptor molecules; the so-called bulk heterojunction concept. At the interface between electron-donor and electron-acceptor areas, the difference in electron affinities drives the exciton dissociation by injecting free electrons (holes) into the electron-acceptor (electron-donor) areas. Provided that continuously connected paths between the interfaces and the electrodes exist, the free electrons and holes will be collected therein. From these considerations a number of morphological criteria can be extracted for optimum solar cell performance: first, the segregated electron-donor and acceptor domains must have a typical size of the order of the exciton diffusion length, in order to avoid wasteful radiative recombination events; second, the interface area between donor and acceptor domains, where exciton dissociation takes place, must be maximized; and, finally, donor (acceptor) domains must be continuously connected to the cathode (anode) to favour efficient charge transport. A morphology that would satisfy these three criteria could be a lateral superlattice of donor and acceptor areas with typical dimensions of some 10 nm. In this work we describe variable-temperature Scanning Tunneling Microscopy (STM) experiments that show how monolayer-thick blends of the electron donor molecule (exTTF) with the electron acceptor (PCBM) on a reconstructed Au(111) surface, segregates laterally into 'nanostripes' whose width is of the order of the exciton diffusion length; it thus corresponds closely with the morphology for optimum solar cell performance. The reason for such a peculiar nano-scale morphology can be traced back to the different interactions between the two molecular species and the herringbone reconstruction of Au(111). Our results demonstrate the potential of atomistic studies about the growth of organic semiconductors to open new directions for the design and construction of highly-efficient organic electronic devices.

10:20am **EN+SS+TF-ThM8 Solar Water Splitting for Renewable Hydrogen Production: The Role of N and Surface Modification in the Improved Stability of III-V Nitride Photoelectrodes**, *T. Schiros, J. Leisch, **L.-Å Näslund**, H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*, T. Deutsch, J. Geisz, S. Kurtz,* National Renewable Energy Laboratory*, R. Kirby, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

III-V semiconductors are promising materials for photoelectrochemical (PEC) hydrogen production, however, material stability is a serious issue. The addition of dilute amounts of nitrogen to GaP and surface modification such as platinization result in dramatic increases in photocorrosion resistance, but the underlying mechanism is not known. We combine surface-sensitive core-level x-ray spectroscopy and microscopy with electrochemical measurements to study changes in the chemical environment and local morphology at the semiconductor-electrolyte interface during PEC hydrogen production and reveal the role of nitrogen and the platinum catalyst treatment in preserving the integrity of the surface. A detailed understanding of the interface is essential to improve control of photocorrosion and increase device stability.

10:40am **EN+SS+TF-ThM9 Surface Nanostructure and Nanochemistry of CuInSe$_2$ by Scanning Tunneling Microscopy**, *M. Mayer, L. Ruppalt, J. Lyding, **A. Rockett***, University of Illinois

Results of the characterization of the surface physical, chemical and energy band structure of CuInSe$_2$ (CIS) are reported based on scanning tunneling microscopy (STM) studies of epitaxial CIS thin films. Cu(In, Ga)Se$_2$ (CIGS) is the absorber layer in the highest efficiency thin-film solar cells. However, this material does not perform as well as expected, most likely due to local defects and composition fluctuations. These lead to the formation of electronic defect levels in the energy gap and band edge fluctuations, both of which can cause carrier recombination. STM images compare the structure of cleaved (110) type surfaces, which have been shown previously to be energetically unstable, with epitaxial layers of various stable surface orientations that had been cleaned by sputtering and annealing. The energetically favorable close-packed tetragonal (112) surface showed triangular facets in agreement with AFM and SEM images. The (110) face showed structural and chemical correlations with the local density of states and evidence of a Cu-deficient surface consisting of extended In-rich rows. The surface structure of the cleaved surface is consistent with suggestions that the surfaces of group III rich CIGS should be highly In-rich and should contain Cu vacancies. No significant reconstruction associated with the Se sublattice was observed. The local density of states obtained from tunneling spectroscopy exhibited large fluctuations in the energy gap and Fermi energy, providing direct evidence of the band edge fluctuations observed by photoluminescence. The gap fluctuations are correlated with the surface topography and have direct implications for the device performances.

Thin Film

Room: 613/614 - Session TF-ThM

Thin Films for Electronic Applications

Moderator: P.D. Rack, The University of Tennessee

8:00am **TF-ThM1 Superconductivity in Very Clean and Doped MgB$_2$ Thin Films**, ***Q. Li**, A.V. Pogrebnyakov, J.M. Redwing, X.X. Xi*, Pennsylvania State University **INVITED**

MgB$_2$, with a T$_c$ of 40 K, is arguably the first superconductor to show clear multiband superconductivity and two energy gaps. It has the highest T$_c$ among BCS superconductors, which makes it very attractive for many applications. The interplay between the interband and intraband scattering has resulted in many unusual properties. In this talk, I will review our results on MgB$_2$ thin films made by hybrid physical-chemical vapor deposition (HPCVD). Very clean epitaxial MgB$_2$ thin films on (0001) SiC and sapphire substrates have been obtained with a slight increase of T$_c$ from the bulk value due to the epitaxial strain. From the normal state magnetoresistance measurement, we have shown a complex dependence on the orientation of the applied magnetic field, with a maximum magnetoresistance (MR~136%) observed at the field H parallel to c plane at low temperature. However, the angular dependence changes dramatically as the temperature increases, and at high temperatures, the magnetoresistance maximum changes to the H perpendicular to c direction. We attribute the results to the multiple bands with different Fermi surface topology and different electron-phonon coupling in MgB$_2$. By introducing carbon carrying gas during HPCVD deposition, C-doping in the films was achieved. The upper critical field was found to increase with C doping. The upper critical field can be increased to above 60 T in H parallel to ab direction and 40 T in H perpendicular to ab direction. C-doped polycrystalline films coated on SiC filbers also show H$_{c2}$ above 55 T, which make it possible as a coated conductor for high field applications.

[1] Work supported by NSF and conducted in collaboration with B. T. Liu, Y. F. Hu, J. Chen, V. Ferrando, P. Orgiani, Q. R. Feng, H. Gao, L. Shan, H. H. Wen, A. Gurevich, D.C. Larbalestier, J. B. Betts, C. H. Mielke.

8:40am **TF-ThM3 Optical Radiation Selective Devices Based on III Nitrides**, ***D. Starikov**, J.C. Boney, P. Misra, N. Medelci, R. Pillai*, University of Houston

Wide direct band gap of the III nitride materials allows for several advanced optoelectronic applications in a very wide spectral range from 200 nm to 1.77 µm. Both light emission sources and photodetectors with advanced properties can be achieved through tailoring layered III nitride structures with various layer order, chemical composition, conductivity and thickness. In addition, substrate selection plays an important role in the fabrication of these devices as well as in achieving desired device properties. Along with the efficiency of light emission or detection, in most cases it is important to provide selectivity of the optical radiation generated or sensed by the optical device. Such selectivity can be achieved by using spectral and polarization properties of optical radiation. In this paper we present results on the growth, processing, and modeling of multi-band photodiode structures, broad-spectrum avalanche LEDs, and polarization-sensitive photodetectors based on III nitrides grown by Radio Frequency Molecular beam epitaxy on silicon, sapphire, and lithium-aluminum oxide (LiAlO$_2$) substrates. Dual-band visible- and solar-blind UV/IR photodetectors as well as broad spectrum UV-enhanced avalanche LED structures have been demonstrated. The peak responsivities of the dual band photodetectors are 0.0038 and 0.055 A/W at the wavelengths of 349 nm and 1000 nm, respectively. The broad spectrum emission from the avalanche LEDs extended from 300 to 650 nm with a maximum at ~425 nm. Results on optimization of the dual-band photodiodes as well as on testing of polarization-sensitive GaN and InGaN photodetectors grown on non-polar LiAlO$_2$ substrates, which are currently in progress, will be presented in the final paper. Various advanced applications of the optical radiation sensitive devices based on III nitrides will be discussed.

9:00am **TF-ThM4 EXAFS Study of Local Bonding Structures of Ge$_2$Sb$_2$Te$_4$, Ge$_2$Sb$_2$Te$_5$, and Ge$_2$Sb$_2$Te$_7$ with Bond Constraint Analysis**, ***D.A. Baker**, G. Lucovsky, M.A. Paesler,* North Carolina State University*, P.C. Taylor*, Colorado School of Mines

Studies of amorphous (a-) semiconductors have been driven by technological advances as well as fundamental theories. Observation of electrical switching,[1] for example, fueled early interest in a-chalcogenides. More recently a-chalcogenide switching has been applied successfully to programmable memory devices[2] as well as DVD technology where the quest for the discovery of better-suited materials continues. Thus, switching grants researchers today with an active arena of technological as well as fundamental study. Bond constraint theory (BCT) and rigidity theory provide a powerful framework for understanding the structure and properties of a-materials. Application of these theories to switching in a-chalcogenides holds the promise of finding the best composition suited for switching applications. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy[3] is an ideally suited technique to investigate the switching properties of these materials. Films of amorphous $Ge_2Sb_2Te_4$, $Ge_2Sb_2Te_5$, and $Ge_2Sb_2Te_7$ exhibit differing bonding structures and bond statistics, which result in different electronic and optical properties. Results of new EXAFS experiments on these three critical compositions in the Ge-Sb-Te system are presented in light of BCT and rigidity theory.

[1] S.R. Ovshinsky, Phys. Rev. Lett., 20, 1450 (1968).

[2] C. Peng and M. Mansuripur, Appl. Optics, 43, 4367 (2004).

[3] D.E. Sayers, F.W. Lytle, and E.A. Stern, Phys. Rev. B., 11, 4836 (1975).

9:20am **TF-ThM5 CVD of Ru from $C_6H_8Ru(CO)_3$**, ***T.S. Lazarz***, *Y. Yang, N. Kumar, W. Noh, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

Ruthenium is being investigated for multiple uses in microelectronics, including DRAM capacitors,[1] metal gates in p-MOSFETs,[2] and in the copper dual damascene process.[3] Previous studies have generally prepared Ru films by evaporation or by CVD from ruthenocene or its ring-substituted analogues. Other ruthenium compounds such as β-diketonates, arenes, dienes and carbonyls have also been investigated as CVD precursors. In all cases, however, the growth rates been unsatisfactory (< 2 nm/min), the films have been contaminated by heteroatoms due to ligand incorporation, or there have been nucleation problems on covalent substrates.[4] We have used the single-source liquid precursor tricarbonyl(1,3-cyclohexadiene)ruthenium(0), $C_6H_8Ru(CO)_3$, to deposit metallic ruthenium films by CVD at substrate temperatures ranging between 150 and 600 °C on several types of substrates, including covalent. Ligand removal is expected to be relatively facile from this Ru(0) compound due to the ruthenium atom being in oxidation state zero on the precursor molecule. The Ru growth rates are rapid, with a maximum of 19 nm/min. The oxygen content is below AES detection limits (< 1 at. %), and the carbon content is estimated to be low. In-situ spectroscopic ellipsometry indicates negligibly short delays before film nucleation on Si, SiO_2, or sapphire substrates. The resistivities are comparable to the bulk resistivity, ranging between 11 and 21 μΩ-cm. The texture of the films depends on deposition temperature. At lower temperatures, films are strongly textured mostly in the (0002) direction, whereas at higher temperatures the films are less textured. Since $C_6H_8Ru(CO)_3$ gives high growth rates, low resistivities, and nucleates readily on all surfaces tested, $C_6H_8Ru(CO)_3$ is an excellent precursor for depositing thin ruthenium films.

[1] T. Aoyama and K. Eguchi, Japanese Journal of Applied Physics, Part 2 (Letters) 38 (10A), 1134 (1999).

[2] V. Misra, G. Lucovsky, and G. Parsons, MRS Bulletin 27 (3), 212 (2002).

[3] T.N. Arunagiri, Y Zhang, and O Chyan, Applied Physics Letters 86 (2005); Hoon Kim, Toshihiko Koseki, Takayuki Ohba et al., Journal of The Electrochemical Society 152 (8), G594 (2005).

[4] Sang Yeol Kang, Cheol Seong Hwang, and Hyeong Joon Kim, Journal of The Electrochemical Society 152 (1), C15 (2005).

9:40am **TF-ThM6 The Properties of Ultra Thin Ru-P Amorphous Films Deposited with $Ru_3(CO)_{12}$ and $P(CH_3)_3$ for Cu Metallization**, ***J. Shin***, *H. Kim, L.B. Henderson, G.S. Hwang, J.G. Ekerdt*, University of Texas at Austin

For advanced VLSI devices, Cu metallization has replaced Al due to its low resistivity and high intrinsic electromigration resistance. It is well known that Cu requires liner materials that function as a diffusion barrier, a seed layer for electroplating, and an adhesion promoting layer. Ru has been considered as a promising liner material for Cu metallization, however it has been reported that Ru itself is not an effective Cu diffusion barrier due to its microstructure, which is polycrystalline and features a columnar structure. Therefore, controlling the microstructure of Ru films is crucial in obtaining the required liner properties. Here we report ultra thin Ru alloy films having amorphized microstructure by incorporating P into the films. The metal (Ru) - metalloid (P) amorphous films were grown at 300°C by co-dosing triruthenium dodecarbonyl ($Ru_3(CO)_{12}$) and trimethylphosphine ($P(CH_3)_3$) into a cold wall chemical vapor deposition system having base pressure of $5x10^{-8}$ Torr. X-ray photoelectron spectroscopy (XPS) was employed to analyze the film composition and chemical states of the elements in the films, and grazing angle X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used for microstructure analysis. Amorphous films were formed when more than ~ 15 at% of P was incorporated, and the amorphous microstructure remained stable after 3 hrs of annealing at 400°C. Electrical resistivity was measured with a four point probe, and a 15 nm thick amorphous Ru-P film showed a resistivity of ~ 200 Ωcm. Strong adhesion between Ru-P and Cu films was observed in annealing experiments, which revealed adhesion strength in the order of Ru-P alloy > Ta > TaN. More conformal films were grown on trench features by introducing $P(CH_3)_3$ as a result of the improved film step coverage due to the inhibited reaction and lowered sticking coefficient of $Ru_3(CO)_{12}$ by the adsorption of the $P(CH_3)_3$ molecules on the Ru surface. The barrier capability of the Ru-P films against Cu diffusion evaluated by bias temperature stress (BTS) technique will be discussed. First principles density functional theory calculations and ab-initio molecular dynamic simulation results will also be presented to elucidate the interaction between Ru and P, short range order of amorphous structure, and the causes for P stabilizing the Ru based metal - metalloid amorphous films.

10:00am **TF-ThM7 Surface Morphology of Epitaxial Cu Layers: The Effect of Roughness on Electron Scattering**, ***J.M. Purswani***, *D. Gall*, Rensselaer Polytechnic Institute

Single crystal Cu layers, 12 to 600 nm thick, were grown on MgO(001) by ultra-high vacuum magnetron sputtering. X-ray diffraction θ-2θ, ω-rocking curve, and pole figure scans show that layers grown at temperatures $T_s \leq 100$ °C exhibit a cube-on-cube epitaxy, while $T_s \geq 200$ °C results in polycrystalline copper layers. The surfaces of the single crystal layers exhibit regular mound structures, as observed by in-situ scanning tunneling microscopy. The mounds grow in width with increasing layer thickness t, from 21 nm for t = 24 nm to 33 nm with t = 119 nm. In-situ vacuum annealing at 200 and 300 °C leads to a successive smoothening of the surfaces for all thickness values. For example, for t = 24 nm, the RMS roughness is 1.3 nm for the as-deposited layer and decreases to 0.7 nm after the post-deposition anneal. The measured resistivity increases for decreasing layer thickness, from 1.70 μΩ-cm for t = 604 nm to 2.91μΩ-cm for t = 24 nm. This increase is consistent with the Fuchs-Sondheimer model, indicating completely diffuse surface scattering. The diffuse surface scattering is attributed to atomic level roughness, as quantified by the average width of atomically smooth surface terraces, which increases from 0.5 nm for the as-deposited layer to 1.5 nm for the film annealed at 300 °C. Therefore, even the smoothest layers exhibit terraces that are only 8 atoms wide, which is insufficient to result in specular electron surface scattering.

10:20am **TF-ThM8 Investigation of Ru-Ta-N Ultrathin Films as Diffusion Barrier for Cu Metallization**, ***C.-W. Chen***, *J.-S. Chen*, National Cheng Kung University, Taiwan

In this study, the diffusion barrier properties of ruthenium-based thin films which contain different atomic percentage of tantalum and nitrogen are investigated in Cu/barrier/SiO_2/Si system. The Ru-Ta-N films were deposited by co-sputtering from Ru and Ta targets in Ar+N_2 atmosphere. Pure Ru and Ru-N films sputtered in Ar and Ar+N_2 ambient, respectively, were studied as the comparison. The thickness of Ru, Ru-N and Ru-Ta-N samples is all set at 10 nm. The thermal stability of the Cu/barrier/SiO_2/Si multilayers is assessed by annealing the samples in vacuum at 400~700 °C for 30 min. No significant change of sheet resistance is detected for the Cu/Ru-Ta-N/SiO_2/Si system after annealing up to 700°C. However, the sheet resistance of the sample with pure Ru barrier increases abruptly after annealing at 400°C, and the sheet resistance of the sample with Ru-N barrier increases abruptly after annealing at 500°C. The performance of Ru-Ta-N barriers are also confirmed by Auger electron spectroscopy and Rutherford backscattering spectrometry in which Cu shows no obvious diffusion into underlayers after annealing at 500°C. As compared to pure Ru and Ru-N, the Ru-Ta-N films exhibit better electrical properties and capability for preventing Cu diffusion regardless of the different Ta contents. Correlation between the film resistivity and the microstructral characteristics of sputtered Ru, Ru-N and Ru-Ta-N films in the Cu/barrier/SiO_2/Si multilayer systems upon annealing are discussed.

10:40am **TF-ThM9 A Study on the Amorphous Ta-Zr Films as Diffusion Barrier in Cu Metallization**, ***C. Li***, Nanyang Technological University, Singapore, *J. Hsieh*, Ming-Chi University of Technology, Taiwan

Binary alloys with amorphous structure have been used as diffusion barrier in many electronic components for their better resistance to the movement of thermally and electrically conductive atoms. Some other advantages for using such amorphous films including their high crystallization temperature and good electrical conductivity are also important for the function of electronic components. For instance, films such as Cu100-xTax, Zr40Cu60, Ta50Co50, Ta100-xNix (x=35,50) and Co55W45, all exhibit low resistivity (<200 µ?-cm) and high crystallization temperature (Tx ~800oC, except Ta-Co and Cu-Zr) in literature. However, when they are employed as diffusion barriers for Al, Cu or Au metallization, some of the films (Cu100-xTax, Ta100-xNix (x=35,50) and Co55W45) demonstrate a failure at temperatures much lower than their crystallization point. This may due to the low reaction temperature of these metal with Si substrate which is only around 200-300oC. Based upon these earlier studies, one improvement can be made on the existing amorphous films is to replace the noble or near noble metals (Cu, Ni etc.) with some refractory metals such as Ta, W, Ti or Zr because their reaction temperatures with Si are usually higher than 500oC.

Examples of such films as Ta-W and Ti-W can be found in the literature. In this study, a modeling and experimental works on the amorphous binary alloys will be presented for its barrier performance on the metal diffusions. For experiments, a layer of Cu/Ta50Zr50/SiO2/Si stack is made by the deposition of Ta and Zr on thermally oxidized Si substrate by co-sputtering in the Ar plasma. Experimental results indicate that the amorphous barrier can indeed suppress the penetration of Cu atoms into Si substrate upon annealing at temperature higher than 500oC. Further investigations on the thermal stability reveal that the top Cu layer may enhance the formation of metal silicides such as TaSi2 and ZrSi2 inside the barrier. These silicides can increase the activation energy of Cu diffusion and therefore enhance the barrier's performance. In addition, a failure mechanism of the diffusion barrier is proposed based on both thermal stability and residual tensile stresses. A qualitative model for this proposal shall be analyzed by numerical simulations also.

Surface Science

Room: 611 - Session SS2+EM+TF-ThA

Organics and Carbon Films on Silicon

Moderator: A.A. Baski, Virginia Commonwealth University

2:00pm **SS2+EM+TF-ThA1 Reactivity of n-type/p-type H:Si(111) for Photoadsorption of CH_3Br**, ***T. Yamada***, RIKEN, Japan, *H. Ozawa*, The University of Tokyo, Japan, *H.S. Kato*, RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

Ultraviolet photo-assisted adsorption of CH_3Br gas was examined on hydrogen terminated Si(111)-(1x1) surfaces of n-type (P-doped, resistivity 7-10 Ωcm) and p-type (B-doped, 10-40 Ωcm) substrates. After treatment of Si substrates at $1x10^{-5}$ Pa of CH_3Br pressure with simultaneous irradiation by high-pressure Hg lamp (100W) for 10 min - 3 hours at room temperature, high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS) were applied to detect the adsorbate. On n-type H:Si(111), hydrocarbon adsorbates were observed, and on p-type H:Si(111), Si-Br stretching signal (450 cm^{-1}) was exclusively detected. To survay the mechanism of reaction, we divided this adsorption process into UV irradiation in ultrahigh vacuum (UHV) and following CH_3Br introduction without UV. Although a small amount of hydrocarbon contaminant was deposited on both n-type and p-type substrates during UHV UV irradiation, the post-adsorption of CH_3Br resulted in increase of only hydrocarbons on n-type, and only Br on p-type. This result indicates that the irradiation of UV on H:Si(111) promoted photo-assisted desorption of H and leaves hydrogen vacancies, namely, dangling bonds. The difference of adsorption product between the n-type and p-type should be associated with the electronic structure of substrate modified with dopant atoms. We performed molecular-orbital calculations of various H-terminated Si(111) model clusters (sized from 32 Si atoms to 400 Si atoms) with H vacancies on the surface and a few Si atoms replaced with P or B atoms, on the basis of density functional theory (DFT). It was demonstrated that the orbital protruding over the dangling bond was the highest filled electronic orbital on P-doped cluster, whereas on B-doped, it was the lowest unoccupied orbital. This result did not change if we change the number of dangling bonds or dopant atoms. Although this approximation is too rough because of orders-of-magnitude higher dopant level than the real substrates, the result matches the classical formalism of semiconductor band bending near the surface. We further performed DFT calculations on the dangling bond coordinated with a CH_3Br molecule. The dangling bond on n-type/p-type substrate attracts theCH_3 group/Br atom, respectively. It was recognized that the effects of dopant are crucial for the adsorption selectivity of surface dangling bonds towards organic molecules.

2:20pm **SS2+EM+TF-ThA2 Effects of Dative Bond Formation on Si(114) Reaction Pathways**, ***D.E. Barlow***, Nova Research, Inc., *S.C. Erwin, A.R. Laracuente, L.J. Whitman, J.N. Russell, Jr.*, Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface with a single domain-like surface reconstruction composed of parallel rows of dimers, rebonded atoms, and tetramers.[1] We have used transmission FTIR, STM, and DFT to compare the reactions of ethylene and acrylonitrile at the Si(114)-(2x1) tetramer sites. These sites have a diene-like structure, allowing us to investigate the potential Diels-Alder reactivity of an unusual Si surface structure.[2] In particular, we have investigated the effects of conjugated, electron-withdrawing substituents on the dieneophile. For organic reactions, such substituents typically increase the reaction rate, often by several orders of magnitude. Ethylene reacts as the dieneophile in a Diels-Alder reaction at the tetramer site with a reaction probability of $\sim10^{-2}$. Surprisingly, however, we find that acrylonitrile does not undergo the Diels-Alder reaction at the tetramer sites. Rather, exposure of the clean Si(114) surface to acrylonitrile leads to three distinguishable ketenimine (-C=C=N-) structures in the FTIR spectra. Polarized transmission FTIR results indicate the presence of ordered ketenimine arrays, with strong registry to the Si(114) surface and site-dependent orientation. We have distinguished the acrylonitrile adsorption structures at the tetramer sites from those at the dimer and rebonded atom sites by analyzing site-dependent heterofunctionalized Si(114) surfaces on which we have first passivated a large portion of rebonded atom and dimer sites with ethylene, allowing the acrylonitrile to preferentially react with the remaining tetramer sites. From the polarized FTIR spectra, we conclude that the -C=C=N- structures are aligned parallel to <110> at the rebonded atom and dimer sites, but perpendicular to <110> at the tetramer sites. The differing ethylene and acrylonitrile reactivities on Si(114) further emphasize the variable reaction pathways possible for dative bonding on reconstructed Si surfaces.

[1] S. C. Erwin, A. A. Baski, and L. J. Whitman, Phys. Rev. Lett. 77, 687 (1996).

[2] D. E. Barlow, et al., J. Phys. Chem. B 110, 6841 (2006).

2:40pm **SS2+EM+TF-ThA3 Surface Chemistry of Silicon: Making the Connection to Molecules**, ***J.M. Buriak***, *D. Wang, Y. Qiao, J. Chai*, University of Alberta, Canada **INVITED**

The chemistry of semiconducting surfaces is a field of intense interest, not only for the prospect of exciting cutting edge applications, but also from a fundamental perspective.[1] Control over the surface reactivity of silicon and other semiconducting materials is critical for interfacing new molecular devices on chips and other nanotechnological applications, and to perhaps replace oxide overlayers as feature sizes on transistors become smaller than 50 nm. In this talk, we will attempt to provide a preliminary reactivity 'road map' towards understanding the organometallic surface chemistry of silicon that, interestingly, can vary greatly from that of silicon-based molecules. For example, by using the silicon surface as an electrode, electrochemistry can drive reactions that have no obvious parallels with molecular chemistry. As a result, molecules as diverse as alkynes and tetraalkylammonium salts can serve as organic sources to prepare organic monolayers directly on silicon, bound through Si-C bonds.[2] We will also discuss our latest results concerning the patterning of silicon surface reactivity on the nanoscale (features sizes<30 nm); both conjugated organic monolayers and monodisperse metallic nanocrystallites can be interfaced directly to the surface of silicon for a variety of applications.

[1] Buriak, J. M. "Organometallic Chemistry on Silicon and Germanium Surfaces", Chemical Reviews, 2002, 102, 1271-1308.

[2] Wang, D.; Buriak, J. M. "Trapping Silicon Surface-Based Radicals", Langmuir, 2006, 22 6214-6221.

3:40pm **SS2+EM+TF-ThA6 Liquid Methanol Reaction with H-terminated Silicon Surfaces**, *D.J. Michalak*, University of California, Berkeley, *S. Rivillon Amy*, Air Products and Chemicals, Inc., *A. Esteve*, LAAS, France, ***Y.J. Chabal***, Rutgers University

The reaction of hydrogen-terminated Si(111) and oxide terminated silicon surface with neat anhydrous liquid methanol (CH_3OH) has been studied with high resolution Fourier transform infrared spectroscopy (FTIR) to determine several factors regarding the surface chemistry. First, a high temperature reaction of atomically smooth H-Si(111) surfaces in neat anhydrous CH_3OH liquid produces methoxylated surfaces that are virtually free of subsurface oxidation. At long reaction times (t > 3h), the surface saturates with Si-OCH_3 sites covering ~30% of a monolayer, with a residual ~70% comprised of Si-H sites. The virtually-oxide free surface facilitates two important conclusions. First, surface reaction mechanisms involving the insertion of oxygen atoms in the subsurface Si-Si back bonds can be ruled out. Because subsurface oxidation often presents deleterious surface electrical trap states, the absence of significant oxidation also holds important implications for the use of alcohol-terminated precursors in the functionalization of surface chemistry for use in electronics devices. Second, the vibration modes of the clean surface are very sharp and allow a more careful analysis of surfaces that contain subsurface oxidation. Specifically, it has been observed previously that, despite the presence of subsurface oxidation on some methoxyl-terminated surfaces, no evidence for subsurface oxygen atoms has been observed directly below Si-H sites. This is surprising from the standpoint that the surface still retains nearly 60-70% unoxidized Si-H sites. It was proposed that the oxidation may reside underneath Si-OCH_3 sites. In this work, comparison of partially oxidized surfaces with the virtually oxide-free surfaces demonstrates that the presence of blue shifted Si-OCH_3 vibrational modes is correlated with the presence of subsurface oxidation. This assignment is corroborated by studies performed on oxide-terminated surfaces that present similar, but blue shifted modes to those observed on the oxide-free H-Si(111) surface. Thus, this work demonstrates that while virtually oxide-free surface can be made, there is a large selectivity towards the formation of oxide underneath atop Si-OCH_3 sites relative to the Si-H sites, which retain almost exclusively unoxidized backbonds. Finally, mechanisms for the formation of oxide are presented with regard to these new results.

4:00pm **SS2+EM+TF-ThA7 Dissociative Electron Attachment Induced Growth of Thin Graphite Films or Graphene on Si(111)-7×7**, ***D. Oh***, *H. Abernathy, N. Sharma, P.N. First, M. Liu, T.M. Orlando*, Georgia Institute of Technology

There is currently keen interest in developing good strategies for the growth of a few layers of graphite or graphene on substrates such as Si. We are exploring the use of low-energy electron induced dissociation of adsorbed benzene, naphthalene and phenylacetylene in the production of graphite/graphene films with good lateral heterogeneity. In this study, benzene, naphthalene or phenylacetylene is chemisorbed onto reconstructed Si(111)-7×7 surfaces. These adsorbates are fragmented via low-energy electron bombardment at energies which are dominated by dissociative electron attachment resonances. In general, the incident electron beam can be captured by low-lying π^* states of the chemical precursors and can lead to controlled dissociation and the formation of reactive radicals and negative ions. These fragments can then react to form a network structure of predominantly sp^2 hybridization. The deposited carbon overlayer is examined with Auger electron spectroscopy, Raman spectroscopy and scanning tunneling microscopy. The quality of the deposit and the viability of this non-thermal growth strategy will be discussed.

4:20pm **SS2+EM+TF-ThA8 Adsorption Irregularities of 1,3 Cyclohexadiene and Naphthalene on Silicon(100) Investigated by STM, DFT and an Extended Frontier Orbital Analysis**, ***P.M. Ryan***, CRANN, Trinity College Dublin, Ireland, *L.C. Teague,* National Institute of Standards and Technology, *J.J. Boland*, CRANN, Trinity College Dublin, Ireland

We consider the reactions of 1,3-cyclohexadiene (1,3-CHD)[1,2] and Naphthalene on Si(100) and examine possible origins for the surface adsorption selectivity evident from STM measurements. The major adsorption products for both molecules are identified by STM. DFT calculations are carried out in order to examine the energetics of the major products and their associated structural analogs. The calculations reveal that the theoretical product distributions based on thermodynamics alone, for both systems, differ significantly from the experimental ones. We explain, using an extended frontier orbital analysis, that secondary orbital interactions which can discriminate between certain concerted reactions and are unavailable at the Γ point due to symmetry considerations become feasible at other κ points in the surface Brillouin zone. We propose that these interactions play a role in the kinetics of the adsorption process and may account for the observed reaction selectivity.

[1] Teague, L.C. and J.J. Boland, STM Study of Multiple Bonding Configurations and Mechanism of 1,3-Cyclohexadiene Attachment on Si(100). Journal of Physical Chemistry B, 2003. 107(16): p. 3820-3823.

[2] Teague, L.C., D. Chen, and J.J. Boland, DFT Investigation of Product Distribution Following Reaction of 1,3-Cyclohexadiene on the Si(100)Surface. Journal of Physical Chemistry B, 2004. 108(23): p. 7827-7830.

4:40pm **SS2+EM+TF-ThA9 CNTs on a Si(100) Surface: Dry Deposition, STM/STS, and Contacts**, ***B. Naydenov***, Trinity College Dublin, Ireland, *J.J. Boland*, Trinity College Dublin and CRANN, Ireland

We present a cryogenic STM study of carbon nanotubes (CNTs) deposited on Si(100) surfaces. Imaging and spectroscopic results by means of LT-STM will be demonstrated and analyzed. Using STM-manipulations, contacts (different metals) with the CNTs are formed and characterized. Aspects of the CNTs purity, preparation, and interaction with the substrate will be discussed.

Thin Film

Room: 602/603 - Session TF1-ThA

Photovoltaics, Fuel Cells, and Alternative Energy Materials and Applications

Moderator: M. Drees, Luna Innovations Incorporated

2:00pm **TF1-ThA1 High Throughput Fabrication and Screening of Thin Film Electrocatalysts for Fuel Cell Applications**, *J.M. Gregoire, **M. Kostylev**, J. Jin, R.B. van Dover, F.J. DiSalvo, H.D. Abruna*, Cornell University

We describe methodologies for the generation and screening of combinatorial libraries of electrocatalyst materials for fuel cell applications. Composition spread thin films are codeposited via DC magnetron sputtering. The films are then screened for catalytic activity using a fluorescence indicator. The high-throughput nature of both the fabrication and screening processes, coupled with the versatility of the deposition system, allow for the rapid testing of a broad range of potential fuel cell electrocatalyst materials. Details of the techniques, fluorescence test results and characterization data for some catalytically active films will be presented.

2:20pm **TF1-ThA2 Atomic Layer Deposition of Alternative Energy Materials**, *X. Jiang, J.S. King,* ***S.F. Bent***, Stanford University

Atomic layer deposition (ALD) is a method for depositing thin films of semiconducting, insulating and metallic materials using an alternating series of self-limiting reactions between gas phase precursors and the substrate. Over the past several years, ALD has grown steeply in popularity as a choice for the semiconductor industry. However, ALD's real potential for impact may lie in even more novel applications, including those in alternative energy. This presentation will describe our recent studies using ALD for the deposition of thin films for both fuel cell and solar cell applications. For solid oxide fuel cells (SOFCs), we have explored ALD for the fabrication of an ultra-thin Pt film for use as the electrocatalyst, and a Pt mesh structure for a current collector, as a means of improving catalyst performance at lower temperatures. Pt ALD was carried out using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe$_3$) and O$_2$ as precursors and N$_2$ as a carrier and purging gas. Ex situ analysis of the as-deposited Pt films shows that the platinum film is of excellent uniformity, with no measurable impurities and low electrical resistivity. In addition to the blanket deposition of platinum, we have used the technique of area selective ALD, by combining the methods of ALD and microcontact printing, for fabrication of spatially patterned Pt, to be used as a current collector grid for SOFCs. Working SOFC fuel cells were fabricated with ALD-deposited Pt, and their performance was characterized by a potentiostat-impedance system. The results show that comparable initial performance can be achieved with ALD deposited Pt anodes compared to the RF sputtered Pt anodes with only one-eighth the platinum loading required in the ALD film. For the photovoltaic application, we will describe a vertical nanostructured geometry in which the carrier diffusion length is decoupled from solar radiation absorption, enabling high efficiency cells to be fabricated inexpensively out of low quality materials. We will describe how ALD and other deposition methods can be used to deposit thin films of photovoltaic materials to make nanocomposite solar cells.

2:40pm **TF1-ThA3 Investigation of Bulk and Grain Boundary Diffusion of Oxygen in Yttrium Stabilized Zirconia Via Nuclear Reaction Analysis***, ***M. Finsterbusch***, Montana State University and Technische Universitaet Ilmenau, Germany, *H. Chen, W. Priyantha,* Montana State University, *V. Shutthanandan,* Pacific Northwest National Laboratory, *R.J. Smith,* Montana State University, *J.A. Schaefer*, Technische Universitaet Ilmenau, Germany

Yttria stabilized zirconia (YSZ) is one of the most common solid ionic conductors considered for the electrolyte in solid oxide fuel cells operating at temperatures near 800°C. The addition of yttria into zirconia not only stabilizes the cubic fluorite phase of zirconia over a wide temperature range, but also introduces oxygen vacancies due to the smaller valency of Y^{3+} vs. Zr^{4+}. High oxygen ionic conductivity associated with vacancy hopping is seen in YSZ for yttria doping levels around 10%. Numerous studies have been carried out to understand oxygen transport and surface exchange kinetics in single crystal YSZ.[1-3]However, for polycrystalline YSZ the description of diffusion processes is more complex due to the presence of interfaces and grain boundaries that act as preferential sites for variation in composition and chemical state of the atomic species with respect to the bulk. In this study ^{18}O tracer depth profiles were obtained using $^{18}O(p,\alpha)^{15}N$ nuclear reaction analysis for both YSZ single crystals and sintered polycrystalline pellets. Samples were cleaned and pre annealed in a tube furnace for 8 hours at 800°C in air. Afterwards they were exposed for various times at a pressure of 10 Torr of 99% pure ^{18}O at various temperatures up to 900°C. By contrasting the differences of ^{18}O transport for the two structures, the influence of grain boundaries on oxygen transport and exchange kinetics were extracted.

*HiTEC is funded by DOE as a subcontract from Battelle Memorial Institute and Pacific Northwest National Laboratory under Award No.DE-AC06-76RL01830.

[1] R. Roewer, G. Knoener, K. Reimann, H.E. Schaefer, U. Soedervall; phys. stat. sol. (b) 239, No. 2, R1-R3 (2003)/DOI 10.1002/pssb.200309011

[2] N.I. Joos, P.A.W. van der Heide, J.R. Liu, R. Christoffersen, W.K. Chu, C.A. Mims; Mat. res. Soc. Symp. Proc. Vol. 548, Page 605-610

[3] P.S. Manning, J.D. Sirman, R.A. De Souza, J.A. Kilner; Solid State Ionic 100 (1997) 1-10.

3:00pm **TF1-ThA4 Thermal Stability and Oxidation Resistance of Protective Coating on Stainless Steel Interconnect for Solid Oxide Fuel Cells**, ***H. Chen***, *J.A. Lucas, W. Priyantha, R.J. Smith, P.E. Gannon, M. Deibert,* Montana State University, *V.I. Gorokhovsky,* Arcomac Surface Engineering, *V. Shutthanandan, P. Nachimuthu*, Pacific Northwest National laboratory

Chromia forming ferritic stainless steels are being considered for application as interconnects for planar solid oxide fuel cells (SOFC) because of their low cost and flexibility. Many SOFC designs will operate at temperatures exceeding 700°C. At these temperatures, ferritic steels lack environmental stability in the SOFC environment, and as a result may degrade the performance of the SOFC. In this study, an effective, dense and well adherent TiCrAlYO coating was deposited on 430SS using filtered arc deposition technique. XRD indicates that nanocrystalline spinel is the dominant crystal structure in the coating. Rutherford backscattering with He and non-Rutherford scattering with proton were used to characterize the composition and the thermal stability of the coatings. The chromium volatility of the coated steel plates at 800°C was measured using ion beam analysis. Significant reductions in oxidation rates as well as reduced Cr volatility were observed for the coated alloys.

3:40pm **TF1-ThA6 Optimizing the Structure and Composition of Heterostructured Ceria / Zirconia Multilayers through Oxygen Plasma Assisted Molecular Beam Epitaxy**, *S.V.N.T. Kuchibhatla, P. Nachimuthu, C.M. Wang, V. Shutthanandan, M.H. Engelhard, L.V. Saraf,* ***S. Thevuthasan***, Pacific Northwest National Laboratory, *S. Seal*, University of Central Florida

Mesoscopic fast ion conduction in nanometer-scale planar heterostructures is gaining attention from researchers in the field of solid-state ionic conducting devices. One such device and the most popular among alternative energy sources is solid oxide fuel cell (SOFC). In SOFCs oxygen ions should be effectively conducted from cathode to anode through an electrolyte. Hence, it is quite essential to develop electrolyte materials that offer low and intermediate temperature ionic conductivity. Currently, yttria stabilized zirconia (YSZ) is the most widely used electrolyte, but the need for temperatures in the range of 800oC-1000oC imposes various restrictions in expanding the SOFC technology. Samaria doped ceria has been extensively studied as an alternative to YSZ at intermediate temperatures. Structural configuration of these thin films plays a major role in oxygen ionic conduction and we have initiated several studies to understand the influence of structure and chemistry of these thin films on oxygen ionic conductivity. We have synthesized high quality single- and poly- crystal films of Sm doped ceria(SDC) and Sc stabilized zirconia (ScSZ) using oxygen plasma assisted molecular beam epitaxy and characterized those using several surface and bulk sensitive techniques. The effect of growth temperature on the domain structure and the ionic conductivity are features of interest in the research associated with single- and poly- crystal SDC films. It appears that the strain, chemistry and structure at the interface play a role on ionic conduction in the SDC and ScSZ multi-layer films. The enhancement in oxygen ionic conductivity through some of these films at low temperatures are encouraging.

4:00pm **TF1-ThA7 Controlling the Doping Concentration and Thermoelectric Applications of NaxV2O5 Thin Films**, ***S. Iwanaga***, *M. Marciniak, R.B. Darling, F.S. Ohuchi*, University of Washington

A high thermoelectric coefficient has been reported for Na$_x$V$_2$O$_5$ thin films. Na$_x$V$_2$O$_5$ structure consists of V$_2$O$_5$ layers, where Na atoms are retained between the layers, leading to various phases depending on the Na concentration. From the view point of processing this class of material for thermoelectric device applications, the precise control of the Na concentration and stabilization of the desired phase are the key issues. Recently, we presented a possibility of a solution route to make Na$_x$V$_2$O$_5$ thin films. Here, we report that through this new processing route, we can control the crystal phase of Na$_x$V$_2$O$_5$ thin films, specifically between β- and γ- phases, through annealing conditions and the choice of the substrates. β-phase is preferred for thermoelectric applications due to high Seebeck coefficient and a relatively good electrical conductivity. We found that on quartz substrate, high temperature annealing (600 C) leads to predominantly β- phase. By using soda-lime glass, which contains high Na$_2$O, as a substrate, the Na concentration in Na$_x$V$_2$O$_5$ films increases with increasing annealing time: coexistence of β- and γ- phases (10 minutes annealing) develops into γ- phases dominated film upon annealing for >30 minutes. Our results suggest that the Na concentration can be kinetically controlled in this material system. The possibility of Na$_x$V$_2$O$_5$- based thermoelectric device is proposed.

4:20pm **TF1-ThA8 From Uncontrolled and Controlled Size and Shape Intercalated Nanostructures to Bulk Materials for Thermoelectric Device Applications: Old and New Materials - New Techniques**, ***N. Sorloaica-Hickman***, University of Central Florida

The properties of all materials are highly dependent on structure, composition, size and shape. As we seek to explore and utilize novel phenomenon at the nano, 2-dimensional and 3-dimensional scale, a basic understanding of structure/composition/size/shape property relations alone are not enough unless this understanding is made in the context of a specific device and in relation to the practical, economic considerations. This investigation requires a highly integrated approach to all aspects of development of these integrated devices, including theoretical prediction, synthesis, processing and characterization in concert with device design, optimization and implementation. Theoretical and experimental results predicted that the nano-scale materials have better thermoelectric properties that bulk materials.[1] Previous theoretical work on the effect of the grain boundaries in polycrystalline materials indicated that the scattering of the phonons in smaller grains could be very beneficial for the efficiency of the thermoelectric materials.[2] This presentation will highlight some new directions in size and shape controlled nanostructure (grains) and bulk thermoelectric materials research based on our theoretical and experimental investigations. Specific configurations where size and shape of the nanostructures that will constitue the bulk materials are controlled during fabrication will be discussed. Preliminary calculations of the electronic and thermal properties as a function of the composition, size and shape of the intercalated nanostructure will be also presented. We will also describe the synthesis techniques of the nanostructures and the method to incorporate these structures into bulk materials during fabrication. However, the challenge remains to achieve higher performance results in integrated systems in order to more rapidly incorporate them into standard thermoelectric devices.

[1] M. S. Dresselhaus, J. P. Heremans, in Thermoelectrics Handbook: Macro to Nano (Ed: D. M. Rowe), Taylor and Francis, CRC, Boca Raton, FL 2006, Ch. 39, p. 39-1-39-24.

[2] J. W. Sharp et al , Boundary Scattering and the Thermoelectric Figure of Merit, Phys. Stat. Sol. (a) 187, No. 2, 507-516 (2001).

4:40pm **TF1-ThA9 Fabrication of Multilayered Thin Film Cooling Devices**, ***Z. Xiao***, Alabama A&M University

Multilayered thin film cooling devices were designed and fabricated for the application of highly efficient solid-state micro cooling. Multilayered Bi$_2$Te$_3$/Sb$_2$Te$_3$ (p-type) and Bi$_2$Te$_3$/Sb$_2$Te$_x$Se$_{3-x}$ (n-type) superlattice thin films were used as the material systems for fabrication of the cooling devices. The multilayered films were grown by e-beam evaporation and had a periodic structure consisting of alternating Bi$_2$Te$_3$/Sb$_2$Te$_3$ layers or Bi$_2$Te$_3$/Sb$_2$Te$_x$Se$_{3-x}$ layers, with 5-10 nm thickness each. The cooling device consists of pairs of n-type and p-type legs, which are connected electrically in series and thermally in parallel. Under the applied voltage, both electrons in n-type legs and holes in p-type legs move from the cooling end, carrying heat, therefore, heat is pumped away from the cooling end to the hot end, where the heat is finally ejected away. Large number of pairs of n-type and p-type legs with size ranging from 7 µm by 14 µm to 30 µm by 40 µm is integrated in a single device using microfabrication techniques. Photomasks were designed for the fabrication of the cooling devices, and clean room-based microfabrication techniques were used to fabricate the devices. The developed cooling device is a good candidate for the application of high-efficiency solid-state micro cooling. The electrical and thermal parameters of the material systems such as the electrical conductivity, thermal conductivity, and Seebeck coefficient will be characterized and the cooling efficiency will be measured. The results will be reported in the conference.

Acknowledgements: The author thanks CERDEC for financial support for the research.

5:00pm **TF1-ThA10 Optical Characterezation of InN layers grown by High-Pressure CVD**, ***M. Alevli***, *G. Durkaya,* Georgia State University, *R. Kirste,* Technische Universität Berlin, Germany, *A. Weesekara, A.G.U. Perera,* Georgia State University, *A. Hoffmann,* Technische Universität Berlin, Germany, *N. Dietz*, Georgia State University

A growing number of potential applications such as high-efficient heterojunction solar cells,thermoelectric devices and terahertz detector will become possible as Indium Nitride (InN) and In-rich group III-nitride(N) materials become more mature and can be integrated with other-rich group III-N alloys. Understanding and controlling the physical properties of the InN is of essential importance next to its integration as a component of (Ga$_{1-x}$In$_x$)N alloy system, which is crucial for fabrication of wavelength tailored high-efficient LEDs and displays. The present limitations in this area are in the growth of high quality InN and In-rich group III-N at processing conditions that are compatible with GaAlN aloys.The difficulties arise from the low dissociation temperature of In-rich groupIII-N, requiring extraordinarily high nitrogen overpressure to stabilize the material up to optimum growth temperatures. Our research explores the growth of InN and In-rich group III-N by high-pressure chemical vapor deposition (HPCVD), an approach that allows controlling and stabilizing the vast different partial pressures of the constituents. The results show that the chosen HPCVD pathway leads to high-quality single crystalline InN, demonstrating that HPCVD is a viable tool for the growth of In-rich III-N alloys. The structural analysis of InN deposited on GaN-Sapphire substrate by XRD show single phase InN(0002) peaks with full width half maximum below 400 arcsec. The optical transmission analysis shows that an apparent band gap is around 1.4 eV with absorption centers at 0.8 eV and 0.4 eV. The strength of the low energetic absorption centers are closely related to the precursor ratios and the utilized growth temperatures. Infrared reflectance spectroscopy is used to estimate the high frequency dielectric constant, the free carrier concentrations and carrier mobilities in these layers. The free carrier concentration is found to be in the upper 10^{19} cm^{-3} with the corresponding mobilities around 600 cm^{+2}V^{-1}s^{-1}.A further reduction of residual extrinsic impurities in the precursor and carrier gas is presently explored to further reduce the free carrier concentration in the layers.The modeling of the IR-reflectance spectra indicate the present of two distinct InN layers: one with electron concentrations below $5x10^{17}cm^{-3}$,which is followed by second layer in the upper $10^{19}cm^{-3}$ closer to the surface.

Thin Film

Room: 613/614 - Session TF2-ThA

Computational Aspects of Thin Films

Moderator: B.C. Holloway, The College of William and Mary

2:00pm **TF2-ThA1 Computational Study of the Interfacial Structure of Aluminum/α-Alumina**, ***B.D. Devine***, University of Florida, *A. McGaughey*, Carnegie-Mellon University, *S.R. Phillpot*, *S.B. Sinnott*, University of Florida

Several experimentally observed orientations for the interface between FCC aluminum grown on the (0001) face of α-alumina were studied through molecular dynamics using a modified variable charge potential. This many-body, empirical potential allows for the realistic modeling of both the metallic and ceramic phases in large-scale, atomistic simulations. The effects of temperature, surface terminations and coherency on the interfacial structure and energy were investigated. The efficiency of the molecular dynamics simulation allows for study of periodic systems oriented with minimal strain along the preferred relationship of $<1010>_{Al2O3} || <110>_{Al}$ as well as secondary orientations along $[2112]_{Al2O3} || [011]_{Al}$ and $[2112]_{Al2O3} || [231]_{Al}$. The results are compared to experimental data and to the results of density functional theory calculations. This work is supported by the National Science Foundation (DMR-0426870).

2:20pm **TF2-ThA2 Analytical Simulation of Conformal and Super-Conformal CVD on High Aspect Ratio Vias and Trenches**, *Y. Yang*, ***J.R. Abelson***, University of Illinois at Urbana-Champaign

The need to coat or fill recessed features such as trenches or vias is frequently encountered in micro- and nano-fabrication processes. Chemical vapor deposition is commonly used because of the combination of good conformality and high growth rate. With the continuous scaling down of feature sizes and the increase of aspect (depth/width) ratios, it has become a major challenge to maintain the growth conformality and filling efficiency. We developed a numerical model that is capable of simulating the film thickness profiles produced by CVD in trenches and vias with aspect ratios ≥ 10:1. In this model, the precursor transport is described by Knudson diffusion, and the precursor concentration and reaction rate distributions are solved numerically from the continuity equation. The evolution of the deposition profile during a filling process can also be predicted. We employ this model to understand the critical issues associated with CVD on high aspect ratio features. We show that the precursor reaction probability is the key factor that governs the deposition conformality. The model predicts the precursor reaction probability that is required to conformally coat or to completely fill trenches with aspect ratios ranging from 5:1 to 100:1. These simulations are in close agreement with the experimental profiles we have obtained for HfB_2 and CrB_2 films grown using single-source borohydride precursors. Traditionally the precursor reaction probability is controlled primarily by the growth temperature. We show that if a Langmuir surface reaction mechanisms is operative then the precursor pressure is a far more effective parameter to reduce the reaction probability. We have developed a new approach to obtain super-conformal coating (bottom-up filling) of high aspect ratio features, and we have demonstrated proof-of-concept with CrB_2 and HfB_2 films. In this method, a suppressor species is introduced into the growth system to reduce the surface reaction rate of the precursor. We simulate the deposited film profile as a function of the suppressor pressure, precursor pressure, trench aspect ratio, and the relative reaction rates of the suppressor and precursor species. We will discuss methods to optimize the filling process by varying the suppressor pressure in time during film growth.

2:40pm **TF2-ThA3 Computational Investigation of Surface Polymerization by Ion Assisted Deposition**, *W.-D. Hsu*, University of Florida, *S. Tepavcevic*, *L. Hanley*, University of Illinois at Chicago, ***S.B. Sinnott***, University of Florida **INVITED**

Density functional theory-MD (DFT-MD) simulations are used to study surface polymerization by ion-assisted deposition (SPIAD) of thiophene on alpha-terthiophene oligomers on a silicon surface to determine the dominant mechanisms responsible for the SPIAD process. Polythiophene is a conductive polymer that has attracted much interest in recent years because its properties are desirable for applications that include light emitting diodes, field effect transistors, and photovoltaics. Optimization of the performance of polythiophene in these devices requires the development of processing methods that can simultaneously control its chemistry and morphology on the nanometer scale. One such method is SPIAD, where conducting polymer thin films are grown on substrates by the simultaneous deposition of hyperthermal polyatomic ions and thermal neutrals in vacuum. Both neutral and positively charged systems are considered in the DFT-MD simulations in order to assess the effect of charge on the results, which were compared to experimental data. The incident energies range from 100 to 500 eV. The simulations indicate that the differences in the collision outcomes between the neutral and positively charged events are small in most cases, but the atoms in the +1 charged system experienced slightly larger forces and velocity variations than the atoms in the neutral system. Several key bond dissociation and polymerization mechanisms are predicted in the simulations that are also observed experimentally. The most important prediction is that incident thiophene ions break apart on collision with the 3T film. Both the experiments and simulations indicate that incident thiophene ions chemically modify the structure of the oligomer film by covalently bonding to the 3T oligomers. The insight gained from this integrated experimental and computational work can be used to optimize the SPIAD process for polythiophene and other conducting polymer systems. This work is supported by the National Science Foundation (CHE-0200838).

3:40pm **TF2-ThA6 Modelling, Growth and Characterisation of Stress-Balanced Thin Films on Stress-Free Virtual Substrates**, ***S.G. Turner***, Imperial College London, UK, *L. Yu*, Chinese Academy of Sciences, China, *K. Chua*, *M.R. Levy*, Imperial College London, UK, *X. Li*, University of Oxford, UK, *J. Zhang*, Imperial College London, UK

The Si/SiGe material system on a Si platform gives opportunities to develop Si-based optoelectronic devices, allowing monolithic integration.[1] The 4% mismatch requires strain to be properly managed in structures that exceed the critical thickness for relaxation. Growing a stress-balanced structure on a virtual substrate (VS) allows such control. This work characterises the composition, tilt and strain state of the VS, and that of thin layers. Growth was carried out under ULPCVD & GSMBE modes in a modified VG Semicon system. We grew a fully-relaxed SiGe VS on Si(001), compositionally graded from pure Si. We show that a composition overshoot in the graded layer is needed to achieve the required in-plane lattice parameter, and determine its value. We examined x-ray reciprocal space maps (RSM) about the 004 and 224 reflections, obtaining average tilt of the VS with respect to the substrate and tilt distribution. Results from misoriented substrates show that the VS tilts to reduce the difference between low-index planes and the physical surface by >5%, explained by the preferential introduction of misfits with certain Burgers vectors. A fully-relaxed VS provides a good template for stress-balance between thin metastable layers by considering average force in the structure.[2] Predictions from linear elasticity (LE) theory (assuming linear interpolation of alloy elastic constants) were tested by depositing a DBR on a fully-relaxed VS.[3] The DBR consisted of 25 repeats of a Si/SiGe (32%) bilayer of ~190nm thickness, grown at 590°C and 520°C respectively. RSMs (giving lattice parameters) revealed the bilayer was coherent to the VS, supporting the validity of the linear extrapolation. This was compared to density functional theory calculations of the elastic constants. Reflectivity was 75% at 1.4 microns, and x-ray analysis showed fringes typical of well-ordered interfaces, suggesting a good stress-balance was realised. The composition overshoot part of the VS remains under compressive strain and coherent to the subsequent grown layers. We propose to compensate this using tensile Si, obtaining a true stress-free structure. We demonstrated this for varying VS compositions. We thus show that the precise strain state of thin films can be accurately manipulated.

[1] Kuo et al., Nature Vol. 437 p1334

[2] Ekins-Daukes et al., Crystal Growth & Design Vol. 2 p287.

[3] Kawaguchi et al., APL Vol. 79 p476.

4:00pm **TF2-ThA7 Intra- and Interlayer Mass Transport Rates during Layer-By-Layer Homoepitaxial Pt(111) Growth from Hyperthermal Beams (5-50 eV)**, ***V. Chirita***, *D. Adamovic*, *E.P. Münger*, *L. Hultman*, Linköping University, Sweden, *J.E. Greene*, University of Illinois, Urbana-Champaign

We employ multi-billion time step embedded-atom method molecular dynamics simulations to study homoepitaxial growth of Pt(111) using low-energy (0.2 - 50 eV) hyperthermal Pt fluxes. We deposit 5 monolayers at 1000K and with deposition rates approaching experimental conditions. The results reveal a transition from a three-dimensional (3D) multilayer growth mode to layer-by-layer growth at ~ 20 eV which is maintained for energies of up to 50 eV. In order to determine the mechanisms responsible for the observed change in the growth mode, we resolve, with picosecond resolution, both irradiation-induced and thermally activated processes. This allows us to determine, with unprecedented accuracy, the energy dependence of the net intra- and interlayer migration rates during the deposition process. Results show, that for all energies, irradiation events are completed within 10 ps following energetic impacts and that these processes dictate the growth mode. As expected, thermal migration is not affected by the deposition energy. For Pt deposition energies above 20 eV, the net interlayer migration induced by irradiation is towards the surface. This type of mass transport occurs via exchange mechanisms between surface and sub-surface atoms. On the growing layers, we observe primarily the descent of adatoms at step-edges and the recombination of adatoms with surface vacancies, i.e. mainly thermally activated processes. However, thermally activated net downward migration is an order of magnitude less than irradiation-induced upward migration. Intralayer migration is shown to depend strongly on adatom surface coverage. Results show that adatoms are the primary source of in-layer mass transport, which is observed to peak at a coverage of ~ 0.05 ML. Sputtering is observed to occur for energies higher than 25 eV. However, the yield is too small, less than 1% at 50 eV, to have a significant effect on island nucleation and coalescence kinetics.

4:20pm **TF2-ThA8 Synthesis and Theoretical Modeling of Fullerene-like Phospho-Carbide Compounds**, ***A. Furlan***, *G.K. Gueorguiev, H. Högberg, S. Stafström, L. Hultman*, Linköping University, Sweden

First-principles DFT calculations predict that Fullerene-like (FL) CPx compounds can have resilient mechanical behavior similar to FL-CNx, but for a lower V element concentration. P is a higher period element compared to N. This means a higher freedom with respect to chemical bonding which is likely to affect the structure of the CPx compounds compared to FL-CNx. The results of theoretical simulation of synthetic growth of FL-CPx structures show that the substitution of N with P makes the formation of tetragon defects energetically favorable and that P-P bonds are plausible. This implies stronger curvature and interlocking of graphene planes. Concurrent inter- and cross-linking of the bent graphene planes induced by the P atom leads to cage- and onion-like structures which promise improved mechanical properties of the FL solids. In this paper we also present results from magnetron sputtering deposition of CPx thin films. The films were deposited by DC magnetron sputtering in Ar atmosphere from a compound graphite-P target containing between 5 and 15 at.% of P. Higher proportions of P in the target should be avoided since P-rich species in the deposition flux might result in P-segregation during film growth. The substrates were Si and NaCl wafers kept at a bias voltage in the range of -20 V to -50 V, and substrate temperature ranging from 150 ºC to 780 ºC. As-deposited coatings were analyzed using XPS, nanoindentation, SEM, and TEM. The preliminary results show that incorporation of P into the film is promoted at lower substrate temperatures and higher bias voltages. Nanoindentation experiments show that resistance to indentation and hardness of the CPx increases for decreasing substrate temperature and increasing bias voltage.

4:40pm **TF2-ThA9 High-Throughput Determination of Sputtered Film Composition: The Importance of Resputtering**, *J.M. Gregoire, M.B. Lobovsky, M.F. Heinz, F.J. DiSalvo,* ***R.B. van Dover***, Cornell University

The use of traditional characterization techniques to determine elemental compositions in composition spread thin films is time-intensive. Combinatorial, high-throughput studies of thin film materials demand high-throughput determination film composition. We discuss the possibility of calculating codeposited film compositions from deposition profiles obtained during single-source sputtering. In the context of DC magnetron sputtering, we find that while this technique is appropriate for the Pd,Pt,Ti system, it yields atomic ratios in a Pt,Pb composition spread thin film that vary significantly from values measured with wavelength dispersive x-ray spectroscopy. A model for resputtering during codeposition is presented to account for these discrepancies, and the model is used to calculate resputter rates during Pt,Pb codeposition. We also employ our model to estimate the resputtering susceptibility of commonly sputtered elements.

5:00pm **TF2-ThA10 General Theory of Optical Reflection from a Thin Film on a Solid and its Application to Heteroepitaxy**, *Y.Y. Fei, X.D. Zhu,* ***X. Wang***, University of California at Davis, *H.B. Lu, G.Z. Yang*, Chinese Academy of Sciences

Light reflection from an optically smooth yet atomically rough film on a smooth solid substrate formed by deposition or erosion is a convenient source of information on morphology and chemical make-up of the film. We show that changes in optical reflectivity for s-polarized (TE mode) and p-polarized (TM mode) components, defined as $(r_p - r_{p0})/r_{p0} - (r_s - r_{s0})/r_{s0} = \Delta_p - \Delta_s$, induced by such a film, is generally related to structural and chemical properties of such a film through a mean-field theory. Here r_{p0} and r_{s0} are the reflectivity of a bare substrate, and r_p and r_s are the reflectivity when the film is added onto the substrate. According to the theory, $\Delta_p - \Delta_s$ consists of a term that is proportional to the thickness of the rough portion of the film, a term that is proportional to the density of unit cells embedded in terraces, and a term that is proportional to the density of unit cells situated at step edges. The proportionality constants are functions of the overall thickness and chemical make-up of the film. We apply the theory to analysis of a wide range of growth and adsorption experiments studied with the oblique-incidence reflectivity difference (OI-RD) technique.

Thursday Afternoon Poster Sessions

Thin Film

Room: 4C - Session TF-ThP

Aspects of Thin Films Poster Session

TF-ThP1 Ferroelectric Properties of PbMn$_{1/3}$Nb$_{2/3}$O$_3$-Pb(Zr,Ti)O$_3$ Thin Films Epitaxially Grown on (001)MgO Substrates, ***K. Wasa***, *I. Kanno, H. Kotera*, Kyoto University, Japan, *T. Zhang, F. Li, S.-Y. Zhang*, Nanjing University, China

It is well known bulk ferroelectric oxide ceramics of modified Pb(Zr,Ti)O$_3$ (PZT) , PbMn$_{1/3}$Nb$_{2/3}$O$_3$- PZT, show variety of ferroelectric properties when we change the doping level of Mn and Nb. Thin films of the modified PZT will be useful for a fabrication of micro- and/or nano-level functional device including GHz electronic devices, since the co-doping of Mn and Nb to pure PZT will improve both mechanical Q values and electromechanical coupling of original PZT. However, it is not clear whether the bulk ferroelectric properties will be achieved in the ferroelectric thin films. We have tried to make epitaxial growth of thin films of the modified PZT, xPbMn$_{1/3}$Nb$_{2/3}$O$_3$- (1-x)PZT ,on (001)MgO substrates by rf-magnetron sputtering at x=0.06 and PZT(45/55). Before the epitaxial growth of the modified PZT, (001)Pt electrode with SrRuO$_3$ buffer layer was epitaxially grown on the MgO substrates by the rf-magnetron sputtering. The epitaxial temperature of the modified PZT thin films was around 600^{o}C and the epitaxial films showed (001) single orientation of tetragonal structure. The dielectric constant of the co-doped epitaxial thin films at 1.7 μmm in film thickness was $\varepsilon^*=190$ at 100kHz and showed sharp square shape P-E hysteresis curve with Pr=60μmC/cm^2 and Ec=110kV/cm. The bulk dielectric constant of modified PZT is $\varepsilon^*=300$ to 400. The structural differences between bulk and thin films will cause the sharp square type P-E curve with smaller dielectric constant for thin films. The epitaxial thin films showed high piezoelectric constant, e_{31} =-4C/m^2 , which was almost the same to the highest value of piezoelectric constant observed in the pure PZT(52/48) thin films at MPB condition. The present Mn and Nb doped PZT thin films show tetragonal structure which achieves the fine interface between thin films and the substrates. Since the doping of Mn will increase the mechanical Q values, the modified PZT thin films with lower dielectric constant will be applicable for the fabrication of the nano-level functional devices including GHz film bulk acoustic resonator (FBAR).

TF-ThP2 (Dual) Ion Beam Deposition of Tantalum Pentoxide Thin Film at Room Temperature, ***W. Kulisch***, *D. Gilliland, G. Ceccone, H. Rauscher, L. Sirghi, P. Colpo, F. Rossi*, Joint Research Center, Italy

Tantalum pentoxide is a material with outstanding optical (high refractive index, high transparency) and electrical properties (high dielectric constant), rendering it a promising candidate for applications in rapidly developing fields such as optics, microelectronics, and sensorics. Many modern application are based on plastic substrates such as PMMA, which in turn requires deposition at low or even room temperature. To meet this end, the deposition of Ta$_2$O$_5$ films by means of (dual) ion beam deposition at room temperature on Si, glass and plastic substrates has been investigated. A tantalum target was sputtered by Ar ions from a Kaufman source in the presence of oxygen, while the growing film was simultaneously bombarded with Ar or O ions from a plasma beam source. Films have been characterized with respect to their morphology, thickness, composition, bonding structure, and optical properties by techniques such as atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), variable angle spectroscopic ellipsometry (VASE) and UV-VIS spectroscopy. In a first step, the influence of the oxygen partial pressure on the properties of single ion beam sputtering was investigated. It turned out that the oxygen content in the films increased with the oxygen partial pressure until saturation at the stoichiometric value is reached. These films are extremely smooth (rms roughness < 0.15 nm), possess refractive indices of 2.1 or even higher and extinction coefficients lower than the detection limit of the ellipsometer (ca. 10^{-3}). In a second step, the influence of a densification of the growing films by simultaneous bombardment with either oxygen or argon ions was studied. The parameters investigated were the ion current density and the ion energy. A major aim of this study was to establish a correlation of the basic film properties, especially the bonding environment as revealed by XPS and FTIR, one the one hand, and the optical properties, on the other hand.

TF-ThP3 Characterization of Hafnium Nitride Films Deposited by Plasma ALD, ***N. Singh***, Oxford Instruments Plasma Technology, UK

Conductive hafnium nitride films have been deposited by plasma ald in the Oxford Instruments OpAL reactor. TEMAH was used as the hafnium source and nitrogen was provided from a remotely mounted inductively coupled plasma source. The influence of nitrogen-hydrogen and ammonia plasmas on film properties such as stoichiometry, refractive index, and resistivity is reported. Film thickness and refractive index were determined by ellipsometry. The resistivity was measured using a 4 point probe. The composition of the film was estimated from Auger electron spectroscopy and XRD was used to confirm the amorphous nature of the film. Depending on the plasma composition, the growth per cycle was in the range 0.7 - 1.5 Å/cycle and the refractive index varied from 1.4 - 2.3. The minimum measurable resistivity of the films was 5 μ Ω cm. Hydrogen plasma has signifcant effect on the conductivity of the deposited iflms compared to nitrogen plasma. The thickness of the films remained unchanged when left exposed to ambient air.

TF-ThP4 Al-doped ZnO (AZO) Films Deposited by Gas Flow Sputtering for Transparent Conductive Thin Films, ***H. Takeda***, Aoyama Gakuin University, Japan, *Y. Iwabuchi, M. Yoshikawa*, Bridgestone Corporation, Japan, *Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Al-doped ZnO (AZO) has been attracted much attention as one of alternative materials to Sn-doped In$_2$O$_3$ (ITO) films. Recently, there have been strong demand for high deposition rate with stable discharge and low cost deposition systems for the various commercial applications. Gas Flow Sputtering (GFS) has two important features. The one is the possibility for very high deposition rate because of using an intense hollow cathode discharge and a large amount of sputtering gas (Ar) flow. Another is stability of the reactive sputtering process with the variation in reactive gas (O$_2$) flow. Reactive sputtering is usually highly nonlinear processes for the conventional glow discharge sputtering because of the poisonings of the target surface. In the case of GFS, a large amount of Ar gas flows from the faced targets to the substrate preventing the oxidation of the target surface. AZO films were deposited by GFS on alkali-free glass (corning, #1737) without heating using two Zn-Al alloy targets (Al: 1.5 wt.%). For all the depositions, Ar gas flow and sputtering power were fixed at 1.0 SLM and 1500 W, respectively. O$_2$ flow was controlled from 0 to 10 sccm. The crystal structure was analyzed by X-ray diffraction (XRD). The electrical and optical properties were measured by van der pauw method and UV-IR spectroscopy, respectively. With increasing O$_2$, the intensity of an XRD peak of Zn metal decreased. On the other hand, ZnO XRD peaks appeared from O$_2$ flow of 6 sccm. All AZO films deposited over 6 sccm of O$_2$ exhibited a strong c-axis preferred orientation perpendicular to the substrate surface. Deposition rate was about 70 nm/min. At O$_2$ gas flow of 6 sccm, the AZO film showed the lowest resistivity of 9.82×10^{-4} Ω cm, Hall mobility of 10 cm^2/V s, carrier density of 5.48×10^{20} /cm^3.

TF-ThP5 Annealing and Manganese Activated Electroluminescent Characteristics of Thin Film Gallium Oxide, *J.H. Heo*, ***J.H. Kim***, Chungbuk National University, Korea

Post deposition annealing and alternating current electroluminescence of thin film gallium oxide doped with manganese (Ga$_2$O$_3$:Mn) have been studied. The Ga$_2$O$_3$:Mn films were prepared at room temperature by radio frequency planar magnetron sputtering from a 2 mol% Mn-doped Ga$_2$O$_3$ target in an oxygen-argon mixture atmosphere. The as-deposited Ga$_2$O$_3$:Mn films had an amorphous structure. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses indicated that the Ga$_2$O$_3$:Mn films began to crystallize into a monoclinic β-Ga$_2$O$_3$ phase by the post-deposition anneal at 800°C. The crystallinity of the films was continuously improved as the annealing temperature increased up to 1200°C. The polycrystalline structure was uniformly developed throughout the film by the anneal. The half-stack alternating-current thin-film electroluminescent (ACTFEL) devices were constructed using an inverted single-insulating structure, indium tin oxide (ITO)/Ga$_2$O$_3$:Mn/lead zirconate titanate (PZT)/Au on alumina (Al$_2$O$_3$) substrates. The fabricated ACTFEL devices exhibited an emission peak at around 507 nm in the green range and it was accounted for by the 3d-3d intrashell transition from the $^4T_1$ excited state level to the $^6A_1$ ground-state in divalent Mn ion. The color coordinates of the emission were x=0.197 and y=0.623 in the CIE chromaticity.

TF-ThP6 Effects of Manganese Oxide-Mixed Abrasive Slurry on the Tetra-Ethyl Ortho-Silicate Oxide Chemical Mechanical Polishing for Planarization of Inter-Layer Dielectric film in the Multilevel Interconnection, ***S.-W. Park**, W.-S. Lee,* Chosun University, Korea*, Y.-J. Seo,* Daebul University, Korea*, G.-W. Choi, S.-J. Han, Y.-K. Lee*, Chosun University, Korea

One of the critical consumables in chemical mechanical polishing (CMP) is a specialized solution or slurry, which typically contains both abrasives and chemicals acting together to planarize films. The slurry designed for optimal performance should produce reasonable polish rates, acceptable polish rate selectivity with respect to the underlying layer, low surface defects after polishing, and good slurry stability. In single abrasive slurry (SAS), the solid phase consists of only one type of abrasive particle. On the other hand, mixed abrasive slurry (MAS) consists of a mixture of at least two types of abrasive particles, which can be chosen from inorganic (alumina, silica, ceria, zirconia, titania, manganese oxide, etc) or organic (polymeric resins) groups. In this work, in order to prepare the MAS, KOH-based fumed silica slurry of pH 11 with solid content of 13 % was diluted in de-ionized water (DIW) with 1:10 ratio. The manganese oxide (MnO2) abrasives particles were then added in the diluted silica slurry. The concentration of manganese oxide abrasive was varied from 1 wt% to 5 wt%. The surface quality after polishing is important issue in TEOS-oxide CMP. A surface with a very low scratch level is obtained by chemically modifying the abrasive surface. The particle size distribution of MAS as a function of mixed amount of manganese oxide abrasive particles was also observed a bimodal particle size distribution with the two peaks at mean aggregate particle sizes of 250 nm and 2250 nm. Formation of nanometer and large size particles is perhaps, the result of aggregation of modified manganese oxide particles. This is due to an interplay between the abrasive action of larger manganese oxide particles and chemical-tooth nature of the smaller silica particles surrounding the larger manganese oxide particles. The slurry composition is further optimized to allow an excellent polishing performance yielding good surface quality while maintaining high removal rate. In addition, it is anticipated that there were be few special slurry handling problems in a fabrication production environment because relatively benign chemistry is used. This work was supported by grant No. (R01-2006-000-11275-0) from the Basic Research Program of the Korea Science & Engineering Foundation and by Korea Research Foundation Grant (KRF-2006-005-J00902).

TF-ThP7 The Role of Nitrogen Composition in SiO_xN_y as Diffusion-Barrier Film Deposited by $NH_3/SiH_4/Ar$ Plasma Enhanced Chemical Vapor Depositon, ***P. Thuy**, J.H. Lee, I.K. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

For the next generation display devices, flexible display panels formed on plastic substrates are considered and one of the important issues in the flexible displays is the formation of transparent diffusion barrier on the plastic substrates or on the devices which prevents the permeation of water and oxygen to the device. In this study, SiO_xN_y thin films were deposited by plasma enhanced chemical vapor deposition (PECVD) using $SiH_4/NH_3/Ar$ at low temperature (temperature < 50°C) and with biasing the substrate and the effect of substrate biasing and gas mixture on the film properties as a water vapor permeation barrier was investigated. The result showed that with the R ratios ($R=[NH_3]/([NH_3]+[SiH_4])$ from 0.4 to 0.6, nitrogen composition in the film was the highest and the roughness of the film was the lowest. Also, the water vapor transmission rate was $\leq 10^{-3}$ mg/(m^2/day). Consequently, these SiO_xN_y thin films were suitable as diffusion barriers on glass or polymer materials. In this presentation, more detailed material properties of SiO_xN_y thin films measured as a function of bias voltage and gas combination will be discussed.

TF-ThP8 Low-Temperature Formation of Polycrystalline Silicon Thin Films via Enhanced Aluminum-Induced Crystallization, ***F.W. DelRio**, J. Lai, T.-J. King Liu, R. Maboudian*, University of California Berkeley

In the manufacture of very large scale integrated circuits and microelectromechanical systems, polycrystalline silicon (polysilicon) thin films are typically formed directly by low-pressure chemical vapor deposition at temperatures above 600 °C, using silane as the precursor gas. Such a high process temperature makes this approach unsuitable for formation of polysilicon films on low-cost glass substrates and on substrates with completed CMOS integrated circuits. To lower the thermal budget, aluminum-induced crystallization (AIC) can be used to crystallize an amorphous silicon (a-Si) film deposited at low temperature. The formation of polysilicon by AIC of non-hydrogenated a-Si relies heavily on the layer exchange of the adjacent Si and Al films. Several factors affect the exchange of the Al and Si layers, and consequently, have an impact on the characteristics of the polysilicon film. In this paper, we study the effect of silicon doping on AIC of non-hydrogenated a-Si. In particular, Al-2%Si is examined, which is commonly used in microelectronics to prevent junction spiking, hillocks, and electromigration. A series of Al-2%Si/a-Si samples are prepared in a sputtering system with multiple process chambers and annealed in vacuum at temperatures in the range of 250 to 375 °C. The silicon doping is found to enhance the crystallization process, thereby reducing the initial crystallization temperature by ~50 °C. The enhancement is attributed to the presence of Si precipitates in the Al-2%Si film, which act as nucleation sites for Si grain growth. As with the Al/a-Si system, adjacent Al-2%Si and a-Si films undergo a layer exchange during isothermal annealing, resulting in a continuous polycrystalline silicon film with good physical and electrical properties. The observed decrease in the Si_{2p} binding energy is consistent with p-type doping of the Si layer, attributed to the presence of Al in the crystallized film. Assuming an Arrhenius-type behavior for the crystallization, the activation energy for the process is found to be 0.97±0.09 eV. This value is in good agreement with the activation energy for Si diffusion in evaporated Al films, indicating that the crystallization is a diffusion-limited process.

TF-ThP10 Thermally Stable Ag Thin Film Structure Modified with Very Thin Al Layers, ***M. Kawamura**, Y. Inami, Y. Abe, K. Sasaki*, Kitami Institute of Technology, Japan

Improvements of thermal stability of Ag thin films, featured with the lowest resistivity among all metals, have been attempted. Especially, Ag thin films on dielectric oxide layers are expected for metallization materials in future electronic devices if the improvement is achieved. One of the common ways is alloying the Ag films, but it is difficult to preserve its low resistivity due to impurity scattering effect of electrons in some cases. We show a result of structural modification, where very thin Al layers (about 1 or 3 nm of thickness) were introduced at top and/or bottom of the Ag, namely Al/Ag/Al, Ag/Al and Al/Ag structures. The Al/Ag/Al structure showed excellent stability on surface morphology and electrical resistivity even after annealing at 600^{o}C in vacuum. It is considered that the deposited thin Al layers changed into thin Al oxide layers and resulted in capping (and/or passivation) of Ag film and better adhesion with oxide substrate. The resistivity of the film was also as low as that of bulk Ag. The Al layer at the top of Ag film showed better result than that at the bottom. Therefore, it is found that inhibition of surface diffusion of Ag films is more important to prevent agglomeration of Ag thin films. Consequently, it is found that the structural modification is very useful to obtain thermally stable Ag thin films without agglomeration even after annealing at 600^{o}C.

TF-ThP11 Transmission Infrared Characterization of Titanium Oxide Thin Films Deposited by Atomic Layer Deposition, ***B.-C. Kang***, Sungkyunkwan University, Rep. of Korea

Metal oxide thin films have a number of perspective applications in microelectronics and sensor technology. However, there is not enough mechanistic understanding of growth chemistry during film deposition process, especially atomic layer deposition (ALD) process. We have constructed a simple ALD reactor which enables transmission infrared spectroscopy to be performed in situ on a layer-by-layer basis. In this study, ALD of TiO_2 was carried out using alternating exposures of titanium isopropoxide ($Ti(O^iPr)_4$) and water (H_2O), separated by an inert gas (e.g., N_2) purge. In situ transmission Fourier transform infrared (FTIR) spectroscopy was used to monitor the sequential surface chemistry during the $Ti(O^iPr)_4$ and H_2O exposures during ALD reaction onto the Si(100) surface. The FTIR spectra showed the growth of TiO_2 bulk vibrational modes versus number of ALD cycles. Also ex situ x-ray photoelectron spectroscopy, scanning electron microscopy and transmission electron microscopy were used to investigate the composition and detail structure of the deposited TiO_2 thin film on the Si(100) substrate.

TF-ThP12 Fabrication of CdS-based Visible Light Photocatalyst by the Use of Ammonia-Free Chemical Bath Deposition Technique, ***S. Biswas**, M.F. Hossain, T. Takahashi,* University of Toyama, Japan*, Y. Kubota,* University of Yokohama City, Japan*, A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

In the recent years, utilization of a second semiconductor of lower band-gap as a sensitizer to TiO $_2$ attracted lot of attention as an emerging technique for preparation of visible light photocatalyst. CdS is one of the effective low band semiconductors which can be used as a sensitizer to TiO_2. However, the preparation of CdS layer by popular conventional chemical bath deposition (CBD) technique with ammonia as a complexing agent create environmental problem as large scale production causes employment of large amounts of ammonia, which is toxic, highly volatile and harmful for the environment. In this present study CdS thin films were deposited on glass substrate by ammonia free chemical bath deposition technique with Sodium citrate as a substitute to ammonia. After deposition, all the samples were annealed at 400 °C in high vacuum of 5 x 10 $^{-5}$ Pa for 30 min. On the top of CdS layers TiO_2 thin films were deposited by dc magnetron sputtering technique with using a mask to leave exposed CdS surface. Different samples were prepared with various amount of thiouria content for the preparation of CdS layer. The CdS thin film prepared by ammonia free recipe shows highly oriented crystallographic structure. The optical property of the CdS thin film exhibits higher red shift in compare to CdS prepared by conventional technique. Different amount of red shift has been observed with different thiouria concentrations. The photocatalytic activity was measured by decomposition of Methanol separately in UV-Vis and visible light. The surface morphology of the CdS and TiO$_2$ surface was studied by field emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM). The result is attributed to the crystallographic structure and microstructure of both CdS and TiO$_2$ layers.

TF-ThP13 Study of Sol-Gel Derived TiO$_2$ Photoelectrode for the Fabrication of Low Cost Dye-Sensitized Solar Cells, *M.F. Hossain, S. Biswas,* ***T. Takahashi***, University of Toyama, Japan, *Y. Kubota*, University of Yokohama City, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

Dye sensitized solar cells (DSCs) are regarded as a low cost alternative to conventional p-n junction solar cell devices. The high light-to-energy conversion efficiencies achieved with DSCs may be attributed to the nano-porous TiO$_2$ electrode. Among the various techniques for the preparation of TiO$_2$ 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, and also it is a low temperature process. In our study, the titanium dioxide porous thin film electrodes were deposited on SnO$_2$: F coated glass slides by sol-gel technique; where, tetrabutylorthotitanate was used as a precursor and was hydrolyzed in a water/alcohol/amine mixture. Polyethylene glycol (PEG), with different concentrations, was added to the coating solution as a structure-directing agent, and the films thus prepared were transparent, crack free. In this present investigation, titanium dioxide thin films were prepared with different PEG concentrations and with different numbers (2-8) of coatings. The surface morphology of the films has been observed by atomic force microscope (AFM) and field emission scanning electron microscope (FE-SEM). The morphology of porous TiO$_2$ thin films strongly depends on the concentration of the template (PEG). The decomposition of PEG during high temperature treating is considered to be responsible for the generation of porous structure in the films as compared with TiO$_2$ film without addition of the polymer. It was revealed from optical study that the dye absorption increases with the increase of PEG concentration. Incident photon-to-current efficiency (IPCE) 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 of TiO$_2$ films deposited with different PEG concentrations is discussed with the analysis of different microstructure of the TiO$_2$ thin films and the corresponding dye-incorporation.

TF-ThP14 Optimization of Sputter-Deposited TiO$_2$ Photo-Electrode for Dye-Sensitized Solar Cell, ***M.F. Hossain***, *S. Biswas, T. Takahashi*, University of Toyama, Japan, *Y. Kubota*, University of Yokohama City, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

Dye-sensitized solar cells (DSCs) have been under investigation for the past decade due to their attractive features such as high energy conversion efficiency and low production costs. The high light-to-energy conversion efficiencies achieved with DSCs may be attributed to the nano-porous TiO$_2$ electrode. Reactive magnetron sputtering is a very promising technique for large-area uniform coating of TiO$_2$ thin film and it has potential to control the crystallographic phase and micro-structure through the process of modification of different sputtering parameters. In this present study effort has been made to prepare low cost DSCs with sputter-deposited TiO$_2$ electrode. Nano-porous TiO$_2$ thin films were successfully deposited on SnO$_2$:F substrate by facing target reactive magnetron sputtering deposition technique with different substrate temperatures ranging from room temperature to 400° C. Low cost chlorophyllin based-dye was used along with carbon paste electrodes (CPEs) on SnO$_2$:F glass as a counter electrode. Incident photon-to-current efficiency (IPCE) was calculated for all the solar cells with different TiO$_2$ thin films to evaluate the economic viability of this technique. The amount of dye incorporation was found to be highly dependent on the microstructure and the thickness of the film, as apparent from optical measurements. The variation of photoelectric conversion efficiency of the solar cells with different TiO$_2$ films deposited at different substrate temperatures is discussed with the analysis of different microstructure of the TiO$_2$ thin films and the corresponding dye-incorporation.

TF-ThP15 Micro Structure Control of RuO2 Nanoparticle Deposition on CNTs by Cyclic Voltammetry Method, ***H.-M. Wu***, Chinese Culture University, Taiwan, *W.-T. Hong*, Institute of Materials Science and Nanotechnology, Taiwan, *L.-C. Chen*, National Taiwan University

The deposition and surface morphology of RuO2 on carbon nanotubes (CNTs) are crucial for the optimal capacitive performance of RuO2/CNTs composite supercapacitors. We investigate the effect of annealing and pulse voltage control on the microstructure of RuO2 nanoparticles during cyclic voltammetry deposition. The results have shown that the capacitance RuO2/CNTs was remarkably achieved to 225 mF/cm2 after annealed at 200? for 2 hours, and 125 mF/cm2 by applying 2 sec on time/ 5 sec off time pulse voltage for half hour, at scan rate 50 mv/sec. The micro texture of RuO2 on CNTs surface was found strongly affected by deposition condition and play a key rule of the capacitive performance.

TF-ThP16 Porosity Analysis on Supported Thin Nanoporous Films, ***K.J. Chao***, National Tsinghua University, Taiwan

Ordered nanoporous materials synthesized through surfactant templating exhibit channel structures of amorphous silicate or oxide framework, uniform apertures in the range of 2–30 nm and large surface area of ~1000 m2/g. Their intrachannel void domain provides the confined space to accommodate nanostructured molecules and clusters, and the hydroxyl groups on the intrachannel surface can be chemically modified through silynation. The applications of this type of nanoporous films are closely associated with their pore properties such as pore size and porosity as well as hydrophobicity of intrapore surface. The dielectric constant of nanoporous silica films was reported to decrease with porosity. Gas transport of these films was found to be somewhat affected by their pore size distribution. Furthermore, the uniform thickness and proper density of the nanoporous coating play key roles in its anti-reflection of light. The film texture of supported thin films was found to be affected by substrate. As those films and their substrates usually appear together in application, it is desirable to perform the characterization with on-substrate thin films instead of the films detached from their substrates. In this paper, three pore characterization techniques and their application on supported silica thin films are discussed. The porosity of nanoporous films on flat and dense substrates, including glass and silicon wafer, has been estimated from refractive index obtained by ellipsometric porosimetry and from film density and thickness obtained by specular X-ray reflectivity(XRR). After removal of organic template, such as nonionic P123 Pluronic block copolymer (EO20-PO70-EO20) and cationic surfactant CTAB (C16H33N(CH3)3Br, the intrachannel surface of nanoporous silica is rich in hydrophilic silanol groups, which can absorb water easily. The water absorbency makes the nanoporous silica difficult to maintain a constant density and low dielectric constant, especially at relative humidity > 25 %. Therefore, it is better to perform the XRR under low humidity using an in-situ sample cell and to use the film as a low dielectric layer after hydrophobic modification. To elucidate the relationship between porosity and pore size distribution, the physical adsorption of krypton on dehydrated samples has been measured, and this technique is performed in the absence of water uptake on the hydrophilic nanoporous materials.

TF-ThP17 Silicon Carbonitrides: On the Attainability of Stable Compounds with High Nitrogen Content, ***M. Bruns***, Forschungszentrum Karlsruhe, Germany, *M. Rudolphi, H. Baumann*, Frankfurt University, Germany, *U. Geckle*, Forschungszentrum Karlsruhe GmbH, Germany

During the last decade great efforts have been made to synthesize pure Si-C-N compounds using various precursor based techniques. These still ongoing activities were mainly stimulated by the expected attainability of materials combining the properties of silicon carbide and silicon nitride. However, most of the approaches result in compounds of deficient nitrogen content and considerable hydrogen and oxygen content, respectively. In contrast, high-purity thin films with tailored elemental composition can be achieved directly from the elements using either RF magnetron sputtering, ion implantation or the combination of both methods. In the latter cases, severalfold implantation at different energies calculated from Monte-Carlo-simulations is necessary in order to synthesize layers with homogeneous element depth-distribution up to the surface. The availability of this powerful preparation tool motivated us to study the ternary Si-C-N phase diagram in more detail. Therefore, the main stoichiometry-defining parameters for sputtering (Si/C target area ratio, N partial pressure, substrate temperature) and ion implantation (energy and fluence) have been varied systematically in order to attain a chosen composition. The chemical composition of the Si-C-N films was characterized by means of X-ray photoelectron spectroscopy (XPS). In addition, Auger electron spectroscopy (AES), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy were used to achieve a comprehensive characterization. For quantification XPS and AES data were calibrated with absolute concentration values from non-Rutherford backscattering spectrometry (n-RBS). Resonant nuclear reaction analysis (NRRA) provides non-destructive depth profiles of ^{15}N. The morphology after subsequent annealing was studied by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM).

As one prominent result the N content of 57.4 at.% required for the formation of Si-C-N compounds on the tie line Si$_3$N$_4$ - C$_3$N$_4$ cannot be reached for Si/C ratios ≤ 1, whereas stoichiometric Si$_2$CN$_4$ can be easily achieved in a reproducible manner. Obviously the compound formation does not follow a simple Si by C substitution. In conclusion these results might give reason to speculate on the attainability of pure C_3N_4.

TF-ThP18 New Method to Correlate Crystalline Orientation and Sputtering rate of Tantalum, ***C.-F. Lo***, Praxair Surface Technologies - MRC

Normally, higher target sputtering rates contribute to higher film deposition rates, which result in increased throughput. Optimizing the cathode design of sputtering tool and the sputtering parameters are common ways to increase film deposition rate. Controlling the grain orientation of the sputtered material is another possible approach to increase the deposition rate. In order to find the desired orientation for higher sputtering rates, the correlation between crystalline orientation and sputtering rate must be identified. In the past, single crystals were used to correlate the crystalline orientation and sputtering rate. This technique was time-consuming regarding sample preparation and limitations on material availability. The new method uses Electron Backscatter Diffraction (EBSD) to identify the orientation of the individual grains on a polycrystalline material prior to being sputtered. By measuring the change in eroded depth of each grain as a function of sputtering kWh, the sputtering rate is obtained, In order to gather higher grain population and ensure the eroded depth of the individual grains are measurable by a height gauge, the grain size diameter is controlled in the range of 3mm to 20mm. This study used a 4 inch diameter by 0,25 inch thickness polycrystalline Tantalum as a test sample to correlate the grain orientation and sputtering rate. By applying 1 kW power with 10 mtorr Ar pressure, the eroded depths of the individual grains at the erosion zone were measured at intervals of 5 kWh. The results showed that the (111) grain orientation has the lowest erosion rate, while the orientations with higher indices tend to be eroded faster. This study demonstrated that the relationship of crystalline orientation to sputtering rate can be easily established by sputtering polycrystalline materials with the assistance of EBSD to pre- identify the orientation of the individual grains. Copyright 2007. Praxair Surface Technologies. All rights reserved.

TF-ThP19 Combinatorial Thin Film Synthesis of Cerium Doped Lutetium Silicate (Lu2SiO5) Scintillation Materials, ***J.D. Peak****, C.L. Melcher, P.D. Rack*, University of Tennessee

Positron Emission Tomography (PET) is a widely employed medical imaging technique that possesses the advantage of being able to image metabolic activity. In PET imaging a patient ingests a radioactive tracer and gamma rays resulting from positron annihilation are detected by a circular array of single crystal scintillators coupled to photomultiplier tubes (PMT). Since the scintillator crystals are the first step in PET detection, their performance is of paramount importance in final image quality and resolution. Large scintillator crystals are often grown via time consuming processes such as the Czochralski and Bridgman crystal growth techniques. The search for new scintillator crystals can be limited by the time consuming nature of the crystal growth. In this work, we will illustrate the use of a combinatorial thin film synthesis process that is being used to explore new scintillator materials. The combinatorial synthesis process utilizes three individual rf magnetron sputtering sources which can be simultaneously powered to generate a wide composition space of binary or ternary systems. In this work, we have investigated cerium doped lutetium oxyorthosilicate (LSO) as it is currently the most widely used scintillator crystal in PET imaging and provides a good benchmark for our proposed approach. LSO thin films with a gradient of cerium doping have been deposited to investigate the effects of cerium concentration and to compare the thin film properties to those of bulk LSO crystals. We have found that the emission spectra of the thin film materials have similar characteristics compared to the bulk crystals, and the emission intensity changes with the cerium concentration. Cerium doped lutetium-silicon oxide gradients have also been grown. X-ray diffraction measurements have been correlated to the equilibrium phase diagram, and the intensity of the luminescence emission spectra have been correlated with the corresponding phases of the lutetium-silicon system. In this presentation, we will discuss the combinatorial thin film synthesis process, and will correlate the observed structural, morphological, and chemical properties of the thin films to the measured optical properties.

TF-ThP20 Electrochoromic Properties of Mg-doped Nickel Oxide Films Deposited by rf Magnetron Sputtering, ***H. Sugawara***, Aoyama Gakuin University, Japan, *I. Yamamoto,* Nissan Motor Co., Ltd., Japan, *Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Electrochromic devices have been expected as the one of the environmental technologies such as architectural "smart" windows which should have large potential to save energy. Ni oxide (NiO) films have been studied extensively as oxidation-coloring materials, which could be used as counter electrode of amorphous WO_3 films. Azens, et al. reported that heavy Mg dopings (atomic ratio of Mg/ (Ni+Mg): 44.4 %) on NiO was effective to improve optical transmittance in visible light region of 380-600 nm at the bleached state.[1] In this study, we investigated Mg doped Ni oxide films in the wide range of the doping concentration and variation of the electrochromic properties were investigated in detail. Ni oxide flims were deposited on unheated ITO-coated glass substrates by rf magnetron sputtering using NiO-MgO targets with various Mg doping concentrations (atomic ratio of Mg/ (Ni+Mg): 0, 5, 10, 20 %). Ar was used as a sputtering gas and O_2 was introduced as a reactive gas (O_2 gas composition changes from 0 % to 100 %). Total gas pressure during the depositions was maintained at 5 Pa and the film thickness was adjusted approximately to 200 nm. Crystallinity and surface morphology of the films were analyzed by X-ray diffraction (XRD) and atomic force microscope (AFM), respectively. The composition and the chemical state of the elements were analyzed by X-ray photoelectron spectroscopy (XPS). In order to analyze the electrochromic properties, the specimens were immersed in a 1M KOH electrolyte and underwent voltammetric cycling in a three-electrode arrangement with a Pt counter electrode and an Ag/AgCl reference electrode. The Ni oxide films with the proper amount of Mg doping showed higher coloration efficiency and higher transmittance at the bleached state than Ni oxide films without doping. The optimized doping concentration in this study was 5 % for the highest electrochromic performance.

[1] A. Azems, J. Isidorsson, R. Karmhag, C. G. Granqvist, Thin Solid Films, 422 (2002) 1.

TF-ThP21 Structural Characterization and Electronic Work Function of Pt-Ru Alloy Thin Films, ***A.P. Warren****, R.M. Todi, B. Yao, K.B. Sundaram,* University of Central Florida, *K. Barmak,* Carnegie Mellon University, *K.R. Coffey*, University of Central Florida

Microstructure and the electronic work function of Pt-Ru alloy thin films spanning the compositional range from pure Pt to pure Ru were investigated. Nominally 50 nm thick films were co-sputtered from elemental targets in an ultra high vacuum chamber. X-ray reflectivity and Rutherford backscattering spectroscopy were used to determine the film thicknesses and compositions. The electronic work function of the alloy film samples was determined by analysis of the capacitance-voltage characteristics of films deposited as part of a metal-oxide-semiconductor capacitor structure and found to range from 4.8 eV for pure Ru to 5.2 eV for pure Pt. To better understand the variation in work function for the intermediate compositions, a variety of characterization techniques were used. Transmission electron microscopy was used to examine the microstructure of the samples, and to assess the grain size variation. X-ray and electron diffraction were used to identify the crystalline phases present and to evaluate the extent of crystallographic texture. A notable increase in the compositional range of the hexagonal close packed (hcp) phase was observed, suggesting a metastable extension of the hcp phase stability as compared to bulk Pt-Ru alloys. The steepest change in the electronic work function for the intermediate alloy compositions coincided with a rapid change in the c/a ratio of the hcp phase.

TF-ThP22 The Importance of the Valence State of Cu in the Formation of Re-BCO using Low Pressure dc-Magnetron Sputtering, ***K. Smet****, R. De Gryse*, University Ghent, Belgium

In this work we propose a novel way of explaining the XRD-spectra of our rotatable dc-magnetron low pressure sputtered $YBa_2Cu_3O_{7-\delta}$ and $NdBa_2Cu_3O_{7-\delta}$ thin films. As is frequently the case at low pressure sputtering our films exhibit an expanded c-axis. This expansion is usually attributed to oxygen deficiency and/or cation-disorder in the Re-$Ba_2Cu_3O_{7-\delta}$ structure. However under certain conditions (low pressure, Cu co-sputtering, lowering deposition temperature,...) the spectra of our films not only reveal an expanded c-axis but the (00n) peaks also tend to split up, whereby one peak has the theoretical c-axis value while the other shows an enlargement. This behaviour suggests the presence of two phases in our thin films. A closer look at XRD-spectra of some of our thin films suggest that a large c-axis expansion in Cu-poor conditions might be attributed to the presence of $Y_2Ba_2O_5$. The conditions triggering the split as well as the possible presence of $Y_2Ba_2O_5$, point to the importance of the energy and/or valence state of the Cu atoms during the deposition process. Therefore in this paper we explore a possible explanation for the peak splitting in the XRD-spectra of our thin films based not only on the abundance of the Cu atoms at the substrate but also on their energy or valence state.

TF-ThP23 Chemical Mechanical Polishing Characteristics of ITO Thin Film Prepared by RF Magnetron Sputtering, *G.-W. Choi,* ***W.-S. Lee***, Chosun University, Korea, *Y.-J. Seo,* Daebul University, Korea, *S.-W. Park, S.-J. Han*, Chosun University, Korea

Indium tin oxide (ITO) thin films have attracted intensive interest because of their unique properties of good conductivity, high optical transmittance over the visible region and easy patterning ability. Thin films of ITO have found many applications in anti-static coatings, thermal heater, solar cells, flat panel displays, liquid crystal displays, electroluminescent devices, sensors and organic light-emitting diodes. ITO thin film is generally fabricated by various methods such as spray, CVD, evaporation, electron gun deposition, direct current electroplating, high frequency sputtering, and reactive sputtering. In this paper, ITO films were grown on glass substrate by RF magnetron sputtering method. To achieve high transmittance and low resistivity, we examined the various film deposition conditions such as substrate temperature, working pressure, annealing temperature, and deposition time. Carrier concentration and carrier mobility of ITO thin films were measured, the transmittance of them also was done. As O2 flow rate and substrate temperature increased, the transmittance of ITO thin film increased because ITO particles formed coarse and good crystalline. Next, in order to improve the surface quality of ITO thin film, we performed the chemical mechanical polishing (CMP) by change of process parameters, and compared the electrical and optical properties of the polished ITO thin film. The thickness of ITO films was measured by ellipsometer. The electrical resistivity was measured by using the four-point probe method. . The best conditions to polish the surface of ITO thin film (which was used as the anode) smoothly were as follows: platen speed, head speed, polishing time, and slurry flow rate were 60 rpm, 60 rpm, 60 sec, and 60 ml/min, respectively. AFM analysis shows that the thin film of ITO was polished smoothly. This work was supported by a Korea Research Foundation grant (KRF-2006-005-J00902).

TF-ThP24 Effect of Plasma Induced Substrate Temperature Rise on AZO Thin Film Properties in ICP Assisted Bipolar Pulsed dc Magnetron Sputtering, ***W.K. Yang***, *J.H. Joo*, Kunsan National University, Korea

To deposit Al doped Zinc oxide film on polymer substrate at room temperature, internal inductively coupled plasma assisted bipolar pulsed dc magnetron sputtering system was used. Pulse frequency was from 50kHz to 250kHz and duty ratio was between 60 - 90%. ICP was generated by a 2MHz rf generator through an L-type matching network and a ceramic shielded Cu antenna. High density plasma could heat the temperature sensitive polymer by high bombarding ion and electron energy flux. The average electron density and temperature in this experiment was 10^{11} #/cm^3 and 2 - 5 eV by Langmuir probe measurements. The distance between the magnetron sputtering target and substrate must be optimized not to give excessive heat flux to the substrate. Variable frequency pulsed dc plasmas showed wide range of shapes at the same gas pressure and power level. Up to 150kHz, the plasma region was extended as the frequency was increased. At higher frequency than 150kHz, the length of plasmas remained same. We measured the transient temperature changes in the plasma region at four different positions and will discuss the correlations between the pulse frequency and transient temperature rise of a polymer substrate.

TF-ThP25 Effect Of Sodium Addition On Cu-Poor CIGS2 Thin Film Solar Cells, ***P.S. Vasekar***, *N.G. Dhere*, Florida Solar Energy Center

Copper-Indium-Gallium Sulfide (CIGS2) is a chalcopyrite material with a near-optimum band gap of 1.5 eV. Recent research in the CIGS2 thin film photovoltaic community is directed towards thinner films because the availability and cost of Indium are limiting factors. The required amounts of metals can be lowered by using thinner films. Initially, small sized grains are formed during the film growth. With continuing growth to larger thicknesses, more favorably oriented grains grow faster at the expense of others and coalesce to form compactly packed large-grain morphology. Hence certain thickness of a thin film is necessary so that the grains start coalescing. The solar cell performance in smaller grained chalcopyrite absorber deteriorates due to detrimental effects of the larger fraction of grain boundaries. It is essential to hasten the grain growth through coalescence to retain high-quality properties even in thinner films. Sodium may play a vital role by enhancing the atomic mobility and improving the coalescence even in thinner films. It will be interesting to study if sodium can play a role in Copper-poor CIGS2 absorbers. In Copper-rich CIGS2 precursors, increased mobility and consequently absorber phase formation is obtained due to pseudo-binary phase region. Hence Sodium may not play a vital role in Copper-rich precursors. Also Copper-rich precursors for this purpose are prepared with 40 percent excess Copper. After sulfurization, the absorber film is etched to remove the excess Copper. This may or may not lead to an exact stoichiometric Cu/In+Ga ratio of 0.92 for the absorber in addition making the film rough. Copper-poor absorber has a comparatively smooth film and better morphology after etching. This work represents a study of morphology and device properties of CIGS2 thin films with Copper-poor absorbers after Sodium is introduced on the substrate in the form of Sodium Fluoride before sputtering Copper, Indium and Gallium.

TF-ThP26 Surface Modification of Polytetrafluoroethylene by Copper Ion Implantation, ***K.-W. Weng***, Mingdao University, Taiwan, *S. Han*, National Taichung Institute of Technology, Taiwan, *Y.-C. Chen*, National Chung Hsing University, Taiwan, *D.-Y. Wang*, Mingdao University, Taiwan

Polytetrafluorethylene (PTFE) was implanted copper by a hybrid metal plasma ion implantation (MPII) with varying ion dose. X-ray photoelectron spectroscopy (XPS) was used for the characterization of chemical structures in the ion-implanted assembly, while scanning electron microscopy (SEM) was used for the characterization of morphology. Five chemical bonds, CF$_3$, CF$_2$, CF, C-O, and elemental carbon bonds, were observed on the surface of the ion-implanted assembly. Numerous microfibers were observed on the ion-irradiated surface. Water contact angle of the ion-implanted samples increased gradually with increasing ion dose, and reached a maximum value of 103.5^0 on the surface of the sample implanted with ion dose of 3×10^{17} ion/cm^2. The decrease of microhardness at high ion dose was resulted, accounted for radiation damage. Wear resistance and resistance were also discussed in the copper modified surface.

Surface Science

Room: 611 - Session SS2+EM+TF-FrM

Organic Films II: Semiconductors and C$_{60}$

Moderator: J.E. Reutt-Robey, University of Maryland

8:00am **SS2+EM+TF-FrM1 Unravelling Molecular Contrast Formation Obtained by NC-AFM on Titania**, ***R. Bechstein***, *J. Schütte, P. Rahe, A. Kühnle*, University of Osnabrueck, Germany

The (110) surface of TiO$_2$ constitutes an interesting model substrate for molecular adsorption studies due to its importance in applications such as organic solar cells and light emitting diodes. Several experiments revealed that organic molecules can be anchored to the surface through carboxylic groups both under ultra-high vacuum conditions[1] as well as from solution.[2] We investigated a perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide (PTCDI) derivative without carboxylic anchor groups by non-contact atomic force microscopy (NC-AFM) under ultra-high vacuum conditions. The molecules were deposited at room temperature onto TiO$_2$ (110) by evaporation from a Knudsen cell. We achieved true atomic resolution on the bare substrate as well as submolecular resolution on individual molecules. The molecules were observed to align along the [001] direction with the ability to move along this direction. They are found to be homogeneously distributed on the terraces without any tendency to cluster at step edges even at elevated temperature. Two molecular contrast modes are clearly distinguished. In one mode the molecules appear cloudy and are observed to be centred on top of bright rows. In the other mode the molecules are imaged with a dark bone-shaped centre and a bright rim, centred on top of dark rows. Scanning tunnelling microscopy measurements allow to conclude that the molecules are always centred on top of the bridging oxygen rows, demonstrating a contrast reversal between the two NC-AFM imaging modes. By comparing these results with previous NC-AFM studies,[3] we can assign the two modes to positive and negative terminated tips showing that in NC-AFM imaging strongly depends on the tip termination.

[1] A. Sasahara, H. Uetsuka, and H. Onishi, J. Phys. Chem. B 105, 1 (2001)

[2] C. L. Pang, T.-a. Ishibashi, and H. Onishi, Jpn. J. Appl. Phys. 44, 5438 (2005)

[3] J. V. Lauritsen, et al., Nanotechnology 17(14), 3436 (2006).

8:20am **SS2+EM+TF-FrM2 Characterization of Para-Sexiphenyl Thin Films Grown on KCl Substrates**, ***A. Andreev,*** Univ. of Leoben, Austria, *A. Montaigne,* Univ. Linz, Austria, *T. Haber,* Graz Univ. of Tech., Austria, *A. Kadashchuk,* National Academy of Sci. of Ukraine, *G. Hlawacek,* Univ. of Leoben, Austria, *D.-M. Smilgies,* Cornell Univ., *R. Resel, A. Winkler,* Graz Univ. of Tech., Austria, *H. Sitter, N.S. Sariciftci,* Univ. Linz, Austria, *C. Teichert*, Univ. of Leoben, Austria

Para-sexiphenyl (6P) films grown on mica(001) and KCl(001) substrates show large morphological and optical anisotropy, which makes them attractive for nano-scale photonic devices. In this work we use Atomic Force Microscopy (AFM), electron microscopy, x-Ray diffraction (XRD), and photoluminescence (PL) in order to find the parameters controlling film morphology, structure, and quality. It is shown that the initial growth stage of 6P on KCl(001) is characterized by the formation of µm-long needles, generating a rectangular network in accordance with the substrate surface symmetry. With increasing coverage, terraced mounds composed of upright standing molecules developing between the needles are observed and subsequent growth is characterized by a coexistence of both features. It is demonstrated that both features grow directly on the substrate surface, i.e., there is no wetting layer during the deposition of 6P on KCl(001). It is also found that both needles and terraced mounds grown on KCl(001) are single crystalline, in contrast to mica(001), where different oriented 6P domains are formed inside of the chains. PL studies have shown that, as in 6P films on mica, the emission spectra contain two different components - a conventional structured spectrum due to intrinsic excitons and a broad red-shifted band ascribed to some kind of defects. The latter band most clearly can be distinguished in delayed fluorescence spectra of the studied films. It is remarkable, however, that the relative intensity of the defect band was much weaker in the films grown on KCl substrates comparing to that on mica, which corresponds well with results of morphological and structural investigations. This finding confirms the high quality of the films and implies that the defect band is rather sensitive to the structure and morphology of the films. We also discuss a correlation between growth condition of 6P and a relative intensity of the defect PL band.

8:40am **SS2+EM+TF-FrM3 A Nanoengineering Approach to Regulate The Lateral Heterogeneity of Self-Assembled Monolayers***, J.-J. Yu, Y.H. Tan, X. Li,* University of California, Davis*, P.K. Kuo,* Wayne State University*, **G.-Y. Liu***, University of California, Davis **INVITED**

Using a scanning probe lithography method known as nanografting in conjunction with knowledge of self-assembly chemistry, regulation of the heterogeneity of self-assembled monolayers (SAMs) is demonstrated. It is known that phase segregated domains would form if SAMs are grown from thiol solutions of mixed compositions. The size and distribution of these domains depend on the interplay between reaction kinetics and dynamics, which can be regulated by varying the reaction conditions including concentration, temperature and reaction time. The reaction mechanism in nanografting, however, differs significantly from self-assembly in the conventional mix-and-grow methods. The spatial confinement in nanografting bypasses the lying-down to standing up transition process, and thus leads to a much fast kinetics. Knowledge of the reaction pathways enables development of methods for shifting the interplay between the kinetics and thermodynamics in SAM formation, and thus the heterogeneity of mixed SAMs. By varying fabrication parameters such as shaving speed, and reaction conditions such as concentration and ratio of the components, the lateral heterogeneity can be adjusted ranging from near molecular mixing to segregated domains of several to tens of nanometers.

9:20am **SS2+EM+TF-FrM5 Mechanistic Aspects of Organic Thin Film Growth from Energetic Sources: Insights from Experiment and Molecular Dynamics Simulations***, **J.E. Goose**, A.S. Killampalli, P. Clancy, J.R. Engstrom*, Cornell University

We have used a combination of experiments and molecular dynamics simulations to investigate the fundamental molecular mechanisms contributing to the evolution and final morphology of thin films of pentacene deposited at hyperthermal incident kinetic energies (E$_i$ = 1-10 eV). Experimentally, using supersonic molecular beam scattering techniques and atomic force microscopy we have characterized the adsorption probability as a function of both E$_i$ and the angle of incidence (θ$_i$). Interestingly, we observe differences in the dynamics of adsorption for pentacene interacting with a clean SiO$_2$ substrate (submonolayer growth) vs. a SiO$_2$ substrate covered by a pentacene thin film (multilayer growth). Specifically, for E$_i$ greater than ~ 1-2 eV, contribution of a new mechanism for pentacene adsorbing on pentacene is implicated. To determine the nature of this mechanism, we have used the non-reactive empirical MM3 potential to model the collision of pentacene molecules with a pentacene thin film using molecular dynamics. Our simulation cell consists of ca. 100 molecules, and includes an upper terrace of 4 x n unit cells, bounded by (010) step edges. Accounting for impacts both near the middle of the terrace and near the step edge, our results from simulation for the probability of adsorption compare very well with those measured experimentally. In particular, adsorption is found to decrease with increasing E$_i$, and, in general, with increasing θ$_i$. More importantly, the simulations give us insight into nature of the events that occur at high incident kinetic energies. For thermal incident kinetic energies we observe mostly simple trapping (molecular adsorption), with near unit probability. At higher E$_i$ of 1-5 eV, a significant fraction of molecules (~ 30%) are found to directly insert into the upper terrace, whereas a higher fraction (~ 90%) of molecules impacting near the step edge in this same energy regime also end up incorporating into the upper terrace. Indeed, direct molecular insertion into the pentacene crystal structure is the dominant interlayer process when both the molecule's orientation and incident angle are aligned normal to the surface, which leads to the formation of interstitials for the time scale of these simulations.

9:40am **SS2+EM+TF-FrM6 Growth of Pentacene Thin Films from a Supersonic Source: Unexpected Behavior in the Presence of Molecular Cluster Formation***, A. Amassian, S. Hong, S. Bhargava, A.R. Woll, T.W. Schroeder, A.S. Killampalli, J.D. Ferguson, J.D. Brock, G.G. Malliaras, **J.R. Engstrom***, Cornell University

We have examined the growth of pentacene thin films on SiO$_2$ using supersonic molecular beam techniques and in situ real-time synchrotron x-ray scattering. At low-to-modest rates of deposition [ca. 0.001 to 0.1 monolayer(ML)/s] we observe an abrupt transition from 2D, layer-by-layer growth to 3D, islanded growth after deposition of the first few monolayers of pentacene on SiO$_2$. At high rates of deposition (ca. 1 ML/s), however, we find persistent 2D crystal growth, and the development of a highly textured film possessing significantly flatter and smoother surface morphology than at low rates of deposition. Concomitantly, in this regime we also observe new polymorphs of pentacene, as significant changes occur in the crystalline structure of the thin films. The transition to this anomalous, yet promising growth behavior corresponds very strongly with the onset of the formation of van der Waals clusters of pentacene within the supersonic expansion. We suggest that the presence of clusters in the incident flux acts to change the dynamics of growth due to a variety of reasons which we discuss. These findings raise the distinct possibility that organic crystals may be synthesized with ultra-flat surface morphology, making them suitable for use in a number of electronics applications where the requirement for abrupt and smooth interfaces has traditionally defaulted to the use of amorphous organic thin films.

10:00am **SS2+EM+TF-FrM7 Vibrational and Structural Investigation of Ferrocene Adsorption on Au(111) Surfaces**, ***G. Pirug***, *M. Kazempoor*, Forschungszentrum Jülich, Germany, *J. Myslivecek*, Charles University in Prague, Czech Republic, *B. Voigtländer*, Forschungszentrum Jülich, Germany

The adsorption of ferrocene ($Fe(C_5H_5)_2$) on Au(111) surfaces has been studied spectroscopically applying HREELS and XPS as well as structurally by means of LEED and STM under UHV conditions. The vibrational modes observed by HREELS indicate reversible molecular adsorption of ferrocene at temperatures of about 110 K. The corresponding frequencies are not significantly shifted with respect to IR or Raman data from solution, indicating a weak adsorbate - substrate interaction. Multilayer adsorption can be distinguished from the physisorbed first layer based on the sequential appearance and relative intensity changes of vibrational modes. In the monolayer regime vibrational modes with a perpendicular dipole moment from ferrocene molecules with an upright standing molecular axis dominate, as concluded from on- and off-specular HREEL spectra applying the surface dipole selection rules. Dissociation into cyclopentadienyl ring radicals (C_5H_5) can be excluded due to the missing related vibrational losses, such as the wagging mode expected at about 760 cm^{-1}. For multilayer coverages the orientation of the condensed ferrocene molecules is no longer exclusively perpendicular to the surface which results in the appearance of additional vibrational losses. Molecular self assembly yields a well ordered surface structure as shown by topographical STM pictures and LEED pattern.

10:20am **SS2+EM+TF-FrM8 Uncovering Molecular Dewetting: Growth and Morphology of C_{60} and PTCDA on Insulators**, ***S.A. Burke***, *J.M. Mativetsky, S. Fostner, P. Grutter*, McGill University, Canada

Despite considerable interest in recent years in the properties and structural characteristics of molecular deposits for organic based devices, there has been only limited study of growth and morphology of molecular materials on insulating substrates. The majority of traditional surface science tools are significantly hindered by the use of an insulating substrate due to complications with charging and surface damage. Over the past decade, non-contact atomic force microscopy (nc-AFM) has proven a powerful surface science tool, and is increasingly being applied to molecular studies on insulators. The power of the technique lies in its ability to image in real-space with sub-angstrom resolution as well as measure structure up to the micron scale allowing for a connection between molecular scale structures and the overall growth morphologies. The nc-AFM technique, operated in UHV, has been applied to two prototypical organic semiconductors: C_{60} and PTCDA, on two well-known insulating surfaces: KBr (001) and NaCl(001). Both systems showed island growth modes with evidence for dewetting, though the resulting morphologies differ considerably. C_{60} on both of these alkali halides forms distinctive branched island shapes. A quantitative analysis of the morphology and its connection to the underlying epitaxy will be discussed. The formation of this branched morphology appears to be a dewetting process which was observed directly in a series of nc-AFM images. The energetics of this system will also be discussed in terms of annealing and deposition onto a heated substrate. PTCDA on NaCl also undergoes a dewetting process, though in a rather different manner. At low coverages, monolayer islands are observed in a highly strained c3x3 epitaxy. However, at larger coverages these single layer islands are seen to coexist with tall crystallites exhibiting the same morphology and herringbone structure as observed for PTCDA on KBr, indicating a coverage induced dewetting transition between 0.7 and 0.8 ML. The dewetting was also induced by annealing of the single layer islands yeilding molecular crystals up to several microns long with the familiar herringbone structure of the PTCDA (102) plane. Dewetting has recently been recognized in several other organic systems as a significant factor in the growth and morphology of thin films. The examples presented here may indicate that dewetting is also an important consideration in molecule-on-insulators systems as well.

10:40am **SS2+EM+TF-FrM9 STM/STS Studies of C_{60}:Pentacene Interface Formation**, ***D.B. Dougherty***, National Institute of Standards and Technology, *W. Jin, W.G. Cullen, G. Dutton, J.E. Reutt-Robey*, University of Maryland at College Park, *S.W. Robey*, National Institute of Standards and Technology

The most efficient small-molecule organic solar cells employ heterojunctions between donor and acceptor materials.[1] In order to push the performance of such devices into a regime of cost-effective power generation, it is necessary to develop a detailed understanding of organic-organic interface morphology and its relationship to electronic band alignment. We have approached this question by studying the technologically relevant[2] system of C_{60} deposited onto pentacene, using STM/STS to provide clues to the relative importance of competing intermolecular interactions. When C_{60} is deposited onto a pentacene bilayer on a Ag(111) surface,[3] STM measurements show two unique structures in the first layer. The pentacene bilayer forms a well-ordered structure on Ag(111) with the long molecular axis nearly parallel to the surface. At the lowest coverages, C_{60} forms linear chains whose direction is templated by the underlying pentacene rows, with C_{60} molecules located between rows of pentacene molecules. The details of the observed structural arrangement are related to electrostatic interactions between C_{60} and the pentacene bilayer structure. Information on local relative band alignment for these structures is measured using constant-current distance-voltage spectroscopy.[4] The local transport gap for C_{60} linear chains is 4.4±0.2 eV compared with a gap of 3.7±0.2 eV for the surrounding pentacene bilayer. The magnitudes of the gaps are influenced by local polarization energies in each structure. At higher coverage, domains of C_{60} with no discernable long range order dominate the first layer. This disorder probably arises from frustrated intermolecular interactions between the two different chemical species. The lateral interactions between C_{60} molecules (favoring hexagonal ordering) cannot be optimized simultaneously with the comparable strength interactions between C_{60} and the underlying pentacene film (favoring an oblique unit cell). *This work has been partially supported by the Dept. of Commerce through the NIST Center of Nanomanufacturing and Metrology and the NSF-funded MRSEC via DMR-05-20471.

[1] P. Peumans, J. Appl. Phys. 93, 3693 (2003).

[2] S. Yoo et al., Appl. Phys. Lett. 85, 5427 (2004).

[3] Eremtchenko et al., Phys. Rev. B 72, 115430 (2005).

[4] S.F. Alvarado, et al., Phys. Rev. Lett. 81, 1082 (1998).

11:00am **SS2+EM+TF-FrM10 Potassium Induced Long Range Superstructure on C_{60}/Ag (111) Surface**, *C.-C. Kuo*, ***W.W. Pai***, National Taiwan University

Various long range superstructures were observed for potassium (K) doped C_{60} monolayer on Ag (111) by scanning tunnelling microscopy (STM). Pristine C_{60} monolayer exhibits a bright-dim contrast in the most stable ($2\sqrt{3}\times2\sqrt{3}$)-R30 phase, whereas the molecular contrast is uniform in other metastable phases (denoted as R12 or R48 phases). Upon K doping, K segregate into compact islands at room temperature and the bright-dim contrast in the R30 phase is eliminated. Furthermore, ordered quasi-hexagonal patterns with periodicities of ~7 nm to ~40 nm appear. The ordered superstructures show distinct characteristics in each C_{60} phase. Close inspection reveals that the super lattices are not exactly hexagonal but exhibit uni-directional distortion. Therefore, the finding is perplexing as it cannot be explained by, e.g., Morie patterns. We propose that the superstructures are due to overlaying an orthorhombic one-dimensional polymerized KC_{60} phase over the hexagonal silver lattice. This is supported by high-resolution STM images showing the signature of [2+2] covalent bond formation.

11:20am **SS2+EM+TF-FrM11 Thiol-Modified Diamondoid Monolayers on Silver and Gold Studied with Near-Edge X-ray Absorption Fine Structure Spectroscopy**, ***T.M. Willey***, Lawrence Livermore National Lab., *J.D. Fabbri*, Stanford Univ., *J.R.I. Lee*, Lawrence Livermore National Lab., *P.R. Schreiner, A.A. Fokin, B.A. Tkachenko, N.A. Fokina*, Justus-Liebig Univ. Giessen, Germany, *J.E. Dahl, R.M.K. Carlson, S.G. Liu*, MolecularDiamond Tech., *T. van Buuren*, Lawrence Livermore National Lab., *N.A. Melosh*, Stanford Univ.

Higher diamondoids, hydrocarbon cages with a diamond-like structure, have evaded laboratory synthesis and have only recently been purified from petroleum sources. Initial calculations on these unique diamond-like molecules show they may have negative electron affinity, a desirable property for electron emission. Readily available adamantane, the smallest diamondoid, can be thiolated and has shown to absorb on gold with high coverage. The availability of diamantane, triamantane, and tetramantanes opens new possibilities for surface-modification as multiple sites are available for thiol or other chemical functionalization. Surface-attached diamondoids have technological possibilities as high-efficiency electron emitters, as well as crystals for diamond growth or other nanotechnological applications, and fundamental studies of the electronic and structural properties of these molecular monolayers are a necessary precursor. We have investigated the effects of thiol substitution position, polymantane order, and metal substrate on diamondoid film morphology. Using Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) we show that the orientation of the diamondoids within each type of monolayer depends highly upon these parameters. We thus demonstrate control over the assembly, and hence the surface properties, of this exciting new class of diamond-like carbon molecules.

Thin Film

Room: 602/603 - Session TF1-FrM

Thin Films for Displays and Flexible Electronics

Moderator: M.A. Creatore, Eindhoven University of Technology, The Netherlands

8:00am **TF1-FrM1 Effects of Processing Parameters on Electroluminescence of RF Magnetron Sputter Deposited ZnS: ErF$_3$**, *D.M. DeVito, A.A Argun, E.S. Law,* University of Florida*, M. Puga-Lambers, M.R. Davidson,* Microfabritech, ***P.H. Holloway***, University of Florida

ZnS:ErF$_3$ alternating current thin film electroluminescent (ACTFEL) devices were fabricated by RF plasma magnetron sputtering. In a full factorial design-of-experiment study, increasing deposition temperature, duty cycle on the doped target and sputter gas pressure all resulted in increases in the 1.55 µm near infrared (NIR) electroluminescence (EL) irradiance at 20V above threshold (B$_{20}$). An increase in the EL threshold voltage (V$_{th}$) upon increasing the duty cycle of the undoped target was also observed. Post-deposition annealing of ACTFEL devices at 425°C for 1 hr improved the NIR EL irradiance by decreasing the F concentrations in the ZnS:Er films. The origins of these effects are discussed in terms of negative ion resputtering, surface mobility of sputtered species, crystallinity, and the effects of atomic concentration upon the EL and radiative relaxation processes. A maximum irradiance, B$_{20}$, of 147 µW/cm^2 is measured for the 1.55 µm NIR EL peak from a ZnS:Er ACTFEL devices produced using a deposition temperature of 150°C, a duty cycle of 75%, an argon sputtering gas pressure of 24 mTorr and post-deposition annealing at 425°C for 1 hour in nitrogen.

8:20am **TF1-FrM2 Local Compositional Environment of Er in ZnS:ErF3 Thin Film Electroluminescent Phosphors**, ***M.R. Davidson***, University of Florida*, S. Stoupin,* Illinois Institute of Technology*, D.M. DeVito,* Oak Ridge National Laboratory*, C. Segre,* Illinois Institute of Technology*, P.H. Holloway*, University of Florida

Phosphors are wide bandgap materials that contain luminescent dopants. Excitation of the dopant can result from electron-beams (cathodoluminescence), photons (photoluminescence) or even mechanical means (piezoluminescence). We have studied the local environment of the erbium (Er3+) luminescent centers in an electroluminescent (EL) ZnS:Er phosphor. The local Er environment is critical to the efficiency and, in some cases, the emission wavelength of the phosphor. Many dopants have radiative relaxation transitions that are quantum dynamically unallowed. While these transitions may be strictly unallowed in the isolated atom, in the phosphor lattice these radiative transitions typically take place with a low probability. The excited states, therefore, must be fairly long-lived in order to allow enough time for the slow radiative transition. Defects and their associated electronic states in the vicinity of the phosphor luminescent center can act to delocalize the excited states and thus provide more effective non-radiative relaxation paths. A detailed knowledge of the local chemical and structural environment is therefore necessary in order to model the quantum efficiency of the radiative relaxation. The dependence of the local composition and order in sputter deposited thin film ZnS:ErF3 electroluminescent (EL) has been investigated using EXAFS as a function of post-deposition anneal temperature. Previous results have shown that the intensity of the EL peaks in the near infrared (1.55 µm) and visible (520 nm) both increase as the anneal temperature is increased, with the NIR intensity maximizing at an anneal temperature of 425 °C . In the as-deposited films, the entire ZnS host lattice is distorted by the presence of the Er, relative to an undoped ZnS film. The long-range crystallinity improves with increasing annealing temperature, especially for 425°C < T < 475°C, the highest annealing temperature studied. The data show that the Er atoms in the as-deposited films have a maximum of one nearest neighbor S atoms, but are surrounded predominantly by F atoms (although the presence of O atoms cannot be ruled out based on EXAFS data). Upon annealing, the spacing of the S around this complex begins to collapse and at 425°C, there is a longer range order that appears.

8:40am **TF1-FrM3 Fabrication and Characterization of Indium Zinc Oxide-Based Thin Film Transistors**, ***D.C. Paine***, Brown University **INVITED**

Active electronics implemented on cheap flexible polymer substrates offer the promise of novel display technologies, wearable electronics, large area memory, and a multitude of other, as-yet-unthought-of, applications that require low cost and high volume manufacturing. Thin film transistors (TFT's) fabricated on temperature-sensitive plastic substrates at low temperatures are the key to this technology. TFT's that use metal (In, Zn, Sn, Ga) oxide channels offer both high mobility (relative to amorphous Si) and the advantage of optical transparency in the visible regime. We report on the fabrication and performance of amorphous oxide transparent thin film transistors that use dc-magnetron sputter techniques to deposit IZO (In2O3-10wt%ZnO) at low oxygen potential (0vol%O2) for the source, drain, and gate-contact metallization and, at higher oxygen partial pressures (10 vol%O2), for the semi-conducting channel. The devices in this study were processed at room temperature except for a single 280°C PECVD deposition step to deposit a 230 nm-thick SiOx gate dielectric. The devices are optically transparent and operate in depletion mode with a threshold voltage of -5 V, mobility of 15 cm2/Vsec, an on-off ratio of >10E6 and, a sub-threshold slope of 1.2 V/decade. We show that control of oxygen in the sputter gas (0 to 30 vol %) during IZO deposition allows control of carrier density.

9:20am **TF1-FrM5 Near IR Electroluminescent Studies Of ZnS Photonic Crystal**, ***E.S. Law***, *P.H. Holloway,* University of Florida*, N. Shepherd*, North Texas State University

The effects of a photonic crystal (PC) structure on outcoupling of light from an alternating current thin film electroluminescent (ACTFEL) device are being studied. The ACTFEL device consists of a thin film of ZnS doped with erbium sputter deposited onto an aluminum-titanium-oxide (ATO) thin insulating layer on an indium-tin-oxide (ITO) transparent conducting electrode on a glass substrate. Al top electrodes are vapor deposited onto the ZnS:Er phosphor, and light is emitted through the glass substrate. ZnS:Er has strong emissions in the near IR at 1550nm, but it has been shown that much of this light is lost laterally to total internal reflection and absorption. The PC structure allows light from these lost modes to be transferred to modes that outcouple from the device. The data show that a triangular array of circles of radius and lattice spacing of 264nm and 660nm, respectively, in the ZnS:Er layer of the ACTFEL device allow coupling of horizontal modes to vertical modes. The sensitivity of this coupling to the dimensions of the PC will be reported. The PC was created with electron-beam lithography using a PMMA resist over the ZnS:Er layer of the ACTFEL device. An Ar ion etch was used to etch the triangular array of holes into the ZnS:Er layer. FOx® flowable silicon oxide was spin coated into the holes to act as the contrasting dielectric layer to the ZnS:Er layer which enables the PC effect. Finally an aluminum electrode was vapor deposited on the backside of the device. The emissions of ACTFEL devices were analyzed using an optical spectrometer. A sevenfold increase in the vertical modes of 1550nm light emission was observed from a device with a PC structure.

9:40am **TF1-FrM6 Conformal CVD of MgO from Mg(H3BNMe2BH3)2 and Water: A New Process for Dielectric Barrier Layers in Plasma Display Panels**, *Y. Yang,* ***D.Y. Kim****, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

MgO is an attractive material for use as a dielectric barrier layer: it is a refractory oxide with a high melting point (2852 °C), high dielectric constant (9.8), wide bandgap (7.2 eV), and high secondary electron emission coefficient. These properties, combined with a good resistance to plasma erosion, make it suitable for use in AC plasma display panels, with the potential to significantly lower the firing voltage. Chemical vapor deposition affords simplicity, high deposition rate, and the ability to produce conformal coatings in deep features such as cylindrical vias. However, previous efforts to deposit MgO by CVD have not been satisfactory due to low deposition rate (~ nm/min), high deposition temperature (> 400 °C), or the presence of carbon or halogen impurities. Such issues derive from the lack of a suitable Mg-containing precursor molecule. We recently developed a completely new type of Mg precursor, bis(N,N,-dimethyldiboranamido)magnesium, here termed Mg(DMDBA)2. The vapor pressure of this precursor at room temperature is remarkably high, ~ 0.8 Torr, such that no carrier gas or heated delivery lines are required. The precursor is thermally stable but reacts readily with water to produce MgO films at temperatures as low as 225 °C. The high vapor pressure of the precursor allows us to achieve extreme conformality, e.g. a completely uniform film on a trench with depth/width ratio of 35:1, or a very rapid growth, e.g. deposition rate of a few hundred nm/min, or any compromise in between. We will present the CVD kinetics and the microstructure, crystallinity, electrical, and optical properties of MgO films grown from Mg(DMDBA)2 and H2O. Films grown at T > 500 °C on Si(100) or glass substrates are crystalline with a (002) texture; films grown at T > 400 °C are columnar; and films grown a lower temperatures are dense and smooth. The refractive index is 1.69-1.72 and the dielectric constant is 9.5, both of which are very close to the values for bulk MgO. The excellent CVD process characteristics and excellent film quality makes this an attractive new means to deposit the dielectric barrier layers in PDPs.

10:00am **TF1-FrM7 Other Impurity-co-doping Effect on the Stability of Resistivity in AZO and GZO Transparent Conducting Thin Films**, ***T. Kuboi***, *Y. Honma, T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

It has been recently reported that the resistivity of Al-doped ZnO (AZO) and Ga-doped ZnO (GZO) transparent conducting thin films with a thickness below approximately 100 nm always increased when tested in heated high humidity environments. For the purpose of improving the resistivity stability in these films for use in heated moist environments, the effect of impurity-co-doping on the stability of resistivity was investigated for AZO and GZO transparent conducting thin films. The impurity (X)-co-doped AZO and GZO (AZO:X and GZO:X) transparent conducting thin films were prepared on glass substrates by dc (both with and without incorporated rf) magnetron sputtering, rf magnetron sputtering and pulsed laser deposition methods. AZO and GZO thin films co-doped with V or In were prepared with thicknesses in the range from approximately 20 to 200 nm at a temperature of 100-200ºC. The resulting thin films were investigated using micro-structural analyses such as EXAFS and TEM. The stability tests were conducted long term (up to 1000 h) in a high humidity environment (air at 90% relative humidity and 60ºC). It was found that the resistivity stability of AZO:V thin films was considerably improved by optimizing the content of co-doping V. In particular, AZO:V films with a thickness of 50 nm were stable enough to be acceptable for use in practical transparent electrode applications. In contrast, thin films with a thickness below approximately 30 nm were always unstable under the above test condition. The resistivity increase of films with a thickness below 30 nm is mainly attributable to carrier transport being dominated by the trapping of free electrons due to oxygen adsorption on the film surface rather than the grain boundary.

10:20am **TF1-FrM8 Sputtered In_2O_3 and ITO Thin Films Containing Zirconium**, ***T.A. Gessert***, National Renewable Energy Laboratory, *Y. Yoshida*, Colorado School of Mines, *T.J. Coutts*, National Renewable Energy Laboratory

The deposition of high-quality tin-doped In_2O_3 (ITO) films by vacuum sputtering is well established. Nevertheless, coating specialists are keenly aware that maintaining high electrical and optical quality in a production environment represents significant challenges. ITO films with high carrier concentration and mobility generally are produced using high substrate temperature (250-350°C) in an ambient where the oxygen partial pressure is controlled to yield a slight oxygen deficiency in the film. Unfortunately, if the sputter ambient becomes too oxygen deficient, the optical transparency of the film decreases. The challenge during ITO deposition is to incorporate enough oxygen to produce films with high transparency while retaining slight oxygen deficiency to yield optimum electrical properties. In a large-area production coating system, this critical oxygen partial pressure must be achieved not only across a large deposition area, but also take into account variations such as target use, seasonal changes, and maintenance activities. Our recent investigations have identified a method to produce ITO-like films that are less sensitive to variations in the oxygen-containing deposition ambient. We are studying the effect of adding small amounts of Zr to both In_2O_3 and ITO ceramic sputtering targets. These targets are then used to produce thin films on glass substrates by r.f. magnetron sputtering. Electrical (Hall) and optical (UV-Vis-NIR spectrophotometry) analysis of these films shows that high-quality Zr-doped In_2O_3 (IZrO target = 9 wt.% ZrO_2+ 91 wt.% In_2O_3) films can be produced at high substrate temperatures (250-350°C) without adding oxygen to the sputter ambient. This result is in contrast to films produced from typical ITO targets (ITO target = 9 wt.% SnO_2+ 91 wt.% In_2O_3), where deposition in pure Ar yields films with very poor optical transparency. Films produced using a target where a small amount of Zr is added to a standard ITO target (ITO:Zr target = 1 wt.% ZrO_2+ 9 wt.% SnO_2+ 90 wt.% In_2O_3) show that the Zr addition allows for a broader range of oxygen partial pressure during deposition. We believe these results may embody significant advantages for large-area ITO film production, and could point the way toward similar benefits in other TCOs such as those based on ZnO or SnO_2 This abstract is subject to government rights.

10:40am **TF1-FrM9 Electronic and Optical Properties of TiO2-based Transparent Conducting Oxide**, ***T. Hitosugi***, University of Tokyo, Japan, *N. Yamada, Y. Furubayashi, S. Nakao, Y. Hirose, A. Ueda*, Kanagawa Academy of Science and Technology (KAST), Japan, *T. Shimada, T. Hasegawa*, University of Tokyo, Japan

Anatase Nb-doped TiO_2 appears to be promising transparent conducting oxide (TCO) for use as a next generation transparent electrode.[1,2] We report on electric properties of transparent conducting anatase $Ti_{0.94}Nb_{0.06}O_2$ polycrystalline films on glass. The films deposited using pulsed laser deposition at substrate temperature of room temperature, with subsequent H_2-annealing at 500°C, showed resistivity of 4.5 x 10^{-4} Ωcm at room temperature, and optical transmittance of 60-80 % in the visible light region. These results indicate that anatase $Ti_{0.94}Nb_{0.06}O_2$ films have excellent potential for practical transparent conducting oxides.

[1] Furubayashi et al., Appl. Phys. Lett. 86, 252101 (2005).

[2] T. Hitosugi et al., Jpn. J. Appl. Phys. 44, L1063 (2005).

11:00am **TF1-FrM10 Reactive Sputtered SnO_2 as the Active Layer in Transparent Thin Film Transistors**, ***W.-Y. Chen***, *J.-S. Chen*, National Cheng Kung University, Taiwan

Thin film transistors (TFTs) are the fundamental driving circuits for flat panel displays. In combination with the 'transparent circuit technology', transparent TFTs can increase the brightness and decrease the power consumption of displays. Therefore, oxide semiconductors are investigated as a substitute for the conventional amorphous silicon on TFTs because of their high optical transparency. In this work, we investigate the possibility of using reactive sputtered tin oxide (SnO_2) as the active layer in transparent TFTs. The transmittance of as-deposited SnO_2 film can reach 90%. Hall measurement shows that the SnO_2 film has higher carrier mobility than amorphous silicon. By changing the Ar/O_2 flow ratio during sputtering, the resistivity as well as the carrier mobility of SnO_2 can be varied. With an adequate preparation condition, the reactive sputtered SnO_2 film can lead to good characteristics as the active n-channel layer in transparent TFTs.

11:20am **TF1-FrM11 Electron Field Emission Study of Reactive Sputter Deposited Palladium Oxide Thin Films**, ***C.-J. Huang***, *F.-M. Pan, T.-C. Tzeng, C.-H. Tsai*, National Chiao-Tung University, Taiwan

Palladium oxide (PdO) is a p-type semiconductor and has many technological applications, such as catalysis, photoelectrolysis, and sensors. Because it is thermally stable up to 800°C, at which the oxide decomposes, and has a relatively low work function (3.9 eV), PdO is a suitable material for field emission applications. It has been used as the electrode material in a surface conduction electron emitter display. In this study, PdO thin films 100 nm thick were prepared on the Pt bottom electrode by reactive sputter deposition and the field emission characteristics were studied. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were used to characterize the chemical composition of the PdO thin film. Under certain deposition conditions, the PdO thin film exhibited a flake-like surface structure. The morphology of the deposited PdO thin film was highly dependent on the sputter deposition conditions, such as the gas flow ratio (Ar /O_2) and the substrate temperature. According to atomic force microscopy analysis, the PdO thin film deposited at 25°C had a root-mean-square (RMS) surface roughness of ~23 nm. The flake structure had a ridge angle smaller than 60° with a height ranging from ~30 nm to 100 nm. The sharp ridge angle can enhance the electric field at the local area around the ridge during the field emission operation. The field emission property of the PdO flake structure were studied using a simple diode configuration under a vacuum condition of ~10^{-6} torr, and the turn-on field was about 8.5 V/µm at the emission current density of 10 µA/cm^2.

Thin Film

Room: 613/614 - Session TF2-FrM

Nanoparticles

Moderator: T.M. Klein, the University of Alabama

8:00am **TF2-FrM1 Preparation and Characterization of Supported Metal Sulfide Nanoclusters Using Size-Selected Deposition**, ***M.G. White***, Brookhaven National Laboratory, *J.M. Lightstone*, SUNY Stony Brook, *P. Liu*, Brookhaven National Laboratory, *M.J. Patterson, J.C. Lofaro*, SUNY Stony Brook **INVITED**

The layered (S-M-S) structure of the bulk metal sulfides leads to unusual structures at the nanoscale (disks, fullerenes, tube) that exhibit a size-dependent band gap and/or unique catalytic properties. For example, MoS_2

is widely used as a commercial catalyst for hydrogenation and hydrodesulfurization, where it is dispersed as nanoparticles (10-30 Å) on a high surface area support. It is generally accepted that the active sites for reaction are associated with Mo atoms (with Ni/Co "promoter" atoms) located at defects or edges of the nanoparticle, however, many questions remain about the inter-relationship between nanocluster size, structure (atomic and electronic) and metal-sulfur composition, and how these physical properties influence catalytic activity. In this work, we are using mass (size) selected cluster ion beams to explore the size dependent reactivity of small nanoclusters of the early transition metal sulfides (Mo, W). Specifically, we use reactive sputtering in a magnetron source to generate gas-phase cluster cations which are then mass-analyzed to yield a beam of clusters with a precisely defined mass (size) and metal-sulfur composition. The mass-selected clusters are deposited at low kinetic energies ("soft landing") onto a solid support, e.g., Au(111) and Al_2O_3, for preparing model nanocatalysts whose properties can be studied by conventional surface science techniques. To date, we have explored the structure and stability of several prominent $Mo_xS_y^+$and $W_xS_y^+$ cluster species (x/y = 2/6, 3/7, 4/6, 5/7, 6,/8, 7/10, 8/12) in the gas phase and deposited on surfaces. These clusters are substoichiometric relative to the bulk material (sulfur to metal ratio < 2), and generally have exposed metal atoms (edge sites) that are available for adsorbate binding and reaction. Using thermal desorption (TPD) and electron spectroscopy (Auger, XPS), we have studied the reactivity and thermal stability of molybenum sulfide nanoclusters deposited on a Au(111) surface. This work was motivated by recent theoretical calculations that predict that the highly symmetric and stable Mo_4S_6 and Mo_6S_8 clusters bind to the Au(111) surface via relatively strong Au-S linkages, but with little distortion of the cluster structure. Experiments indicate that the clusters can be deposited intact, with adsorbate binding energies that depend on cluster size and atomic composition, and the presence of the Au substrate.

8:40am **TF2-FrM3 Chemical States of Sn Present in SnO2 Nanomaterial Sensors*,* *__D.L. Lahr__*, *J.K. Evju, K.B. Benkstein, J.L. Hertz, S. Semancik*, National Institute of Standards and Technology

Tin(IV) oxide (SnO_2) has been studied extensively as a chemiresistive sensing material. Increasingly, it has been shown that morphologies of SnO_2 with nanoscale dimensions have improved sensing properties compared to the bulk material. We report on the observation of chemical states of tin present at the surfaces of a variety of nanoscale SnO_x materials using X-ray Photoelectron Spectroscopy (XPS). Nanoparticles, nanowires and nanostructured thin films with a nominal stoichiometry of SnO_2 actually contain a range of oxidation states of tin, from tin(IV) to tin(0), at their surfaces. Depth profiling reveals the underlying tin(IV) oxide in each of these materials, and provides information on the relative amounts of the various chemical states present as a function of depth. In addition, we present methods to control the extent of oxidation of these materials, as monitored by XPS. We propose that the relative amounts of the chemical states of tin at the surfaces of sensors composed of these materials influence their sensitivity and stability. Control of the composition of the chemical states of tin can lead to improved sensor performance.

9:00am **TF2-FrM4 New Carbon Allotropes Produced by Hydrogen Plasma Exposure of Carbon Nanotubes*,* *__M.J. Behr__*, University of Minnesota, *T. Singh, D. Maroudas,* University of Massachusetts, Amherst, *E.S. Aydil*, University of Minnesota

Plasma-enhanced chemical vapor deposition (PECVD) using hydrocarbons is a common technique used to grow carbon-based nanostructured materials. It has been well established that hydrogen plays a critical role in determining these materials' crystallinity. For example, PECVD of diamond films is possible only when hydrocarbon precursors are heavily diluted in hydrogen. The specific role of hydrogen in these carbon systems, however, is unknown. To investigate hydrogen's role, we have exposed multiwalled carbon nanotubes (MWCNTs) and carbon nanofibers (MWCNFs) at room temperature to atomic hydrogen produced by an inductively coupled radio frequency plasma source. We observed hydrogen-induced crystallization of MWCNTs and MWCNFs at room temperature. Nanometer-size crystals of carbon appear gradually during 2-10 hour H-atom exposure of the nanotubes. We characterized these nanocrystals using high-resolution transmission electron microscopy (HRTEM), electron diffraction, and forward recoil elastic spectrometry (FRES). HRTEM of the H-exposed material at room temperature revealed the presence of carbon nanocrystals, ~5 nm in diameter, embedded in amorphous carbon nanorods. The electron diffraction patterns and lattice spacings could not be accounted for by known crystalline phases of carbon, such as diamond and lonsdaleite, or by contaminants. However, two distinct crystalline phases are observed among a variety of others in this amorphous matrix. The observed electron diffraction patterns and lattice spacings from these two phases are consistent with a body-centered cubic (BCC) phase with lattice parameter a = 0.30 nm and a face-centered cubic (FCC) phase with lattice parameter a = 0.425 nm. The lattice parameter of the FCC phase is approximately the same as that of i-Carbon, a previously observed but unidentified phase belonging to the cubic crystal system. However, electron diffraction from i-Carbon and the FCC phase we observe do not follow the same selection rules. First-principles density functional theory calculations within the generalized gradient approximation are used in conjunction with electron microscopy to suggest possible crystal structures for these new phases. Specifically, we consider the possibility that these new ordered phases may contain hydrogen atoms in addition to carbon and examine the dependence of the structural parameters of the crystalline phases on their hydrogen content.

9:20am **TF2-FrM5 Non-Lithographic Organization of Nickel Catalyst for Carbon Nanofiber Synthesis on Laser-Induced Periodic Surface Structures*,* *__Y.F. Guan__*, The University of Tennessee, Knoxville*, A.V. Melechko,* Oak Ridge National Laboratory*, A.J. Pedraza, P.D. Rack*, The University of Tennessee, Knoxville

We present a non-lithographic technique that produces organized nanoscale nickel catalyst for carbon nanofiber growth on a silicon substrate. This technique involves three consecutive steps: first, the substrate is laser-irradiated to produce a periodic nanorippled structure; second, a thin film of nickel is deposited using glancing angle ion beam sputter-deposition, followed by plasma heat-treatment; and third, a catalytic dc plasma enhanced chemical vapor deposition (PECVD) process is conducted to produce the vertically aligned carbon nanofibers (VACNF). The nickel catalyst is distributed along the laser induced periodic surface structures (LIPSS), and the Ni particle dimension varies as a function of the location on the LIPSS and is correlated to the nanoripple dimensions. The glancing angle, the distance between the collimators, and the total deposition time all play important roles in determining the final catalyst size and subsequent carbon nanofiber property. Due to the gradual aspect ratio change of the nanoripples across the sample, Ni catalyst nanoparticles of different dimensions were obtained. After the PECVD process, it was observed that in order for the carbon nanofibers to grow, the nickel catalyst dimension should be larger than a certain critical value of ~ 25 nm, below which, the Ni is insufficient to sustain carbon nanofiber growth.

9:40am **TF2-FrM6 Matilda : A Mass Filtered Magnetron Nanocluster Source*,* *__G.H. Kwon__*, *T.M. Klein,* The University of Alabama*, W. Hale,* AJA International, Inc.*, G.J. Mankey*, The University of Alabama

Matilda, a nanocluster source, consists of a cluster source, a Retarding Field Analyzer (RFA) and a Magnetic sector. A moveable AJA A310 Series 1"-diameter magnetron sputtering gun enclosed in a water cooled aggregation tube serves as the cluster source. The sputtering pressure in the aggregation tube is controlled in the range of 0.03 - 1 Torr using a mass flow controller. The mean cluster size is found to be a function of gas flow rate, sputtering power, and aggregation length. The kinetic energy distribution of ionized clusters was measured with the RFA. The RFA also serves as a high pass filter which allows only ions having a higher kinetic energy than the cluster charge times the retarding voltage to pass. A silver target was used for initial testing and cluster sizes were measured using a transmission electron microscope. At high Ar flow rates, the mean cluster size is 60 nm and for lower flow, the mean cluster size is reduced to 2 nm. Finer control of cluster size can be achieved using a mixture of He and Ar as the sputtering gas. Our results show the He gas pressure can be optimized to reduce the cluster size variations. The cluster sizes can also be selected using a magnetic sector. The sector is downstream from the RFA, and the magnetic field is applied in a direction perpendicular to the direction of ion motion. The ions are dispersed on a substrate laterally according to size. This new method of fabrication allows the study of size effects on a single substrate to increase throughput. This work was funded by the US DOE under grant number DE-FG02-01ER45867 and shared equipment from NSF-DMR-02-13985.

10:00am **TF2-FrM7 Controlled Synthesis of Single and Multi-Component Metallic and Ceramic Nanoparticles Via Matrix Assisted Pulsed Laser Evaporation*,* *__A.T. Sellinger__*, *E.M. Leveugle, L.V. Zhigilei, J.M Fitz-Gerald*, University of Virginia

The need to obtain nanoparticles with narrow size distributions has prompted the development of alternative processing methods. As an emerging area, laser processing has evolved into several widely accepted fields spanning from thin film growth, etching, lithography, and industrial fabrication to name a few. Within this field, the use of matrix-assisted laser processing has been successfully utilized in the deposition of soft materials in thin film form. One class of materials amenable to solution processing are acetates [$X(OAc)_2$]. Acetates are a widely favored metallorganic precursor for thin film processing on various substrates due to their decomposition behavior under ultraviolet irradiation and/or low temperature. In this research, a dry method to synthesize nanoparticles from frozen salt solutions is reported. Synthesis of Pd, Au, and Ag nanoparticles including their binary and ternary compositions were grown by photo-chemical decomposition of starting metal acetates within host matrices of chloroform and water using an excimer laser operating at 248 nm. Frozen composite targets were ablated at fluences ranging from 0.10 J/cm^2 to 1.0 J/cm^2 at a processing pressures ranging from 10 mTorr to 1 Torr. The ejected nanoparticles were deposited on continuous carbon coated and lacey carbon transmission electron microscopy grids at ambient temperature. Characterization was performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDXS). High-resolution TEM analysis showed definitive evidence of elemental composition and confirmed that the size distributions which were narrow for the Pd system which exhibited mean diameters ranging from 2 to 3 nm while the Ag and Au systems were on the order of 10 nm with evidence of large particles. Additional research concerning the growth of complex, multi-component oxide nanoparticles will be presented as time permits.

10:20am **TF2-FrM8 The Characterization of Stress Induced Crystallization of Polycrystalline Silicon Thin Film Transistor with Vertically Aligned Carbon Nanofibers**, ***J. Park***, *S.Y. Kwon,* The University of Tennessee, *S.-I. Jun,* dpiX, *A.V. Melechko, T.E. McKnight, M.L. Simpson,* Oak Ridge National Laboratory, *P.D. Rack*, The University of Tennessee

Thin film transistors (TFT) with vertically aligned carbon nanofibers (VACNF) are an attractive electronic switching device for nanoscale electroanalysis and delivering biological material into live cells. In our previous work, we have demonstrated an amorphous silicon TFT array integrated with VACNFs for delivering biological material into live cells. To enhance the device performance, we have explored a polycrystalline silicon active layer with a bottom-gate structure. For the poly silicon device, source/drain and gate metals and gate dielectric thin films were RF magnetron sputter deposited. We have examined several enhanced crystallization strategies including DC bias stress during amorphous silicon deposition and stress induced crystallization (SIC) using dielectric silicon nitride caps with relatively lower process temperature and higher crystallinity silicon than conventional annealing. The silicon films have been characterized by x-ray diffraction, scanning electron microscopy, and Raman spectroscopy. In this presentation, we will demonstrate the process flow of fabricating polycrystalline silicon with the stress effects and the characteristics of polycrystalline silicon will be discussed. Furthermore, the electrical characteristics of the TFTs with this active layer will be demonstrated.

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