Thin Film
Room 2022 - Session TF-MoM
ALD and Applications I

Moderator: H. Kim, POSTECH, Korea

8:00am **TF-MoM1 Spatially Controlled Nano-Scale Doping of Er@sup 3+@ in Y@sub 2@O@sub 3@ by Atomic Layer Deposition***, **J. Hoang,** T.T. Van, M. Sawkar Mathur,* University of California, Los Angeles*; J. Bargar,* Stanford Synchrotron Radiation Laboratory*; B. Hoex,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; R. Ostroumov, K. Wang, J.P. Chang,* University of California, Los Angeles

We report in this work the utilization of radical enhanced atomic layer deposition (RE-ALD) to synthesize ultra thin films with controlled dopant incorporation. Er-doped Y@sub 2@O@sub 3@ is a potential waveguide core material for compact optical amplifiers because Y@sub 2@O@sub 3@ allows for incorporating of a higher concentration of Er and enables a compact geometry and a larger signal admittance angle. Extended X-ray Absorption Fine Structure (EXAFS) analysis showed that Er was in the optically active trivalent state in all samples, confirmed by their X-ray absorption near-edge spectroscopy. Modeling of the EXAFS data revealed that Er@sup 3+@ is coordinated with 6 O at 0.224 and 0.232 nm. The critical inter-ionic distance between two Er@sup 3+@ was determined to be 0.4 nm, thus setting an upper limit on the Er@sup 3+@ concentration in Y@sub 2@O@sub 3@ at about three orders of magnitude higher than the Er@sup 3+@ solubility limit in the conventional SiO@sub 2@ host. X-ray diffraction (XRD) and selected-area electron diffraction patterns revealed a preferential film growth in the [111] direction, showing a lattice contraction with increasing Er doping concentration, likely due to Er@sup 3+@ of a smaller ionic radius replacing the slightly larger Y@sup 3+@. The optical properties of Er@sup 3+@ ions incorporated in Y@sub 2@O@sub 3@ were investigated by using cavity ring-down spectroscopy (CRDS), and the peak absorption cross section of Er@sup 3+@ in Y@sub 2@O@sub 3@ at 1.53-µm was estimated to be ~2.0x10@sup -20@ cm@sup 2@, about two times of that for Er@sup 3+@ in SiO@sub 2@. This is consistent with our previously reported larger effective absorption cross session of Er@sup 3+@ based on the photoluminescence yield as a function of the pump power. An important implication of this higher absorption cross section is that the population inversion can be achieved at a lower pump power and hence higher pumping efficiency.

8:20am **TF-MoM2 MnO@sub 2@ and MgO Atomic Layer Deposition Using Bis(Ethylcyclopentadienyl) Precursors and H@sub 2@O***, **B.B. Burton,** F.H. Fabreguette, D.N. Goldstein, S.M. George,* University of Colorado at Boulder

The atomic layer deposition (ALD) of manganese oxide (MnO@sub 2@) and magnesium oxide (MgO) was studied using Fourier transform infrared (FTIR) spectroscopy and quartz crystal microbalance (QCM) measurements. MnO@sub 2@ ALD was performed at temperatures between 100-300°C using sequential exposures of Mn(CpEt)@sub 2@ [bis(ethylcyclopentadienyl)manganese] and H@sub 2@O. MgO ALD was performed at temperatures between 125-400°C using sequential exposures of Mg(CpEt)@sub 2@ [bis(ethylcylopentadienyl)magnesium] and H@sub 2@O. The FTIR spectra were consistent with a loss of O-H vibrational features and a gain of C-H vibrational features during the M(CpEt)@sub 2@ exposure. The H@sub 2@O exposure produced a gain in O-H vibrational features and a loss of C-H vibrational features. The M-O bulk vibrational modes were also observed to grow in both cases between 500-1000 cm@super -1@. The QCM showed a maximum mass gain per cycle (MGPC) of 56 ng/cm@super 2@/cycle for MnO@sub 2@ at 150°C and a MGPC of 44 ng/cm@super 2@/cycle for MgO at 150°C. Both reactions were very efficient and required reactant exposures of only 2 x10@super 5@ L (1 L = 1 x 10@super -6@ Torr s). The X-ray reflectivity (XRR) measurements were consistent with growth rate of ~1.1 Å/cycle at 150°C and ~1.41 Å/cycle at 150°C for MnO@sub 2@ and MgO, respectively. Based on thicknesses measured by XRR and the MGPC obtained by QCM, the density for the MnO@sub 2@ ALD films was 4.95 g/cm@super 3@ and the density for the MgO ALD films was 3.15 g/cm@super 3@. Transmission electron microscopy (TEM) was also performed after 40 AB cycles of MnO@sub 2@ ALD and 50 cycles of MgO ALD on ZrO@sub 2@ particles. In agreement with the growth rates obtained from the XRR measurements, the film thicknesses observed by TEM were 54 Å and 85 Å for MnO@sub 2@ and MgO, respectively.

8:40am **TF-MoM3 A New Fabrication Method of Nanostructural Materials by Using Selective Atomic Layer Deposition***, **M.M. Sung,*** Hanyang University, South Korea **INVITED**

We report a new fabrication method of nanostructural materials by using selective atomic layer deposition of thin films on patterned self-assmebled monolayers and nanoporous templates. The patterned monolayers define and direct the selective deposition of thin films. This technique has been used successfully to deposit nanostructural materials on technologically important substrates including silicon and gold. Oxide nanotubes with diameter of 30 ~ 200 nm were successfully fabricated by this technique. It allows one-step processing for the fabrication of the freestanding oxide nanotubes. Sub-Ã.ngstrom wall thickness controls in oxide nanotubeâ?T structures can be achieved by this method. The nanostructural amaterials have been investigated by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), water contact angles analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV spectrometer.

9:20am **TF-MoM5 Mechanism of Al@sub 2@O@sub 3@ Atomic Layer Deposition Using Trimethylaluminum and Ozone***, **D.N. Goldstein,** S.M. George,* University of Colorado at Boulder

Al@sub 2@O@sub 3@ atomic layer deposition (ALD) is typically performed using trimethylaluminum (TMA) and H@sub 2@O. However, ozone can be used as the oxidant instead of H@sub 2@O. Ozone may lead to reduced Al@sub 2@O@sub 3@ leakage current for dielectric applications. Ozone may also purge faster than H@sub 2@O and lead to faster Al@sub 2@O@sub 3@ ALD. The mechanism of Al@sub 2@O@sub 3@ ALD using TMA and ozone is still under debate. To study the chemical species on the growing Al@sub 2@O@sub 3@ ALD surface, we have performed transmission FTIR vibrational spectroscopy investigations. High surface area ZrO@sub 2@ nanoparticles were utilized to obtain high surface sensitivities. The vibrational spectrum was recorded after each TMA or ozone reaction. The ozone generator produces 3.7 wt.% ozone in a 300 sccm O@sub 2@ flow in a viscous flow ALD reactor. Argon is utilized as the carrier gas to reduce reactive NO@sub x@ species. At the growth temperatures of 175 and 275°C, the FTIR results reveal that O@sub 3@ reacts with Al-CH@sub 3@ surface species produced by the TMA reaction and forms primarily formate groups and a mixture of methoxy and hydroxyl species on the surface. Production of formate groups may involve oxygen insertion into the Al-CH@sub 3@ bond to form methoxy species that are known to condense into formate groups at the reaction temperatures. The TMA then displaces the formate and methoxy groups and reforms Al-CH@sub 3@ surface species. FTIR difference spectra after TMA and O@sub 3@ reactions at 275°C are shown in the accompanying figure. These spectra are consistent with the loss and gain of formate and methoxy groups. The surface features are temperature dependent. At temperatures greater than 375°C, the FTIR vibrational spectrum reveals only formate groups on the surface.

9:40am **TF-MoM6 Atomic Layer Deposition of Y@sub 2@O@sub 3@-Al@sub 2@O@sub 3@ Nanolaminate Thin Films and Compounds***, **J.C. Rowland,** M. Davidson, P.H. Holloway,* University of Florida

Alternating nano-scale thin films of Y@sub 2@O@sub 3@ and Al@sub 2@O@sub 3@ were grown by atomic layer deposition (ALD) with AlCl@sub 3@, Y(thd)@sub 3@, and H@sub 2@O precursors. The surface roughness was determined by AFM versus growth parameters such as substrate temperature (250-550°C), gas sweep time, etc. Growth rates of 0.4 nm/cycle were demonstrated. The composition was analyzed by Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS), and shown to have low concentrations of impurities, especially Cl from the Al precursors. The microstructure and crystallinity / amorphicity were characterized using cross-sectional transmission electron microscopy (TEM), and X-ray diffraction (XRD). These data are interpreted in terms of the layer-by-layer ALD growth mode and compared to the properties of a single oxide film of Y@sub 2@O@sub 3@ or Al@sub 2@O@sub 3@. Solid state diffusion during post-growth annealing was investigated for forming various Y@sub 2@O@sub 3@-Al@sub 2@O@sub 3@ compounds such as Y@sub 2@Al@sub 5@O@sub 12@ (YAG), YAlO@sub 3@ (YAP), and Y@sub 4@Al@sub 2@O@sub 9@ (YAM), having cubic garnet, orthorhombic perovskite, and monoclinic structures, respectively.

10:20am **TF-MoM8 Plasma Enhanced Atomic Layer Deposition of TiO@sub 2@ and HfO@sub 2@: Plasma Source Configuration and Film Properties***, S.M. Rossnagel,* IBM T.J. Watson Research Center*; J. Joo,* Kunsan National University, Korea*; **H. Kim,*** POSTECH, Korea

Plasma enhanced atomic layer deposition has advantages over thermal atomic layer deposition method in deposition rate, deposition temperature window, film density and choice of precursors. The role of plasma can be summarized into two categories; selective dissociation of precursors and enhancement of nucleation site density. Four different configuration of high density plasma sources were developed and applied to deposit TiO@sub 2@ and HfO@sub 2@ on 200 mm Si wafers using TIIP(titanium isoproxide) and TEMAH(tetrakis ethyl methyl amido hafnium) as precursors. For reactants, oxygen and water plasma were used. In addition, these same materials were evaluated by thermal ALD in the same tool. Optical emission spectroscopy was used as a real time diagnostic tool. Thickness and refractive index uniformity was monitored by ellipsometry. Chemical composition was evaluated by XPS and RBS. TiO2 was rather insensitive to the configuration of plasma sources; the distance to the wafer, or the size of the plasma sources. 2% of non-uniformity in thickness and refractive index was typically obtained from 1 inch diameter inductively coupled plasma source, which means radical dominant process both in abstraction and nucleation steps. Leakage current and C-V characteristics showed good results in higher film thickness than 3.5nm of TiO@sub 2@. HfO@sub 2@/TiO@sub 2@ multilayer and Hf@sub x@Ti@sub (1-x)@O@sub 2@ films were deposited to seek good combination for gate stacks.

10:40am **TF-MoM9 Interface Properties of Hafnium Oxide Films Grown by Atomic Layer Deposition on Native, Chemical Oxide and H-Terminated Si Surfaces***, **J.C. Hackley**, L. Takacs, T. Gougousi,* UMBC

A hot wall Atomic Layer Deposition flow reactor equipped with a Quartz Crystal Microbalance (QCM) has been used for the deposition of HfO@sub2@ thin films using tetrakis-ethylmethylamino hafnium (TEMAH) and H@sub2@O as precursors. HfO@sub2@ films were deposited on H-terminated Si, native oxide and SC1 chemical oxide. Spectroscopic ellipsometry and QCM measurements confirm linear growth of the films with a growth rate of ~1.2Å/cycle at 250°C. The films composition and morphology was examined using XPS, FTIR, AFM and XRD. Films are nearly stoichiometric HfO@sub2@ (O:Hf ~1.95) with bonded carbon content less than 3 at. % and the surface rms roughness is ~ 3% of the film thickness. A similar incubation period of ~15 cycles is found for all three starting surfaces and X-ray photoelectron emission spectroscopy shows no SiO@sub2@ formation at the interface for deposition on the H-terminated Si surfaces. However, there is evidence for Hf-O-Si bonding and RTA inert anneals (2 min in Ar) at temperatures as low as 300°C destabilize the interface and lead to the formation of interfacial SiO@sub2@. X-ray diffraction data indicate that the films start to crystallize upon anneals at 300°C. From the XPS and XRD data we conclude that initially the H termination of the surface and the as deposited amorphous HfO@sub2@ network protect the interface from oxidation. However, once the film begins to crystallize then diffusion of moisture and impurity O@sub2@ along the grain boundaries is enhanced resulting in the formation of interfacial SiO@sub2@.

11:00am **TF-MoM10 Atomic Layer Deposition of Aluminium Silicate Films***, **P.J. Evans**,* ANSTO, Australia*; P.H. Mutin,* Universite Montpellier, France*; G. Triani, Z. Zhang, A. Atanacio, J. Bartlett,* ANSTO, Australia

The ALD of silicate films has been the subject of several recent studies.@footnote 1-3@ Interest in these materials has been stimulated in part by research into suitable candidates for the high-k dielectric layer in future semiconductor devices. While the ALD of hafnium and zirconium silicates have figured prominently in work to date, other metal silicates, such as those of aluminium, have also been reported.@footnote 4,5@ The present study investigates the deposition of aluminium silicate films by means of the reaction between aluminium chloride (AlCl@sub 3@), tetramethoxysilane (TMOS) and water at temperatures in the range 200 - 300 °C. An in-situ quartz crystal microbalance (QCM) was used to monitor the growth process in real time. The results of these measurements indicated that a single AlCl@sub 3@/H@sub 2@O pulse sequence followed by 3 - 5 pulse sequences of TMOS/H@sub 2@O enhanced both the growth rate and amount of Si in the film. These conditions were then used to deposit films on silicon wafers for ex-situ characterisation with ellipsometry, SIMS and XPS. It was found that films with approximately equal amounts of Al and Si could be obtained with the above precursors at 250 °C. At lower temperatures, the film growth rate decreased rapidly to the extent that negligible growth occurred at 200 °C. This finding is similar to that observed in other cases where ALD film growth has been found to depend on the effect of temperature on reaction kinetics. @FootnoteText@ @footnote 1@Vainonen-Ahlgren, E.; Tois, E.; Ahlgren, T.; Khriachtchev, L.; Marles, J.; Haukka, S.; Tuominen, M.; Comp. Mater. Sci. 2003, 27, 65. @footnote 2@Kukli, K.; Ritala, M.; Leskelä, M.; Sajavaara, T.; Keinonen, J.; Hegde, R.I.; Gilmer, D.C.; Tobin, P.J. J. Electrochem. Soc., 2004, 151, F98. @footnote 3@Kang, S-W.; Rhee, S-W.; George, S.M. J. Vac. Sci. Technol. A 2004, 22, 2392. @footnote 4@Brei, V.V.; Kasperskii, V.A.; Chuiko, A.A.; Russ. J. Appl. Chem. 1996, 69, 335. @footnote5@Lim, J.W.; Yun, S.J.; Lee, J.H.; Electrochem. Solid-State Lett. 2005, 8, F25.

11:20am **TF-MoM11 Structure and Electrical Properties of BN Atomic Layer Deposition Grown in a Quasi-static Viscous Flow Reactor***, **R.K. Grubbs**,* Sandia National Laboratories

Boron nitride (BN) is a desired material due to its thermal, electrical and tribological properties. The ability to deposit certain phases of BN via atomic layer deposition (ALD) could potentially solve a number of materials issues related to packaging and to MEMS systems. This talk describes the deposition, materials characterization and resulting electrical properties of ALD grown BN at a deposition temperature of 480 °C. Initial work on the ALD of BN was performed by Ferguson and George using FT infrared spectroscopy on ZrO@sub 2@ particles.@footnote 1@ Their work determined that large reactant exposures were necessary to complete the ALD surface chemistry. To produce ALD films of BN, an ALD viscous flow reactor was run in a quasi-static mode to obtain the necessary exposures required to saturate the surface chemistry. NH@sub 3@ and two different boron precursors were used to make BN thin films. Both BCl@sub 3@ and B(CH@sub 3@)@sub 3@ precursors were successful at producing BN ALD. The resulting thin films were analyzed with depth profile Auger electron spectrometry and x-ray diffraction. The BN films were amorphous as grown and did not convert to a crystalline phase under rapid thermal annealing conditions. The BN ALD grew at a rate of 0.7 Å/cycle at the 480 °C reaction temperature. Electrical measurements were performed on the BN ALD thin films as a function of film thickness. The breakdown voltage, leakage current and dielectric constant were measured for each BN synthesis and compared. Although BN ALD is a time consuming process, it can provide amorphous, low dielectric constant, pinhole free films for potential electrical, and diffusion barrier applications. @FootnoteText@ @footnote 1@ J.D. Ferguson, A.W. Weimer, S.M George, Thin Solid Films 413 16 (2002).

11:40am **TF-MoM12 Plasma Controlled Atomic Layer Deposition for Sealing Pores in Low-k Materials***, Y.-B. Jiang, **J.L. Cecchi**,* University of New Mexico*; C.J. Brinker,* Sandia National Laboratories

On a porous substrate, atomic layer deposition (ALD) takes place not only on the top of the substrate, but also penetrates into the internal porosity. For sealing the pores of a nanoporous low-k materials, it is important to prevent any deposition in the internal pores, which would alter the material's dielectric constant. Consequently, an approach capable of confining ALD to the top surface of the porous substrate is needed. We have developed such a method by combining ALD with plasma processing. The ALD process is carried out such that deposition reaction will not take place unless triggered by a plasma. TEOS and O2 have been used as the precursors for SiO2 ALD in a plasma-ALD reactor. Although both precursors will be incident on all exposed surfaces, including the internal pores, they are not reactive to each other unless triggered by active plasma radicals. Since the radicals in the plasma do not penetrate into the nanoporous matrix, no ALD will take place in the internal pores. Another approach we have developed is an ALD process for which adsorption can not proceed unless the surface is activated by plasma. Using TMCS (trimethyl chlorosilane) and H2O vapor as SiO2 ALD precursors, ALD proceeds via the cycle of TMCS/Ar purge/O2-plasma/H2O vapor/Ar purge. After each TMCS exposure, the sample surfaces are passivated with -CH3 groups. Upon the following exposure of an O2 plasma, -CH3 groups on the top surface are removed, leaving the surface reactive to subsequent precursor adsorptions. But the internal pores remain passivated, since plasma cannot reach them. In this manner, ALD is also confined to the top surface of the porous substrate. We present transmission electron microscope (TEM) images that establish that the SiO2 ALD thus obtained was a several-nm-thick pore-sealing layer conformally on the top of patterned nanoporous silica without filling the internal pores.

Thin Film
Room 2022 - Session TF-MoA
ALD and Applications II

Moderator: S.M. Rossnagel, IBM T.J.Watson Research Center

2:00pm **TF-MoA1 Molecular Layer Controlled Deposition of Polymer Thin Films***, **A.A. Dameron**, Y. Du, N.M. Adamczyk, S.M. George,* University of Colorado at Boulder

Conformal polymeric thin films can be fabricated using sequential, self-limiting surface chemistries that are similar to atomic layer deposition (ALD). The simplest repetitive surface chemistry for this molecular layer controlled polymer growth is based on the reaction of two bifunctional monomer reactants. This type of polymer film growth was originally demonstrated in the 1990s in various Japanese laboratories. Subsequently, little work has been done to understand or to utilize this polymer growth method. To further develop this important technique, we have explored the condensation reaction of 1,6-hexanediamine (H@sub 2@N-(CH@sub 2@)@sub 6@-NH2) with adipoyl chloride (ClOC-(CH@sub 2@)@sub 4@-COCl) to fabricate Nylon 66 (polyamide) films. By monitoring the infrared absorbance for the C-H, N-H and C=O stretching vibrations using Fourier transform infrared spectroscopy, we have observed the linear growth of the Nylon 66 films versus number of AB reaction cycles. Polymeric condensation reactions provide a wide spectrum of other possible reactant candidates. Currently, we are exploring surface chemistries for the molecular layer controlled deposition of other polymers such as polyester. In addition, polymeric materials can be combined together with inorganic materials to form laminate structures. We have demonstrated the growth of Nylon 66/Al@sub 2@O@sub 3@ nanolaminate films. Other polymeric/inorganic films can be fabricated to create new multifunctional materials.

2:20pm **TF-MoA2 Gas Diffusion Barriers on Polymers Using Al@sub2@O@sub3@ Atomic Layer Deposition***, M.D. Groner, A.A. Dameron,* University of Colorado*; R.S. McLean, P.F. Carcia,* DuPont Central Research & Development*; **S.M. George**,* University of Colorado

Diffusion barriers are required to protect thin film devices from the corrosive effects of various gases. One example is flexible organic light-emitting diode (OLED) devices that are susceptible to degradation because of facile permeation of O@sub2@ and H@sub2@O through the plastic substrates. Our recent work has utilized quantitative Ca-tests to measure water vapor transmission rates (WVTRs) through polymers coated with Al@sub2@O@sub3@ ALD films. These Ca-tests have measured WVTRs of 1.4 x 10@super-5@ g/m@super2@/day at 38°C and 5.5 x 10@super-5@ g/m@super2@/day at 60°C for an Al@sub2@O@sub3@ ALD film thickness of ~25 nm on polyethylene naphthalate (PEN). Based on the apparent activation energy, the WVTR at 23°C is estimated to be only 6 x 10@super-6@ g/m@super2@/day. These WVTR values are excellent and close to the targeted WVTRs required for OLEDs. Our earlier measurements used radioactive tracer tests based on HTO permeability to measure WVTRs. These radioactive tracer tests measured higher WVTRs of ~1 x 10@super-3@ g/m@super2@/day at room temperature for an Al@sub2@O@sub3@ ALD film thickness of ~26nm on Kapton polyimide and PEN. The difference between the Ca-test results and the HTO radioactive tracer test results suggests that the HTO test may be influenced by tritium diffusion in addition to HTO diffusion. Additional work is focusing on improvements in diffusion barrier performance using multilayer films composed of Al@sub2@O@sub3@ ALD and other materials.

2:40pm **TF-MoA3 Atomic Layer Deposition of In@sub 2@O@sub 3@ Using Cyclopentadienyl Indium: A New Synthetic Route to Transparent Conducting Oxide Films***, **J.W. Elam**,* Argonne National Laboratory*; A.B.F. Martinson,* Northwestern University*; M.J. Pellin,* Argonne National Laboratory*; J.T. Hupp,* Northwestern University **INVITED**

Indium Oxide (In@sub 2@O@sub 3@) forms the basis for an important class of transparent conducting oxides (TCO) that see wide use in optoelectronic devices, flat-panel displays and photovoltaics. Here we present a new method for depositing In@sub 2@O@sub 3@ thin films by atomic layer deposition (ALD) using alternating exposures to cyclopendadienyl indium and ozone. Using a precursor vaporization temperature of 40°C and deposition temperatures of 200-450°C, we measure growth rates of 1.3-2.0 Å/cycle. A significant advantage of this synthesis route over previous techniques is the ability to conformally coat porous materials such as anodic aluminum oxide membranes. The deposited films are nanocrystalline, cubic phase In@sub 2@O@sub 3@ and are highly transparent and conducting. In situ quadrupole mass spectrometry and quartz crystal microbalance measurements reveal a mechanism in which approximately 1 in 6 of the initial Cp ligands remain on the surface following each InCp exposure, and the remaining Cp ligand is burned off during the subsequent O@sub 3@ exposure to form CO@sub 2@. Using this method, we demonstrate for the first time the conformal coating of very high aspect ratio porous membranes with ALD In@sub 2@O@sub 3@. This technique will enable the functionalization of porous materials with In-based TCO films for the fabrication of novel photovoltaic devices.

3:20pm **TF-MoA5 Fabrication of Integrated Scanning Electrochemical-Atomic Force Microscopy Probes by Atomic Layer Deposition of Aluminum Oxide***, **D.J. Comstock**, M.C. Hersam,* Northwestern University*; J.W. Elam, M.J. Pellin,* Argonne National Laboratory

Integrated scanning electrochemical-atomic force microscopy (SECM-AFM) is a powerful tool for characterizing electrochemical and biological processes ranging from corrosion to membrane transport. SECM-AFM utilizes probes consisting of a tip electrode integrated onto a conventional atomic force microscopy cantilever, allowing for simultaneous but independent topographic and electrochemical imaging. In this study, we describe a novel process for fabricating integrated SECM-AFM probes using atomic layer deposition (ALD) techniques. ALD allows for the deposition of highly conformal, continuous insulating films with precise thickness control and is thus well suited for this project. Fabrication starts with commercially available conductive AFM probes, onto which a 50 nm thick aluminum oxide film is deposited by ALD. This insulating film serves to encapsulate the probe body, cantilever, and tip and eliminate electrical leakage currents when operating in an electrochemical environment. The tip nanoelectrode is fabricated using focused ion beam milling to selectively remove aluminum oxide from the tip apex and expose the underlying conductive film. The integrated probes are characterized by scanning electron microscopy (SEM) throughout fabrication to determine both the quality and morphology of the insulating film and the dimensions of the electrode. The films and fabricated probes are electrochemically characterized by cyclic voltammetry, in which the diffusion-limited redox current is used to determine the area of the exposed nanoelectrode. In addition, silver electrodeposition is used to visually confirm that the electrochemical activity of the probe is limited solely to the nanoelectrode at the tip apex. Both SEM imaging and electrochemical characterization have revealed tip electrodes with diameters as small as 50 nm. Finally, we demonstrate the application of these probes to SECM-AFM by acquiring topographic and electrochemical images of a model substrate.

3:40pm **TF-MoA6 Stand-Alone TiO@sub2@ Nanotubes for Nano-Sensors using Atomic Layer Deposition and Focused Ion Beam***, **D.K. Cha**, B.K. Lee, M.J. Kim,* University of Texas at Dallas*; J. Kim,* University of Texas at Dallas, U.S

Various tubular metal oxide nanomaterials such as TiO@sub2@ nanotubes have attracted considerable interest due to their excellent properties for nano-sensors and integrated circuits. In this study, we focus on the characteristic of single TiO@sub2@ nanotubes which are grown by atomic layer deposition (ALD) on nano porous membranes with self-assembled monolayers (SAMs) treatments. The TiO@sub2@ nanotubes are 20-200 nm in diameter with a wall thickness of 5-20 nm. For the electrical characterization of single TiO@sub2@ nanotubes, electrical test structure devices are fabricated on SiO@sub2@/Si wafer patterned with Au/Cr electrodes by focused ion beam (FIB), which has site-specific platinum deposition capability. A single TiO@sub2@ nanotube with a diameter of 200nm shows that the current increases linearly with the applied voltage (-3V to 3V) and resistivity is calculated to be approximately 100 @ohm@ cm. It is also found that the conductance of a single TiO@sub2@ nanotube is affected by the ambient, indicating the surface of TiO@sub2@ nanotube is sensitive to the presence of absorbed species such as water molecular. This conductance changing suggests that individual TiO@sub2@ nanotubes can be used for nano-sensor application. In addition, photo-conduction behaviors of single TiO@sub2@ nanotubes will also be discussed for photovoltaic nano-device applications. This research was supported by a grant (code #: M105KO010026-05K1501-02611) from Center for Nanostructured Materials Technology under 21st Century Frontier R&D programs of the Ministry of Science and Technology, Korea and The State of Texas.

4:00pm **TF-MoA7 Atomic Layer Deposition of Electrocatalytic Platinum for Solid Oxide Fuel Cells*, X. Jiang*,** *S.F. Bent,* Stanford University

Atomic layer deposition (ALD) has been actively explored for a number of applications. It is currently being investigated as an enabling technology to fabricate thin film solid oxide fuel cells (SOFCs). ALD can potentially be used to grow several fuel cell components, including electrolyte, catalyst, and electrode materials, at ultrathin, nanometer-scale thickness. Here we explore the use of ALD for the deposition of the Pt electrocatalyst for an SOFC. We have successfully carried out the Pt ALD process using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe@sub3@) and O@sub2@ as precursors and N@sub2@ as a carrier and purging gas. Ex situ analysis has been carried out on the as-deposited Pt films using a variety of analytical techniques, including atomic force microscopy (AFM),scanning electron microscopy (SEM), X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS), and four-point probe method. The analysis on native oxide-coated silicon wafers shows that the as-deposited platinum film is of excellent uniformity, with no measurable impurities and low electrical resistivity. We have also shown that Pt films of high quality can be deposited by ALD on RF-sputtered yttria stabilized zirconia (YSZ), a good candidate for the SOFC electrolyte. Deposition on YSZ is found to occur with a shorter incubation period than that on SiO@sub2@. The expected operating temperature of the SOFC ranges from 300°C to 1000°C. Post-ALD annealing studies of the morphology and resistivity of the Pt film as a function of temperature and film thickness show that for temperatures up to at least 550°C, resistivity remains relatively constant. However, film roughness, which is desirable for catalytic activity, increases with temperature. In addition, we have carried out area selective ALD of Pt on YSZ using microcontact printing for fabrication of the electrode and current collector for the SOFC. Results of these studies will be presented.

4:20pm **TF-MoA8 Co and CoSi@sub 2@ Films Prepared by Plasma-Enhanced Atomic Layer Deposition for Contact Applications*, H.-B.-R. Lee,*** *H. Kim,* POSTECH, Korea

The CoSi@sub 2@ has been studied as an alternative contact material to TiSi@sub 2@ in microelectrtonics technology since the CoSi@sub 2@ has immunity to shrinkage of line width, low resistivity, and thermal stability. However, typical process consisting of Co sputtering followed by a post annealing has several problems such as poor conformality and Si consumption in nanoscale regime. Therefore we investigated plasma-enhanced atomic layer deposition (PE-ALD) of Co thin films using several metal organic precursors and NH@sub 3@ plasma. The Co PE-ALD processes were studied as a function of key growth parameters including precursors and reactant exposure times and growth temperatures. Rutherford backscattering and X-ray photoemission spectroscopy results indicate that the impurity contents in PE-ALD Co thin films are low resulting in a very low resistivity down to 10µ@ohm@cm. After the deposition, the Co films were annealed to form CoSi@sub 2@ with Ti/TiN capping layers and the results were compared with physical vapor deposition (PVD) Co. In addition, direct ALD process of CoSi@sub 2@ was investigated using additional Si precursor. The microstructures of CoSi@sub 2@ films prepared by annealing and direct deposition were investigated by synchrotron radiation X-ray diffraction and transmission electron microscope.

Thin Film
Room 2022 - Session TF-TuM
Materials for Flexible Substrates, Displays, and Optoelectronics

Moderator: S. Gupta, University of Alabama

8:00am **TF-TuM1 Rapid Thermal Annealing of Indium Tin Oxide (ITO) Films on Flexible Substrates***, **R. Thunuguntla,*** University of Alabama*; D. Bottesch,* ASU Flexible Display Center*; S. Gupta,* University of Alabama

Indium tin oxide (ITO) films are widely used for transparent electrodes in various optoelectronic device and display applications, for instance, organic light emitting diodes (OLEDs), and solar cells. Typically, optimization processes for ITO films include either an in-situ or post-deposition annealing step at temperatures ranging from 200-500°C to improve the sheet resistance and transmission properties, achieving resistivities as low as 250 µ@ohm@-cm and close to 100% transmittance. However, for flexible substrates, processing temperatures must be restricted to about 180 °C, resulting in as-deposited films with higher resistivity and lower transmittance. We report the optimization of ITO film properties on flexible substrates by rapid thermal annealing (RTA). ITO films were deposited on flexible substrates by reactive DC magnetron sputtering over a range of processing conditions. Resistivity and transmission was measured before and after atmospheric rapid thermal annealing with tungsten-halogen lamps at temperatures below 180 °C. Atomic force microscopy and X-ray diffraction studies were also carried out before and after annealing to study the effect of the RTA step on crystal growth and orientation as well as on surface morphology and grain size. These results were compared with those on glass substrates where in-situ annealing at high temperatures during deposition was carried out. Rapid thermal annealing shows great promise as a production-compatible technique for ITO on flexible substrates, with more than 50% reduction of resistivity being achieved in several instances. A detailed RTA optimization study for ITO films on flexible substrates by varying annealing parameters such as time, temperature, thermal profiles and ambient gas is presented.

8:20am **TF-TuM2 Gate Dielectric Development for Flexible Electronics***, **P.C. Joshi**, A.T. Voutsas, J.W. Hartzell,* SHARP Labs of America, Inc.

TFTs integrated on flexible substrates are becoming increasingly attractive for low cost displays, sensors, and rf communication applications. The successful development of high performance flexible devices will be dictated by the enhancement in the thermal stability of the substrates and the low temperature (< 300 °C) processing of the high quality gate dielectric. The PECVD technique has successfully met the demands of the gate dielectric for display devices at processing temperatures lower than 600 °C. However, a further reduction in the processing temperatures below 300 °C is essential to realize low cost, highly functional devices on flexible substrates. The low temperatures processing of gate dielectric films necessitates the development of processes and techniques with plasma controlled reaction kinetics dominating the thin film growth rather then the thermal state of the substrate. At the same time, the gate dielectric reliability need to be maintained or enhanced. In the present work, we report on the low temperature processing of high quality gate dielectric films by high-density PECVD technique at process temperatures lower than 300 °C. The bulk and interfacial electrical quality and reliability of the MOS capacitors as a function of process temperature are discussed in this report. A comparison with the high temperature gate oxide films deposited by PECVD technique employing CCP source has been made to establish the film quality and reliability. The films processed at low temperatures in the range of 150-300 °C showed high electrical performance and reliability as evaluated in terms of the leakage current, flat band voltage, mid-gap interface trap concentration, and BTS characteristics. The observed results are promising and suggest the suitability of HDP technique for novel device development on low temperature flexible substrates.

8:40am **TF-TuM3 Thin-Film Amorphous Silicon Transistors on Flexible Substrates***, **D. Loy,*** U.S. Army Flexible Display Center **INVITED**

The Flexible Display Center (FDC) at Arizona State University is focused on developing thin film transistor (TFT) devices on flexible substrates, for use in a variety of reflective and emissive display technologies. We are currently fabricating amorphous silicon TFT backplanes on a 6” Wafer-Scale Pilot Line linked to a Manufacturing Execution System and supported by a comprehensive suite of in-Fab metrology tools. We are simultaneously installing a GEN II (370 x 470 mm) Display-Scale Pilot Line, with qualified operation slated for late 2006. This talk overviews the critical steps in our backplane technology evolution, from qualification of our baseline low temperature a-Si process on the 6” line with rigid substrates, to transferring the process to flexible plastic and metal foil substrates, to form factor scale-up of the TFT arrays, and finally Pilot Line scale-up to GEN II. Keywords: Flexible displays, backplane electronics, Thin Film Transistors (TFTs), electrophoretic ink, OLEDs

9:20am **TF-TuM5 DC Magnetron Sputtered ITO Thin Film on Plastic Substrate with Hard Coating***, **H.-P. Cheng**, C.-W. Sun,* National Taipei University of Technology, Taiwan, R.O.C.*; T.-H. Chen,* National Chiao Tung University, Taiwan, R.O.C.

The conventional substrates used on monitor are mostly made of glass. Glass has disadvantages of inconvenience in transporting, heavy, fragile, low impact tolerance. The thickness of the glass substrate is facing bottleneck in technical development. Thus, the development of plastic substrate is the growing application. This study focused on the application of DC magnetic sputtering on plastic substrate for sputtering ITO transparent conducting films, and discussed the relationship between the structure and photoelectric properties. The results showed that due to the heat-resistance problem of the plastic substrate, when the substrate temperature is over 60 degree C, ITO film would fracture due to heat stress. Thus, using sputtering under room temperature and lower power could prevent the fracture. Also, the thin film has low adhesiveness due to the characteristics of the plastic substrate, thus, the plastic substrate treated with hard coat could improve the adhesiveness. In terms of the electric properties, the conductivity of ITO film improves as the sputtering time increases, the oxygen pressure decreases, and the proper working pressure is selected. In terms of photoelectric properties, the transmission of light for the ITO film increases as the sputtering time increases, the oxygen pressure increases, and the proper working pressure is selected. After four-point probe test on the electric properties and spectrometer used to measure the transmission of light, the results showed the best resistivity to be 6.96E-4 Ohm.cm, whereas the transmission of light on the test sample is as high as 80%.

10:40am **TF-TuM9 The Surface States of MgO Thin Films Deposited with a Flow of Gases by e-beam Evaporation***, **T.W. Heo,** S.H. Moon, S.Y. Park, J.H. Kim, H.J. Kim,* Seoul National University, South Korea

MgO thin film plays important roles in AC-Plasma Display Panels: the emission of the secondary electrons and protecting the dielectric layer against the ionized ions. Especially the secondary electron emission coefficient becomes more important recently.@footnote 1,2@ However, the secondary electron emission coefficient should be strongly related to the surface state of MgO thin film: only several nanometers of the surface might be the important part to determine the secondary electron emission coefficient. In addition, the density of states (DOS) of the valence band is one of key parameters, which can explain the mechanism of the secondary electron emission. Because, the two electrons involved have energies initially at two levels in the valence band.@footnote 3@ It is known that during e-beam evaporation the addition of gas improved the electrical property of MgO thin film depending on the kind of the gas. But the reasons for that are not clearly understood. MgO thin films were deposited with a flow of O@sub 2@, N@sub 2@ and H@sub 2@ gases by e-beam evaporator. The deposited MgO thin films were investigated by XPS and SEM. Discharging characteristics was also determined. To evaluate the discharging characteristics, 2-inch test panels were fabricated. MgO film deposited with O@sub 2@ flow shows the most dense microstructure(on the SEM image) and the highest density of states of the valence band(on the XPS spectra) as well as the lowest discharging voltage. The discharging voltages of panel that have MgO film deposited with O@sub 2@ flow are lower than those of panels with other gases flows by 4~5 V. The discussion about the reason for the improvement will be discussed in the presentation. @FootnoteText@ @footnote 1@H. Uchiike et al., IEEE Trans. Elec. Dev., ED-23 1211 (1976). @footnote 2@ T. J. Vink et al., Appl. Phy. Lett., 80 (12), 2216 (2002). @footnote 3@Homer D. Hagstrum, Phy. Rev., vol.122, no.1, 83 (1961) .

11:00am **TF-TuM10 Local Bonding Arrangements in Ge-Sb-Te Alloys for Optical Memory Applications: Correlations between Device Performance and Te and Sb Bonding***, **D.A. Baker**, M.A. Paesler, G. Lucovsky,* NC State University*; P.C. Taylor,* Colorado School of Mines

EXAFS studies of as-deposited Ge@sub 2@Sb@sub 2@Te@sub 5@ films yield Ge K@sub 1@ spectra essentially the same as previously reported. The earlier studies assumed only Te nearest neighbors, but the more comprehensive analysis of this paper indicates significant concentrations of

both Ge-Ge and Ge-Te bonds. Bond-lengths and coordinations determined from EXAFS, combined with relative bond enthalpies yield the following molecular structure: G@sub 2@Sb@sub 2@Te@sub 5@ = Ge@sub 2@Te@sub 3@ + Sb@sub 2@Te@sub 3@ with 17% of the Te-atoms 3-, rather than 2-fold coordinated. The average bond coordination, , and number of valence bonding constraints/atom, , have been determined from an extension of bond-constraint theory (BCT) that includes broken bond-bending constraints for Ge-Ge bonds. This paper addresses additional compositions to better understand the role of broken bond-bending constraints for Sb-Sb bonds that are present in alloys with Sb@sub 2@Te@sub 2@ molecular structures. Broken constraints reduce for Ge from 7 to 4.33, and Ge@sub 2@Sb@sub 2@Te@sub 5@, and optical memory alloys on the Sb@sub 2@Te@sub 3@-GeTe tie-line have ideal values of ~3.05Â±0.05. Similar decreases in occur for Sb-Sb bonds, and are important in identifying network idealicity in other GST alloys. The fraction of 3-fold coordinated Te increases from 7.1 to 25% along the Sb@sub 2@Te@sub 3@-GeTe tie-line, and the amorphous to crystalline optical transmittivity transition occurs over a narrow temperature range, 30°C, and with a different bond scaling relationship.

11:40am **TF-TuM12 Sputter Deposition of Al Doped ZnO Films with Various Incident Angles***, **Y. Sato**, K. Yanagisawa, A. Miyamura, Y. Shigesato,* Aoyama Gakuin University, Japan

Film structures or properties are heavily affected by varying incident angle of depositing particles. When sputtered particles are incident on a substrate perpendicularly, columnar structures normal to substrate surface are usually observed. However, when sputtered particles are incident on a substrate obliquely, columnar structures could be grown toward the incident angle of sputtered particles. In this study, we studied how film structure and some properties of Al doped ZnO (AZO) affected by the various incident angles of sputtered particles. AZO films were deposited on alkali-free glass heated at 200@super o@C by dc magnetron sputtering using an AZO ceramic target with substrate angles from 0 to 80@super o@. The substrate angle of 0@super o@ was defined that the direction of incident sputtered particles was normal to the substrate surface, whereas the substrate angle of 90@super o@ was defined that the one was parallel to the substrate. Film structures, electrical and optical properties of AZO films were analyzed by XRD, Hall-effect measurement and NIR-UV spectrometer. Especially, distributions of crystallographic orientations for the crystallites in the films were analyzed by using X pert-MRD (PANalytical) in details. AZO films deposited with the substrate angle at 0@super o@ showed a strong preferred orientation of c-axis normal to the substrate surface. On the other hand, AZO films deposited with the substrate angle at 80@super o@ possessed c-axis inclined corresponding to the incident angle of sputtered particles. As one of the explanations, such c-axis inclined could be caused by shadowing effect. Resistivity of AZO films decreased with increasing the substrate angle up to 60@super o@ and remained almost constant with the further increase in substrate angle up to 80@super o@. This work was partially supported by a Grant-in-Aid for the 21st COE program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

Thin Film
Room 2022 - Session TF+SS-TuA
Surface Functionalization for Selective Area ALD

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

2:00pm **TF+SS-TuA1 Surface Functionalization for Selective Area ALD***, R. Chen, J. Hong,* ***S.F. Bent,*** Stanford University **INVITED**

Atomic layer deposition (ALD) is a powerful ultra-thin film deposition method for preparing a variety of materials. Typically, the process permits nano-scale control of materials in the vertical direction. To develop the method for three-dimensional control of materials, we have been investigating an area-selective ALD technique which will enable micro- and ultimately nano-scale definition of the lateral structure. Our approach is to chemically modify the substrate surface in order to impart spatial selectivity to ALD. Our focus is on both oxide materials (e.g. HfO@sub 2@ and ZrO@sub 2@) and metals (e.g. Pt) deposited by ALD. We have investigated several different types of self-assembled monolayers (SAMs) as resists against ALD using both solution and vapor delivery methods. Oxide-coated substrates (e.g. SiO@sub 2@) have been protected using organosilane-based SAMs, and hydrogen-terminated Si and hydrogen-terminated Ge protected by reaction with alkenes or alkynes. We have followed the SAM properties as a function of molecular structure and formation time using a variety of experimental techniques and have correlated the properties of the SAMs with their efficacy as ALD resists. With the successful ALD resists, area-selective ALD has been carried out using different patterning methods to define the lateral structure. Both microcontact printing of the SAMs and selective functionalization of a SiO@sub 2@/Si structure have been used to achieve area-selective ALD. We have compared the selectivity between the two methods, and will discuss the differences in the context of the SAM resist requirements. We will also show that by choosing either silylation- or hydrosilylation-based chemical functionalization, a single patterned oxide substrate can be used for either positive or negative pattern transfer into the ALD film.

2:40pm **TF+SS-TuA3 Surface Mechanisms in Oxygen-Based Noble Metal Atomic Layer Deposition***, K.J. Park, S.M. Stewart,* ***G.N. Parsons,*** North Carolina State University

Atomic layer deposition of noble metals, including Pt, Ru, Re, and Rh is often achieved using a binary exposure sequence of metal-organic precursors and oxygen, and processes show saturation near one monolayer per growth cycle for varying oxygen exposure and for varying metal-organic exposure. The surface typically oxidizes during the oxygen exposure step, and then the metal precursor ligand is oxidized during the precursor exposure, leaving a single layer of metal deposited on the surface. We have recently observed that for the case of Ru ALD from bis-(cyclopentadienyl) ruthenium and oxygen, the growth thickness per cycle saturates at a value that depends on the extent of oxygen exposure in the ALD sequence. On-line Auger spectroscopy analysis shows that the extent of metal surface oxidation increases with the extent of oxygen exposure, suggesting that the extent of Ru ligand oxidation is determined by the amount of oxygen available at the surface. This is consistent with the observed increase in Ru film growth/cycle during the Ru(Cp)2 exposure step. This dependence of film growth/cycle on oxygen exposure can explain the previously observed pressure dependence of growth thickness per cycle during Ru deposition which is not expected in an ALD process. We believe these observations lead to new insights into methodologies to significantly expand and control the process window and nucleation in Ru ALD, and this can likely be extended to other noble metal ALD processes.

3:00pm **TF+SS-TuA4 Atomic Layer Deposition of Hafnium Silicate Gate Dielectric Layers***,* ***A. Delabie,*** *G. Pourtois, M. Caymax, S. De Gendt, L.-A. Ragnarsson, M.M. Heyns,* IMEC, Belgium*; Y. Fedorenko, J. Swerts, J.M. Maes,* ASM Belgium **INVITED**

Downscaling Equivalent Oxide Thickness (EOT) by decreasing the physical thickness or increasing the permittivity of the gate dielectric is required to reach the CMOS (sub) 45 nm node performance specifications. Hafnium silicate is widely investigated as a high-k gate dielectric due to its thermodynamic stability with silicon. In this work, we study the growth mechanism of hafnium silicate Atomic Layer Deposition (ALD) by combining experiment and theory. Thorough understanding of the ALD mechanisms can contribute to improved film quality and downscaling. The hafnium silicate reaction cycle consists of well separated precursor reactions in the sequence (H@sub 2@O/HfCl@sub 4@)@sub x@/(H@sub 2@O/X)@sub y@ with X a HfCl@sub 4@ compatible Si precursor.@footnote 1@ The composition of hafnium silicate is varied by adjusting x and y. Hafnium silicate films are characterized ex-situ by Rutherford Backscattering (RBS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOFSIMS) and X-Ray Photoelectron Spectroscopy (XPS). Electrical properties are evaluated on TaN gated capacitors. The interaction of ALD surface sites with the precursors is investigated by Density Functional Theory based calculations on cluster models. Our insight in the ALD reaction mechanism allows optimization of the hafnium silicate deposition, resulting in a leakage current reduction of one order of magnitude. @FootnoteText@ @footnote 1@ will be revealed at the conference .

3:40pm **TF+SS-TuA6 Mechanistic Details of TiN Atomic Layer Deposition (ALD) Processes***, H. Tiznado,* ***F. Zaera,*** University of California, Riverside

The reaction mechanisms of atomic layer deposition (ALD) processes have been characterized by a combination of surface sensitive techniques. In this talk our study of the deposition of TiN films from TiCl@sub 4@ and ammonia will be used to illustrate the power of this approach. First, each of the two half steps comprising the ALD process was studied independently. It was found that exposure of the surface to TiCl@sub 4@ leads to the initial deposition of titanium in the +3 oxidation state; only at a later stage most of it appears in the +4 state expected for TiCl@sub 4@. Also, the Cl:Ti final ratio at the end of the TiCl@sub 4@ deposition reaches a value of ~ 3.5, indicating some chlorine removal. Subsequent treatment with ammonia removes most of the remaining Cl and deposits the required nitrogen, as expected. Nevertheless, some chlorine is still seen on the surface, most likely because of HCl readsorption. The buildup of thicker films was tested by performing multiple cycles with alternating exposures to TiCl@sub 4@ and NH@sub 3@. Similar films could be deposited on glass and on W, Ni and Cu foils. Interestingly, depth-profiling studies show that the resulting film consists of a Ti@sub 3@N@sub 4@ layer on top of TiN. This suggests that the reduction of titanium takes place during the exposure of the surface to TiCl@sub 4@, not NH@sub 3@, and that it is the first reaction of the cycle the rate limiting in the whole ALD process.

4:00pm **TF+SS-TuA7 Surface Processes of Plasma-Assisted Atomic Layer Deposition***,* ***W.M.M. Kessels,*** Eindhoven University of Technology, The Netherlands, Netherlands **INVITED**

Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin films with a high conformality and with precise thickness control. The extension of the technique with plasma processes (i.e., plasma-assisted ALD) provides several potential advantages over thermal ALD such as an enhanced growth rate, improved material properties, and lower deposition temperature. However mechanistic studies are scarce and detailed insight into the surface processes of plasma-assisted ALD is still lacking while being imperative for further process optimization. In this contribution surface processes during plasma-assisted ALD are addressed on the basis of studies of oxide (Al@sub 2@O@sub 3@, HfO@sub 2@) and metal nitride (TiN, TaN) film growth employing several in situ diagnostics. From in situ spectroscopic ellipsometry and quartz crystal microbalance measurements precursor adsorption reactions are discussed addressing the formation of surface species, substrate-inhibited growth, and film nucleation. The surface reaction products as well as the consumption of precursor and plasma species are discussed from time-resolved mass spectrometry studies as well as from optical emission spectroscopy, a unique feature provided by the plasma process. On the basis of the results, the paradigms for plasma-assisted ALD are reviewed and differences with thermal ALD processes are discussed.

Thin Film
Room 3rd Floor Lobby - Session TF-TuP
Thin Film Poster Session

TF-TuP1 Effect of Particle Transport Process on Mode Transition and Film Composition during Reactive Sputtering of Metal Oxides*, **T. Nakano**, Y. Iimura, S. Baba,* Seikei University, Japan

Target mode transition and film composition during the DC reactive sputter deposition process has been studied for various metal oxides, especially focused on the effect of the particle transport process of sputtered atoms. Si, Ti and Nb targets were sputtered in a gas mixture of argon and oxygen. These targets were chosen to elucidate the effect of the atomic mass on the reactive sputtering through the particle transport process of sputtered atoms. At a fixed argon gas flow rate of 20 sccm, evacuation valve was throttled to achieve a gas pressure between 0.5~2 Pa. At this fixed pumping speed, oxygen flow rate was modified and the transition between the metal and oxide modes was monitored by the cathode voltage. Deposition rate was measured in-situ by a quartz crystal monitor, and the composition of deposited films was measured by X-ray photoelectron spectroscopy. In case of Si sputtering, the mode transition occurred at distinctly lower oxygen flow rate as the pumping speed was decreased and argon gas pressure increased. In addition, at each pumping condition, the oxygen content of deposited film was saturated at lower flow rate than that of the mode transition, which means that the film was totally oxidized while the target was in the metal mode. These results cannot be explained by the Berg's model@footnote 1@ in which the metal to oxide mode transition accompanies the oxidization saturation of deposited metal atoms on the chamber wall, and the reduction of the oxygen gettering. On the contrary, these effects were much more subtle in heavy Nb case. It can be ascribed to the transport behavior of Si sputtered atoms which are lighter than argon atoms and are easily backscattered by them. At higher gas pressures, Si sputtered atoms tend to redeposit on (or around) the target surface, which results in the reduction of both the total gettering speed and its uniformity. @FootnoteText@ @footnote 1@ S. Berg and T. Nyberg: Thin Solid Films vol. 476 (2005) 215.

TF-TuP2 Hydrogen Uptake in MgO Thin Films Grown by Reactive Magnetron Sputtering*, **J.S. Agustsson**,* Mentis Cura ehf, Iceland*; B.V. Agustsson,* Royal Institute of Technology, Sweden*; A.K. Eriksson,* University of Iceland*; K.B. Gylfason,* Lyfjathroun Biopharmaceuticals, Iceland*; S. Olafsson,* University of Iceland*; K. Johnsen,* Mentis Cura ehf, Iceland*; J.T. Gudmundsson,* University of Iceland, Iceland

We explore the hydrogen uptake in MgO thin films, grown by reactive magnetron sputtering. When introducing hydrogen during the growth of MgO thin films, the electrical properties dielectric are affected. A lattice matched heteroepitaxial metal--insulator--metal (MIM) structure was grown. CrMo alloy was used as the metal electrode and the composition chosen so that the film is lattice matched to the substrate when the direction of the alloy is parallel to the direction of the substrate. The hydrogen uptake was determined by nuclear resonance analysis measurements using @super 1@H(@super 15@N,@alpha@@gamma@)@super 12@C. The electrical properties of the MgO films were assessed by impedance spectroscopy. We relate hopping conduction observed in the MgO to the introduction of hydrogen into the sputtering chamber during the growth of the dielectric films.

TF-TuP3 Structure and Electronic Properties of Molybdenum Oxide Thin Films Fabricated by DC Magnetron Sputtering*, **V.V. Atuchin**, B.M. Ayupov, T.A. Gavrilova, T.I. Grigorieva, V.A. Kochubey,* Institute of Semiconductor Physics*; C.V. Ramana, U. Becker,* University of Michigan

Molybdenum oxide (MoO@sub 3@) exhibits interesting structural, chemical, electrical, and optical properties, which are dependent on the growth conditions and the deposition technique. In the present work, MoO@sub 3@ films were produced by DC magnetron sputtering using a Mo target under varying conditions of substrate temperature (T@sub s@) and oxygen partial pressure (pO@sub 2@). The effect of Ts and pO@sub 2@ on the structure and electronic properties of Mo oxide films was examined in detail using reflection high-energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and laser ellipsometry (Î» = 0.6328 Î¼m) measurements. The analyses indicate that the microstructure and phase of sputtered Mo oxide films is sensitive to T@sub s@ and pO@sub 2@. The growth conditions were optimized to produce stoichiometric and polycrystalline MoO@sub 3@ films. A uniform refractive index profile with n = 1.59 and optical absorption k ~ 0.001 was found for a typical textured MoO@sub 3@ film. The results will be presented and discussed in detail to establish a correlation between the microstructure and optical properties of Mo oxide films.

TF-TuP4 Transparent Conducting AZO Thin Films Prepared by Magnetron Sputtering with DC and RF Power Applied in Combination*, **T. Minami**, Y. Ohtani, T. Miyata, T. Kuboi,* Kanazawa Institute of Technology, Japan

In this paper, we describe the preparation of transparent conducting Al-doped ZnO (AZO) thin films using new deposition techniques that added an rf component to dc magnetron sputtering (dc+rf-MSP) with or without the introduction of hydrogen gas into the deposition chamber. AZO films were deposited using a planar magnetron sputtering apparatus with a sintered AZO target. The dc+rf-MSP depositions were carried out in a pure Ar or an Ar+H@sub 2@ (0-3%) gas atmosphere at a pressure of 0.4 Pa by adding an rf component (13.56 MHz) to a constant dc power of 80 W. The deposition rate in dc+rf-MSP incorporating an rf power of 100 W was approximately 57 nm/min, an increase from approximately 35 nm/min in dc magnetron sputtering (dc-MSP) with a dc power of 80 W; the sputter voltages in these depositions were approximately 170 V and 365 V, respectively. In addition to improving the AZO thin film deposition rate and lowering the sputter voltage, it was found that dc+rf-MSP depositions with or without the introduction of hydrogen gas also resulted in improving the electrical property distribution on the substrate surface and reducing the damage on the deposited films and substrates caused by the bombardment of particles during the sputtering deposition. A low resistivity on the order of 10@super -4@@ohm@cm and an improved resistivity distribution could be obtained in AZO thin films deposited on substrates at low temperatures below 200@super o@C by dc+rf-MSP with the introduction of hydrogen gas; the necessary amount of added hydrogen gas increased as the substrate temperature was decreased.

TF-TuP5 Effect of Target Density and Sputtering Parameters on Film Structure and Resistivity of Tungsten*, **C.F. Lo**,* Praxair Surface Technologies - MRC

Low resistivity is desired for the tungsten film used for the diffusion barrier, via and gate material in semiconductor devices. To achieve low resistivity, purity and film structure are the two factors needed to be controlled. It is known that higher the purity, better the performance of the tungsten film. On the other hand, it is not clear how the film structure that may effect the resistivity. In this study, we controlled the target density and ran a design of experiment for the sputtering power and gas pressure to obtain different film structures. Using the four-point probe, X-ray diffractometer and scanning electron microscope, the relationship between the film structure and resistivity was established. Key words: Tungsten, diffusion barrier, via, gate material, semiconductor, target density, Sputtering, film structure, resistivity.

TF-TuP6 Combinatorial Synthesis and Characterization of Magnetic Fe@sub x@Al@sub 1-x@N Thin Films for Biomedical Applications*, **Y. Guan**, P.D. Rack,* The University of Tennessee, Knoxville*; X. Wang, Y. Liu,* Alfred University*; K.D. Sorge,* Florida Atlantic University

The electromagnetic behavior of nano-scale layered and particulate structures of Fe@sub x@Al@sub 1-x@N materials have potential applications in medical device technologies. Iron and aluminum have been co-sputtered in an Ar-N@sub 2@ ambient to form a combinatorial array of Fe@sub x@Al@sub 1-x@N thin films. Using this approach, we are able to achieve an Fe/(Fe+Al) cation range from ~ 12-60 % over 10 cm long substrate. The deposited films were annealed in vacuum at various temperatures and the films have been characterized by x-ray photoelectron spectroscopy, energy dispersive x-ray spectroscopy, scanning electron microscopy and x-ray diffraction. Furthermore, the ac and dc magnetic properties of the films have been characterized. In this presentation, we will describe in detail the reactive combinatorial Fe@sub x@Al@sub 1-x@N sputtering approach. The chemical, structural, and morphological properties as a function of Fe/(Fe+Al) content will be demonstrated and correlated to the measured dc and ac magnetic properties. *This work was sponsored by Biophan Technologies.

TF-TuP7 Investigation of Luminescence and Microstructure of Sputter-deposited Zinc Gallate Thin Films Doped with Manganese*, **J.H. Kim**,* Chungbuk National University, Korea*; P.H. Holloway,* University of Florida

Luminescent characteristics and microstructural properties of manganese-doped zinc gallate (ZnGa@sub2@O@sub4@:Mn) thin films have been studied. The ZnGa@sub2@O@sub4@:Mn films were prepared by radio

frequency (RF) planar magnetron sputtering from a 2 mol% Mn-doped ZnGa@sub2@O@sub4@ target in an oxygen-argon mixture atmosphere. The half-stack alternating-current thin-film electroluminescent (ACTFEL) devices were constructed using an inverted single-insulating layer structure, ITO/ZnGa@sub2@O@sub4@:Mn/BaTiO@sub3@/Al. First, approximately 600 nm of ZnGa@sub2@O@sub4@:Mn was deposited on the 200µm-thick BaTiO@sub3@ ceramic substrates. The samples were then annealed at 800°C in air for 3 hours, followed by ITO sputter deposition and Al metal evaporation. The fabricated devices were tested using a bipolar trapezoidal drive waveform with rise and fall times of 5 µs and a hold time of 30 µs. The drive frequency was 2.5 kHz (5k light pulses per second). Green emission peaked at 508 nm was obtained from the device and it was attributed to the @super4@T@sub1@ - @super6@A@sub1@ transition in Mn@super2+@ ion. The color coordinates of the emission were x=0.11 and y=0.7 in the CIE chromaticity diagram. The threshold voltage for the emission was ~100 V and the brightness was 28 cd/m@super2@ measured at 30 volts above the threshold voltage. The photoluminescent and cathodoluminescent characteristics of the ZnGa@sub2@O@sub4@:Mn films deposited on Si substrates were also investigated. The emission peaks of both PL and CL were at ~505 nm, and the emission spectra were identical to the EL spectra. Both PL and CL brightness was strongly correlated with the microstructural differences in ZnGa@sub2@O@sub4@:Mn films produced by difference in gas pressure during sputter deposition.

TF-TuP8 Compositional Characterization of High-k Dielectric Material via XPS and TOF-ERDA, *D. Martin, J. Enlund,* ***O. Kappertz****, J. Jensen,* Uppsala University, Sweden

New materials with a high dielectric constant (high k) are needed for future integrated capacitor structures. Aluminium oxy nitride (AlON) is potentially one such material. 150 nm thick AlON thin films are grown via reactive dc magnetron sputtering in an oxygen and nitrogen ambient. The film composition depends on the ratio between the two gas flows, although this relation is highly nonlinear. This complex processing behaviour requires careful analysis of the stoichiometry of the deposited films. Furthermore, the functionality of the films also depends both on the stoichiometry and the impurity levels, making chemical analysis even more important. The film composition was analyzed with both X-ray photoelectron spectroscopy (XPS) in combination with sputter depth profiling and time-of-flight elastic recoil detection analysis (TOF-ERDA), revealing a variation in film composition through the whole film thickness. These findings in the film composition are closely matched between the analysis methods. The methodology of the analysis methods and both their individual and complementary benefits are discussed. Finally, the above observation of the varying stoichiometry indicates that the films are deposited under non-steady state conditions, that is the deposition process does not reach steady state for such film thicknesses.

TF-TuP9 Transparent Conducting Amorphous ZnO-In@sub 2@O@sub 3@ Films Deposited on PC or PET Substrate, *T. Moriga,* ***H. Suketa****, K. Takita, D. Takada, K. Shimomura, K. Inoue, K. Murai, K. Tominaga,* The University of Tokushima, Japan

Transparent conductors on organic polymer substrates have many applications, such as in plastic liquid crystal display devices, flexible electro-optical devices and so on. However, the deformation temperature of organic polymer substrates such as polycarbonate (PC) and polyethylene terephthalate is usually as low as ca. 100°C, low-temperature depositions should be performed to prevent the deformation of the films. We have reported that the amorphous ZnO-In@sub 2@O@sub 3@ films on a glass substrate deposited by simultaneous DC magnetron sputtering with facing dual targets showed the minimum resistivity of 2x10@super -4@@ohm@cm at substrate temperatures of 150°C or the less. Amorphous ZnO-In@sub 2@O@sub 3@ films with low resistivity comparable to ITO films will have an advantage over ITO films in low-temperature depositions. Two disk targets of ZnO and In@sub 2@O@sub 3@ were sputtered simultaneously in Ar gas at a pressure of 1mTorr, and electric current ratio @delta@=I@sub Zn@/(I@sub Zn@+I@sub In@) was adopted as a deposition parameter to change film composition. Discharge current of each target was changed from 0 to 80mA in order to change the contents of Zn and In in the film. The amorphous films both on the PC and PET substrates showed the minimum resistivity at @delta@=0.50, which corresponds to the film composition [Zn]/([Zn]+[In])=0.33. A monotonous increase in resistivity with an increase of zinc content was observed while the films maintained amorphous.

TF-TuP10 Thermophysical Properties and Electrical Properties of Amorphous In@sub 2@O@sub 3@-ZnO Films*,* ***T. Ashida****, A. Miyamura, Y. Sato, Y. Shigesato,* Aoyama Gakuin University, Japan*; T. Yagi, N. Taketoshi, T. Baba,* National Institute of Advanced Industrial Science and Technology, Japan

Thermal diffusivity of Indium Zinc Oxide (IZO) thin films with thickness of 200nm has been measured using newly developed nanosecond thermoreflectance system.@footnote 1@ IZO films sandwiched by molybdenum (Mo) films were prepared on fused silica substrate by dc magnetron sputtering using IZO and Mo multi-targets. The IZO layers were deposited under different oxygen or hydrogen flow rate of 0-10% or 0-20%, respectively. Such Mo/IZO/Mo layered structure was fabricated without exposure to the atmosphere between each depositon. The Mo films with thickness of 70 nm are necessary because the wavelengths of pulse laser used in this study are 782 nm and 1064 nm, at which wavelength IZO films are transparent. The resistivity, carrier density and hall mobility of IZO films ranged from 4.2x10@super -4@ to 22.7@ohm@cm, from 2.6x10@super 16@ to 4.2x10@super 20@ cm@super -3@, from 10 to 51 cm@super 2@/Vs, respectively. The interface between the Mo films and the fused silica substrate was irradiated by nanosecond laser pulse. Heat generated by the pump laser pulse diffuses toward the top Mo surface across the three-layered films. Then the temperature changes at the Mo film surface, which was probed by reflectance of another nanosecond laser pulse. The heat diffusion time changed significantly with changing the gas flow rate. The thermal diffusivity of the IZO films deposited at the unheated substrate, under total gas pressure of 0.7 Pa was 1.2x10@super -6@ m@super 2@/s. This thermal diffusivity was approximately, equivalent that of amorphous ITO films.@footnote 2@ Based on Wiedemann-Franz law, approximately 50% of the thermal conduction was considered to be carried by free electrons. @FootnoteText@ @footnote 1@T. Baba, N. Taketoshi, K. Hatori, K. Shinozato, T. Yagi, Y. Sato, Y. Shigesato, Proc. 25th Jpn. Symp. Thermophys. Prop., (2004, Nagano) pp.240-242.@footnote 2@T.Yagi, K. Tamano, Y. Sato, N. Taketoshi, T. BAba and Y. Shigesato: J. Vac. Sci. Technol. A, 23(4), (2005), pp. 1180-1186.

TF-TuP11 Transparent Conductive Oxide Films of In2O3-ZnO with Additional Ga2O3 Impurities*,* ***K. Tominaga****, D. Takada, H. Suketa, K. Takita, K. Shimomura, K. Inoue, K. Murai, T. Moriga,* The University of Tokushima, Japan

In2O3-ZnO films have amorphous phase. These films are expected as a transparent conductive oxide (TCO) film in optoelectronics. We deposited In2O3-ZnO films with additional Ga2O3 impurities and investigated the influence of Ga2O3 on TCO film properties. Using a facing target sputtering system of ZnO:Ga and In2O3 targets, two targets were sputtered simultaneously in Ar gas at 1 mTorr, and electric current ratio @delta@=IZn/(IZn+IIn) was adopted as a deposition parameter to change film composition. Discharge current of each target was changed from 0 to 80 mA in order to change the contents of Zn and In in the film. Compositional ratios of Zn/(Zn+In) in films were nearly equal to @delta@ value according to the data estimated by X-ray fluorescence analysis. Four ZnO:Ga targets containing 0,4.5,6 and 7.5 wt% Ga2O3 were used for Ga adding in the films. In2O3-ZnO films in amorphous phase were deposited between Zn/Zn+In=0.27-0.57. The lowest resistivity in amorphous In2O3-ZnO was 2.7x10-4 Î©cm. The resistivity for the amorphous film was low between @delta@=0.27 and 0.5, but the resistivity for homologous film increased rapidly between @delta@=0.5. and 0.8. For amorphous films at @delta@=0.33 and 0.5, optical bandgap energy for the film of @delta@=0.33 shifted to higher energy side for that of @delta@=0.5. Similarly, with increasing the Ga2O3 content, optical bandgap energy shifted to a higher energy side.

TF-TuP12 High Resistive ZnO Thin Films Sputtered from ZnO@sub 2@-doped ZnO Target*,* ***K. Wasa****,* Kyoto University, Japan*; Y.J. Shan,* Utsunomiya University, Japan*; I. Kanno, T. Suzuki,* Kyoto University, Japan

Thin films of ZnO were fabricated on a fused silica substrate by a direct sputtering from ZnO powder target. The sputtering was done typically at the sputtering argon gas pressure: 0.5Pa, the deposition temperature: 500@super o@C, the sputtering rf power: 90W for 4 inch target, and the deposition time: 90 min. The film thickness was 1.8µm with the deposition rate of 1.2µm/hr. The sputtered films showed c-axis highly oriented ZnO thin films. The dark resistivity of the ZnO thin films was 5x10@super 3@ ohm-cm and/or conductivity was 0.2x10@super -3@ /ohm-cm at room temperature. The effect of doping of ZnO@sub 2@ was investigated using mixed powder target of ZnO and ZnO@sub 2@(15mol %). It was found the doping of ZnO@sub 2@ reduced the deposition rate. Typical deposition rate was 0.9µm/hr. The electrical resistivity increased by three orders in a

magnitude. High resistivity of 1.6x10@super 6@ohm-cm was obtained by the direct sputtering from the ZnO@sub 2@-doped ZnO target in a pure argon atmosphere. The sputtering mode will be changed by the doping of ZnO@sub 2@ since the deposition rates remarkably decreased by the doping. The high energetic oxygen atoms sputtered from the ZnO@super 2@ will play important roll for the oxidization of the sputtered ZnO resulting in the increase of resistivity of sputtered ZnO thin films.

TF-TuP13 Abnormal Resistivity Change in Indium-Tin Oxide Films*, **S. Takayama**,* Hosei University, Japan

Indium tin oxide (ITO) films are well known as a transparent conducting film and used for various display devices. Their conducting characteristics are contributed by free electrons arising from four valent doping Sn substituting in the In lattice and doubly charged oxygen vacancies. The structure of ITO films can be changed from amorphous to crystal phase depending on the process conditions. In this report, to get further insight into the conducting properties of ITO films, the in-situ resistivity measurement of various structures of ITO films was performed on annealing in a various flowing gas atmosphere (air, O@sub 2@, H@sub 2@). It was found that an abnormal increase of restivity showing a sharp peak was observed at 220-250@degree C@ for the fully and partially amorphous ITO. The temperatures at the peak were shifted to a higher range in the order of air, H@sub 2@, and Osub 2@flowing gas atmospheres. The Hall measurement revealed that the carrier density and Hall mobility both sharply decrease at the resistivity peak. The activation energy of the abnormal resistivity change was measured to be 0.67-1.7 eV by using the Kissinger's method. The activation energy thus measured are different depending on the annealing atmosphere. The X-ray diffraction profiles and TEM observations revealed that the crystallization took place at ~180@degree C and continuously progressed with further increase of annealing temperature. Note that any further visible structure changes were not observed after the peak resistivity. Taking into account the fact that the activation energy of an oxygen vacancy in an In oxide is reported to be about 5eV which is much higher than the present measured values, and also an In in amorphous ITO films is reported to play a large role of the amorphous to crystalline phase transition at ~150@degree C@, the realignment of Sn-O bond to generate a locally ordered structure most likely responsible for the present abnormal resistivity change observed.

TF-TuP14 Multi-layered Depleted Uranium and Gold Coatings on Cylindrical Substrates*, **H. Wilkens**,* General Atomics*; J.L. Klingmann,* Lawrence Livermore National Laboratory*; A. Nikroo, D.R. Wall, J.R. Wall,* General Atomics

The indirect drive approach to inertial confinement fusion (ICF) requires that a hydrogen-filled target capsule is surrounded by a cylindrical cavity called a hohlraum which converts the incident laser energy to x-rays that drive the implosion of the target.@footnote 1@ The efficiency of the x-ray conversion increases with the addition of depleted uranium (DU) to a Au-only hohlraum by making the wall more opaque to the driver energy.@footnote 2@ To manufacture these hohlraums, multiple alternating layers of 30 nm DU and 8 nm Au are sputter deposited onto rotating cylindrical substrates, for a total thickness of 2-7 µm.@footnote 3@ These cylindrical substrates, 5.1 mm in diameter, are micro-machined to less than 25 nm rms roughness. A structural gold layer is electroplated after sputter deposition, then the material is back-machined away at the edges to expose the underlying mandrel, which is leached away leaving a free-standing hohlraum. DU oxidizes rapidly in air (0.5 nm/min),@footnote 4@ so measures must be taken to ensure that it is encapsulated. Oxidation is problematic for two reasons. First, the presence of oxygen in the hohlraum increases the heat capacity, thus canceling the efficiency gains made with the addition of the DU. Second, the DU lattice increases by approximately a factor two upon oxidation, resulting in catastrophic structural failure. Novel production techniques will be presented, along with Auger electron spectroscopy data confirming the absence of oxygen within the multi-layered film. @FootnoteText@ @footnote 1@ Rosen, M., Phys. Plasmas, 6, 1690 (1999).@footnote 2@ Orzechowski, T., et al., Phys. Rev. Lett. 77, 3545 (1996).@footnote 3@ Wilkens, H., et al., Progress in Coating Multi-layered Cocktail Hohlraums. To be published in Fus. Sci. Technol.@footnote 4@ Allred, D., et al., Highly Reflective Uranium Mirrors for Astrophysics Applications, X-ray Mirrors, Crystals and Multilayers, Proc. SPIE 4782, 212, 2002.

TF-TuP15 Nano-Composite Amorphous Carbon (a-C) Thin Films to Improve the Tribological Properties*, **Y.S. Park**, H.J. Cho, B. Hong,* Sungkyunkwan University, Korea

In this work, we studied the change in the tribological properties of amorphous carbon deposited over Si substrate with Ti and a-C:Ti as the adhesive layer. The nano-composite amorphous carbon thin films were prepared by closed-field unbalanced magnetron sputtering method using the graphite and the titanium as targets. We tried various structure for the interlayer under hydrogenated amorphous carbon (a-C:H) film to improve the tribological properties and have observed characteristic changes in the nano-composite structure. In addition, Ti layer (a-C:H/Ti/Si and a-C:H/a-C:Ti/Si) improved the adhesion between the a-C:H film and the substrate and the incorporation of the Ti (a-C:Ti and a-C:H:Ti) in a-C and a-C:H films improved the lubricant properties. We selected the laminated structure in order to minimize the demerits observed in a-C:H/Ti/Si and a-C:H/a-C:Ti/Si structures, such as low hardness and high stress. With Ti-doped a-C and a-C:H in laminated structure, the tribological properties were observed to be improved with high hardness over 29 GPa, high elastic modulus over 235 GPa and a smooth surface below 0.8 nm.

TF-TuP16 Preliminary Study of CuIn@subx@B@sub1-x@Se@sub2@ Absorber Materials*, **N.J. Ianno**, T. Santero, R.J. Soukup,* University of Nebraska-Lincoln

One of the most useful thin film solar cell materials is CuInSe@sub2@ (CIS). However, the efficiency of solar cells fabricated with CIS is limited because of the narrow band gap of the CIS material. This problem has been reduced somewhat by the substitution of Ga for some of the In. The result is a more efficient solar cell, but still of limited voltage output because changes in the band structure limit the maximum amount of Ga that be substituted. We present preliminary results on the substitution of boron for indium. Theoretically, a much smaller amount of boron is needed to obtain a band gap near the optimum level of near 1.5eV. We have estimated this percentage to be about 24%. The films are deposited on bare soda-lime glass and Mo coated soda-lime glass via planar magnetron co-sputtering and are selenized in a separate step. The deposition is accomplished by sputtering from three separate targets of Cu, In, and B. In this way we have complete control over all the constituent elements. Deposition is made under a variety of conditions by varying the deposition rate and substrate temperature. The resulting films are analyzed by a variety of methods. These methods include characterization by x-ray diffractometry, photon transmission/absorption, Fourier Transform Infrared spectroscopy and spectroscopic ellipsometry and are compared to CIS films deposited in our laboratory and CIGS films reported in the literature. We will show the effect of boron substitution on the lattice parameter and the optical band gap.

TF-TuP17 Lubricant Characteristics of Ti doped Hydrogenated Amorphous Carbon Films Prepared by Closed-Field Unbalanced Magnetron Sputtering Method*, **H.J. Cho**, Y.S. Park, B. Hong,* Sungkyunkwan University, Korea

Hydrogenated amorphous carbon (a-C:H) have been shown to have the low friction coefficient, high hardness and low abrasive wear rate. The a-C:H film according to experiments have had the maximum hardness of 25 GPa and the minimum friction coefficient of 0.1. The incorporation of Ti in a-C:H film is able to improve the electrical conductivity, friction coefficient and the adhesion to various substrates. In this study, a-C:H:Ti films were deposited on Si and steel substrates by closed-field unbalanced magnetron (CFUBM) sputtering system with two targets of carbon and titanium in Ar/C2H2 plasma. The lubricant characteristics was investigated for a-C:H:Ti deposited with DC bias voltage from 0 V to -300 V. We obtained the hardness up to 20 GPa and friction coefficient lower than 0.1. The atomic percentage of Ti related to the lubricant properties increased up to 11 % at -300 V. Also, the surface roughness and the surface energy of the films tended to reduce with the DC bias voltage. The surface roughness of the film was found to be extremely low (0.2 nm).These results might be due to the increase of the ions bombardment and Ti implantation with DC bias voltage.

TF-TuP18 Anisotropic Microstructure of PVD Coatings Caused by Anisotropy in Flux Distribution of Arriving Atoms*, S.Yu. Grachev, J.-D. Kamminga,* Netherlands Institute for Metals Research, the Netherlands*; T. Smy,* Carleton University, Canada*; G.C.A.M. Janssen, **R. Machunze**,* Technical University Delft, the Netherlands

We determined that flux angular distribution of deposited atoms from an elongated target in a dc-sputtering system is highly anisotropic. We used an aperture in front of a sample to determine the flux distribution experimentally. Monte-Carlo simulations of the deposition process agreed

with the experiment quite well. The anisotropy and the width of the flux changed with Ar pressure. It is known that the flux distribution can play a decisive role in film's microstructure formation when surface diffusion is suppressed. This condition is satisfied when deposition of a high melting point metal is carried out at room temperature. We studied the microstructure of Cr films as a function of flux angular distribution. In all cases crystallographic texture was biaxial. Texture splitting was observed in different directions depending on Ar pressure. Two types of "domains" with crystallographic orientations tilted with respect to each other develop in thick films (>1µm). We demonstrate that the flux angular distribution is responsible for the texture splitting.

TF-TuP19 Comparative Study on Super-Hardcoating Materials between Ti@sub x@W@sub y@N and Ti@sub x@Al@sub y@Si@sub z@N Deposited by Reactive Co-Sputtering*, M. Yamaguchi, A. Miyamura,* Aoyama Gakuin University, Japan*; K. Hattori,* National Institute of Advanced Industrial Science and Technology, Japan*; T. Aoki, Y. Sato, Y. Shigesato,* Aoyama Gakuin University, Japan

TiN@sub x@ is one of the most promising materials for hardcoating technology. Nowadays we can make them more specialized properties (i.e.; harder, higher melting point, and chemically more stable) by adding some metal elements like Al, Si, W, Cr, etc. The purpose of this study is to present a comparative analysis on nano-structure and mechanical properties of Ti-W-N and Ti-Al-Si-N films, which were deposited by co-sputtering using Ti, W or Ti, Al, Si targets, respectively. The microstructure, phase and chemical composition of films were analyzed by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Electron Prove Micro Analysis (EPMA). Nano-indentation equipped with Nano Intdentation Tester with Berkovich diamond was used to measure the hardness and Young's modulus along the depth of the films. It was clarified that Ti-W-N films consisted of nanocrystalline TiN@sub x@ and WN@sub x@ phase, whereas Ti-Al-Si-N films consisted of nanocrystalline TiN@sub x@ in an amorphous a-SiN@sub x@ matrix. Ti-W-N films showed hardness of 21-23 GPa depending on the compositions, whereas Ti-Al-Si-N films performed much larger hardness of 32GPa. Deposition rate of the Ti-W-N films decreased with increase in rf substrate bias power. Furthermore, concentration of Ti in the film slightly decreased with increasing rf substrate bias power, which could be attributed to the re-sputtering of Ti atoms by the Ar@super+@ ion bombardment. Average roughness (Ra) of the film surface estimated from AFM images decreased from 5.9nm to 1.3nm with the increase in the rf bias power applied on the substrate holder from 0 to 100W, which could be attributed to the secondary nucleation enhancement by the ion bombardment during the film growth. This work was partially supported by a Grant-in-Aid for the 21@super st@ COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

TF-TuP20 Target Surface Compound Layers Formed by Reactive Sputtering of Si Target in Ar+O@sub 2@ and Ar+N@sub 2@ Mixed Gases*, Y. Abe, T. Takisawa, M. Kawamura, K. Sasaki,* Kitami Institute of Technology, Japan

Reactive sputtering is a useful method to form compound thin films by sputtering a metal target in reactive gas atmosphere. The surface state of the metal target change with sputtering conditions and makes important effects on deposition rate, chemical composition of the deposited films, and plasma state. However, quantitative studies on the surface state of the target were scarce. In this study, Si target was sputtered in Ar+O@sub 2@ and Ar+N@sub 2@ mixed gases and SiO@sub 2@, and Si@sub 3@N@sub 4@ thin films were deposited using a RF magnetron sputtering system. The maximum thickness of the oxide and nitride layers formed at the surface of the Si target was measured by ellipsometry. The oxide and nitride layer thicknesses formed at the target surface were found to be 7 nm and 4 nm, respectively. The rate of oxide layer formation at the surface of the Si target in oxygen plasma is thought to be higher than that of nitride layer in nitrogen plasma.

TF-TuP21 Heat Treatment Effect in Palladium Oxide Composite Films Fabricated by Reactive Ion Beam Sputter-Deposition*, T. Ichinohe, S. Masaki,* Tokyo National College of Technology, Japan*; M. Iwase,* Tokai University, Japan*; K. Kawasaki,* TDY, Co, Ltd., Japan

In this study, palladium (Pd) oxide composite films containing metal Pd were fabricated by reactive ion beam sputter-deposition, changing the substrate temperature (T@sub sub@) from RT to 400@super o@C. According to X-ray diffraction analyses, the mixture of PdO(002) and Pd(111) was observed in the film formed at T@sub sub@=200@super o@C, on the other hand, only a metal Pd structure was observed in the film formed at T@sub sub@=400@super o@C. The samples formed at T@sub sub@=200@super o@C and at 400@super o@C showed positive type conduction with a resistivity of 4x10@super -4@ @ohm@cm and negative type with 3x10@super -5@ @ohm@cm in as-deposition, respectively. The structure of both samples obviously changed to PdO(002), the resistivity also increasing up when the samples were oxidized over 400@super o@C. After oxidation at 600@super o@C, both samples showed p type conduction and relatively higher resistivity (1x10@super -2@ @ohm@cm). The absorption edge changed from 1.5 to 2.3 eV after oxidation up to 600@super o@C. On the contrary, the structure and the resistivity of T@sub sub@=200@super o@C and 400@super o@C almost did not change when the samples were annealed under nitrogen atmosphere, except at 600@super o@C in T@sub sub@=200@super o@C. The resistivity in the sample of T@sub sub@=200@super o@C slightly decreased after annealing at lower temperature than 600@super o@C and increased to very large value as same as insulator over 600@super o@C. The absorption edge was too high to measure in the insulating sample. This seemed to indicate that the sample changed to palladium nitride at 600@super o@C.

TF-TuP22 Theoretical and Experimental Study of Thin-Film Precursor Vaporization*, J. Peck, M.M. Litwin,* Praxair, Inc.

A variety of thin-film deposition techniques, including chemical vapor deposition (CVD) and atomic layer deposition (ALD), involve the use of liquid or solid precursors. The precursors used in both CVD and ALD processes frequently exhibit a low vapor pressure (e.g., less than 1 Torr at 25 C). The lack of high vapor pressure typically requires the use of a carrier gas to transport the precursor vapors from a delivery system to a deposition reactor. When using a carrier gas, it is a common misconception that precursor vaporization rate is governed solely by vapor pressure. Based on the kinetic theory of gases, precursor vaporization rate can be increased by using a carrier gas with higher diffusivity. For example, the vapors of a liquid or solid will reach 100% saturation (i.e., partial pressure equal to vapor pressure) faster in the presence of helium, compared to argon. This phenomenon can be exploited to increase the productivity of a film forming process by utilizing precursor/carrier gas mixtures with the maximum diffusivity, to reduce the time required to deposit a specified film thickness. To determine the effect of carrier gas diffusivity on precursor vaporization rate, experiments were performed using a flow-cell vaporizer. These experiments confirmed that the vaporization rate of tetradecane increased by greater than 50% using helium, compared to argon. In addition, experiments performed using naphthalene will also be presented. The naphthalene experiments provide useful insight into the vaporization behavior of solid precursors.

TF-TuP23 Film Improvement of ALD TaN Layers by Application of Additional Energy*, D. Schmidt, C. Hossbach, M. Albert,* Technische Universitaet Dresden, Germany*; S. Menzel,* Leibnitz Institute for Solide State and Materials Research Dresden, Germany*; J.-W. Bartha,* Technische Universitaet Dresden, Germany

TaN is extensively used as diffusion barrier in copper interconnects and might be considered as deep-trench electrode material. These applications require specific material properties; such as low resistivity, high density, low concentration of impurity, in conjunction with the high uniformity inherent to ALD processes. The self-saturating chemical reactions between the gaseous precursor molecules and the solid surface, favour the Atomic Layer Deposition as an excellent method for depositing highly precise and conformal coatings. Tantalum Nitride thin films have been deposited and studied by using tertiarybutylimidotris(diethylamido)tantalum (TBTDET) as organometallic precursor and ammonia as reducing agent in a conventional ALD. The resulting films show a low density of 8g/cm@super 3@ and a high resistivity of more than 1e+05Âµ@ohm@-cm. In comparison we studied methods which supply additional energy for the formation of the film. This includes plasma enhancement of the process (direct as well as remote) or thermal post processing (w/o gas environment). We could show that films deposited with PEALD feature a better conductivity of 1e+03Âµ@ohm@-cm, however several problems are associated with this technique. An alternative plasma enhancement technique, the remote-plasma-assisted ALD (RPALD) is under investigation. By the application of a post process anneal without breaking the vacuum, we could achieve an improvement in film density up to 10,8g/cm@super 3@, in resistivity down to 1e+03Âµ@ohm@-cm and a reduction of the oxygen content of 50%. The impact of the specific deposition conditions as well as additional procedures on film properties are characterized with in Situ metrology like Ellipsometry and Quartz Crystal Microbalance and of course remote analytic techniques including Atomic Force Microscopy, X-ray Photon

Spectroscopy, X-ray Reflectivity/Diffraction and Transition Electron Microscopy.

TF-TuP24 Device-Quality SiO@sub 2@ Dielectric Film Formation using UV-light Excited High Purity Ozone and Organic Silicon Source at 200 @super o@C, ***N. Kameda,*** *T. Nishiguchi, S. Saitoh, T. Noyori, Y. Morikawa, M. Kekura,* Meidensha Corporation, Japan*; H. Nonaka, S. Ichimura,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

It has been strongly required recently to deposit high quality silicon dioxide (SiO@sub 2@) films at lower than 400 @super o@C for the formation of the dielectric film of TFT on low-cost glass or plastic. Thermal CVD using organic silicon source gas and ozone gas O@sub 3@ with concentrations of some 10 vol.% is one of the candidates for the formation. However, insufficient chemical reaction of ozone with the silicon source gas at lower than 400 @super o@C is known to result in rapid decline of the deposition rate as well as the incorporation of impurities such as carbon or OH in the film, decaying the film properties as a dielectric film. The solution for this is to use excited oxygen atom O(1D) that is known to be chemically more reactive than O@sub 3@ to organic materials. We applied the process that irradiates an ultra-violet (UV) light (>210nm) in low pressure (~100 Pa) highly concentrated (>90vol.%) O@sub 3@ (HC-O@sub 3@) and hexamethyldisilazane (HMDS) mixture gas in order to make use of high chemical reactivity of O(1D) atom that is generated by photo-dissociation of O3 by UV light irradiation. To minimize the thermal decomposition of the HC- O@sub 3@ to O@sub 2@ as well as excess reaction of the HC- O@sub 3@ to HMDS gas before arriving at the process wafer, the temperature of the transfer tube of the gas mixture and a process chamber were fixed at room temperature. The dramatically increased deposition rate as well as temperature independent deposition rate between 200@super o@C and 300 @super o@C, at which almost no growth has been reported for low concentration ozone CVD, has been obtained. In addition, leakage current density through thus deposited film with the deposition rate of 10 nm/min at 200 @super o@C has been lower than 10@super -8@ A/cm@super 2@ when 2 MV/cm electric field is applied. The detailed results about the deposited film quality as well as the mechanism of the deposition process will be discussed.

TF-TuP25 Preparation and Photocatalytic Activity of CdS/TiO@subX@N@subY@ Heterojunctions, ***K. Prabakar***, *T. Takahashi, K. Takahashi, T. Nezuka,* University of Toyama, Japan*; T. Nakashima,* Kashiwa Chuo High School, Japan*; Y. Kubota,* University of Yokohama City, Japan*; A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

Currently TiO@sub2@ is the most popular semiconductor used in photocatalysis. However, TiO@sub2@ absorbs only a small fraction of solar light because of its wide band gap energy of 3.2 eV. To extend the light absorbing property of TiO@sub2@ and to enhance its photocatalytic efficiency is to dope TiO@sub2@ with nitrogen and also couple with narrow band gap semiconductors. In this coupled heterojunctions, an improvement of charge separation, increase in life time of the charge carriers and enhancement of the interfacial charge transfer efficiency could be achieved. CdS thin films were prepared by chemical bath deposition. Cadmium sulphate, thiourea and ammonium nitrate were used as precursor to deposit the CdS thin films. On the other hand, nitrogen doped TiO@sub2@ (TiO@subX@N@subY@) films are activated by visible light as well as ultraviolet radiation have been prepared by DC magnetron sputtering in an argon, oxygen and nitrogen atmosphere using titanium metal target. The band gap energy of CdS thin films was tailored between 2.1 to 2.5 eV. The substitutional nitrogen doping to TiO@sub2@ was found to be effective in decreasing the band gap of the films. The band gap energy of the as-deposited TiO@subX@N@subY@ thin films was found to be 2.8 eV. X-ray diffraction, scanning electron microscopy, atomic force microscopy and UV-VIS spectrometers were used to analyze the structural, surface morphology and optical properties of the prepared films respectively. The gaseous photocatalytic activity of CdS/TiO@subX@N@subY@ heterojunctions was studied on 2-propanol and methanol using a FTIR spectrophotometer. The photocatalytic efficiency greatly depends on the surface nature of the CdS films. The effect of preparation conditions, annealing temperature on the photocatalytic activity of CdS/TiO@subX@N@subY@ heterojunctions was studied and the results are discussed.

TF-TuP26 Ferroelectric Properties of Highly Oriented BLT Films using HfO@sub 2@ as Buffer Layers for Ferroelectric-Gate Field-Effect Transistors, *K.T. Kim, G.H. Kim,* Chung-Ang University, Korea*;* ***C.I. Lee,*** Ansan College of Technology, Korea*; C.I. Kim,* Chung-Ang University, Korea

The bismuth layer-structured ferroelectrics (BLSFs) are attractive lead-free material for ferroelectric random access memory (FeRAM) application because of its relative fatigue free character.Metal-ferroelectric-semiconductor field-effect-transistors (MFSFETs) have advantages of high switching speed, nonvolatility, and high density. However, the MFSFETs have been problem such as interdiffusion between the film and Si. To suppress them, a metal-ferroelectric-insulator-semiconductor (MFIS) structure has been demonstrated. The most important thing in developing a MFIS structure is to find a good insulator that acts as a buffer between the Si substrate and the ferroelectric material, and have relative high dielectric constants, low leakage current, good interface characteristics, and compatibility. The buffer layers of HfO@sub 2@ were deposited as a buffer layer on Si and BLT thin films were used as a ferroelectric layer. The electrical and structural properties of the MFIS structure were investigated by varying the HfO@sub 2@ layer thickness. X-ray diffraction was used to determine the phase of the BLT thin films and the quality of the HfO@sub 2@ buffer layer. AES and TEM show no interdiffusion that suppressed by using the HfO@sub 2@ film as buffer layer. The width of the memory window in the C-V curves for the MFIS structure decreased with increasing thickness of the HfO@sub 2@ layer. The experimental results show that the BLT-based MFIS structure is suitable for non-volatile memory FETs with large memory window.

TF-TuP27 Zirconia in Sputter Deposited Oxide Nanolaminate Films: Interfacial Structures, Size Effects, and Metastable Phases, ***C.R. Aita,*** *R.S. Sorbello,* University of Wisconsin-Milwaukee

The interfacial structure of ZrO@sub 2@ with its oxide partner in ZrO@sub 2@-Al@sub 2@O@sub 3@, ZrO@sub 2@-Y@sub 2@O@sub 3@, and ZrO@sub 2@-TiO@sub 2@ nanolaminate films is investigated here. The films were grown on unheated substrates by sequential reactive sputter deposition from metal targets in O@sub 2@-bearing discharges. This set of nanolaminates provides a model of interfaces formed under three different conditions for chemical cation mixing and physical atomic registry (heteroepitaxy or pseudomorphism). Bulk ZrO@sub 2@ and Al@sub 2@O@sub 3@ are insoluble. Neither interfacial cation mixing or atomic registry occurs. Al@sub 2@O@sub 3@ serves as ZrO@sub 2@ growth termination and restart layers in a nanolaminate, leading to tetragonal ZrO@sub 2@ formation in thin ZrO@sub 2@ layers via surface energy considerations. Bulk ZrO@sub 2@ and Y@sub 2@O@sub 3@ are mutually soluble and have a common fluorite-type cubic lattice. Both cation mixing and heteroepitaxy leads to needle-like mixed cation nanocrystals. TheZrO@sub 2@-TiO@sub 2@ system is more complex. Bulk (Zr,Ti)-oxide phases have an orthorhombic lattice, different from any ambient pressure phase of bulk ZrO@sub 2@ or TiO@sub 2@. Although there is a driving force for cation mixing, there is no obvious path to achieve it via formation of a crystalline substitutional solid solution with a lattice structure that is common to the end-members. However, we identify the following path: tetragonal rutile-type (P42/mnm) - orthorhombic columbite-type (Pbcn) - monoclinic baddelyite-type (P21/c) for structure evolution, unusual because it involves the formation of high pressure phases, stabilized here by the Gibbs-Thomson effect. When applied to Zr@sub x@,Ti@sub (1-x)@O@sub 2@ with increasing x where 0<x<1, what is in effect evolving is a change from a metal-oxygen coordination number of 1:6 to 1:7. Support from NSF-CMS Grant No. 9988892, AceLab discretionary funds, and a gift from BadgerMeter, Inc. is acknowledged.

Nanometer-scale Science and Technology
Room 2016 - Session NS+SS+TF-WeM

Nanotribology and Nanomechanics

Moderator: J. Harrison, U.S. Naval Academy

8:00am **NS+SS+TF-WeM1 Nanotribological Properties of Diamond-Like Carbon Thin Films: The Effect of Annealing on Nanoscale Adhesion and Friction*, D.S. Grierson*,** *A.R. Konicek, A.V. Sumant, K. Sridharan, R.W. Carpick,* UW-Madison

Developing micro- and nano-scale devices with contacting or sliding parts continues to be challenging due to the poor tribological performance of conventional materials at the micro/nanoscale. The surface-to-volume ratio at small scales is high, and therefore materials with low nanoscale adhesion, friction and wear are needed to reduce tribological failures. Additionally, in applications where materials are subjected to cyclic thermal loadings, such as nanoscale thermomechanical data storage, the structure and tribological properties must remain stable. Diamond-like carbon (DLC) thin films have exceptional physical, chemical and tribological properties at the macroscale and are promising candidates for tribologically robust micro/nanoscale devices. We have studied the surface chemistry and nanotribology of undoped, Si-containing, and F-containing DLC, and investigated how annealing these films at 300°C in air affects these properties. We used the XANES (x-ray absorption near-edge spectroscopy), a surface-sensitive probe of the core-hole perturbed local density of unoccupied states, to understand the evolution of the surface chemistry and bonding. The sp@super 3@/sp@super 2@ ratio is increased by the addition of Si but not by F. The Si-containing DLC shows increased thermal stability. Atomic force microscopy (AFM) with DLC-coated AFM tips was used to conduct self-mated nanotribology experiments. The AFM results indicate that all DLC films exhibit adhesion on the order of van der Waals forces (~0.03 J/m@super 2@), and the nanoscale adhesion and friction on the Si-containing DLC are not affected by the thermal annealing. This indicates that DLC films, particularly those doped with Si, are highly promising for nanoscale thermomechanical device applications.

8:20am **NS+SS+TF-WeM2 Spectromicroscopy of Tribochemistry: X-PEEM Characterization of Wear vs. Humidity for Ultrahard Carbon Films*, A.R. Konicek*,** *D.S. Grierson, A.V. Sumant,* UW-Madison*; N.N. Naguib, O. Auciello, J.A. Carlisle,* Argonne National Lab*; T.A. Friedmann, J.P. Sullivan,* Sandia National Labs*; J. Birrell,* Advanced Diamond Tech.*; P.U.P.A. De Stasio, R.W. Carpick,* UW-Madison

The outstanding tribological performance of carbon-based films can be seriously affected by variations in humidity. To explore the tribochemical origins of this behavior, self-mated interfaces of tetrahedral amorphous carbon (ta-C) and ultrananocrystalline diamond (UNCD) films were subjected to fretting wear in dry N2 with relative humidity values of 0%, 25% and 50%. Relative friction was measured during fretting, and the resulting wear tracks were examined with atomic force microscopy (AFM) and X-PEEM-XANES (X-ray PhotoElectron Emission Microscopy combined with X-ray Absorption Near-Edge Structure) spectromicroscopy. X-PEEM is capable of discerning chemical and bonding contrast at high spatial resolution, readily distinguishing between the wear track and the unworn film. For both films, friction increases as the relative humidity decreases. However, there are opposing trends in the behavior of graphitization and oxidation due to wear. For ta-C, as the relative humidity is decreased there is an increase in both graphitization and oxidation. This implies that the harsher wear environment has more heavily modified the carbon bonds compared to the wear at a higher relative humidity, inducing graphitization and oxidation. In contrast, the self-mated UNCD interface showed a comparative decrease in graphitization and oxidation in the wear track as the relative humidity was decreased. We will discuss changes observed in both friction and the chemical signature of the surface as the amount of relative humidity in the environment is varied. We will also discuss the relation between the amount of relative humidity in the environment and the level of graphitization that occurs in the wear track. @FootnoteText@ This work was partially supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

8:40am **NS+SS+TF-WeM3 The Role of Atomic Corrugation, Crystal Orientation, and Surface Chemical Bonding in the Nanotribology of Carbon-Based Systems*, R.W. Carpick,*** University of Wisconsin-Madison **INVITED**

A key challenge for nanotechnology lies in developing an understanding of nanotribology, particularly for materials with outstanding tribo-mechanical properties such as carbon-based films. Frictional slip and wear in these materials can be manifested in unique and surprising ways. As a fundamental example, we show that nanoscale friction can exhibit clear transitions from smooth sliding to single slips and then multiple slips. The slips are directly correlated with the atomic lattice of the sample, in this case pure graphite. The observation of the transition to multiple slips is new, and is understood by considering the competition between the stiffness of the interatomic interfacial potential and the elastic stiffnesses of the contacting materials and the force sensor itself. The transition to smooth sliding with ultralow dissipation in open air is observed for the first time, and atomic-scale stick-slip is observed for interfaces orders of magnitude larger than any previously tested. Atomic-scale stick-slip may therefore be a far more prevalent phenomenon than currently appreciated. We have also extensively studied the nanotribological behavior of other carbon-based systems, including single crystal and nanocrystalline diamond. The atomic structure of the surface, verified by detailed surface spectroscopy, critically affects friction and adhesion. Hydrogen termination is particularly effective in reducing friction and adhesion to the limit of van der Waals' interactions. Friction and adhesion are also affected by the crystal orientation. For larger tips, continuum mechanics models of contact area can be applied to understand the interfacial mechanics of these nano-scale contacts, as evidenced by the observation of direct proportionality between friction and contact area, a phenomenon known as "interfacial friction". By using smaller tips coated with a carbonaceous film, the limits of continuum mechanics are explored and discussed.

9:20am **NS+SS+TF-WeM5 Influence of the Solvent Environment on the Contact Mechanics of Tip-Sample Interactions in Friction Force Microscopy of Self Assembled Monolayers*, T.J. Colburn,*** *G.J. Leggett,* University of Sheffield, UK

The application of friction force microscopy (FFM) to the characterisation of surface composition and nanoscale tribological phenomena requires an adequate understanding of the tip-sample contact mechanics. We present new data that show that the properties of the liquid medium influence not only the strength of the frictional interaction in FFM, but also the nature of the contact mechanics model that describes the tip-sample interaction. FFM measurements have been carried out on self assembled monolayers of dodecanethiol (C@sub 10@CH3) and mercaptoundecanoic acid (C@sub 10@COOH) in a variety of liquid media using tips functionalised with alkanethiols (chemical force microscopy). In perfluorodecalin, a liquid with a low dielectric constant, the friction-load relationship fits the behaviour predicted using the Johnson-Kendall-Roberts model for like pairs of interacting molecules, and the Derajuin-Muller-Toporov model for unlike molecules. In contrast, measurements in ethanol, a liquid with a larger dielectric constant, obey Amontons' law (i.e. the friction force is linearly proportional to the load). These findings suggest that single asperity contact mechanics are observed in media with low dielectric constants, where dispersion forces are very strong and frictional interactions are adhesion-controlled. In media with large dielectric constants, sliding is not adhesion-controlled and linear friction-load behaviour is observed.

9:40am **NS+SS+TF-WeM6 Indentation of Individual and Multiple Multi-Walled Carbon Nanotubes with AFM*, H.W. Yap*,** *R.W. Carpick,* University of Wisconsin-Madison

There has been a recent surge of theoretical interest in the axial compression of MWCNTs, but only a limited number of experimental studies have been conducted. The study of axial compression of MWCNTs sheds light on their mechanical properties and has interesting implications in the fabrication of CNT - based composites. Lakes et al.@footnote 1@ have shown that macroscopic tubes have better damping properties in the post kink - buckled, snap-through regime, which is marked by a force drop with increased compression. Waters et al.@footnote 2@ and Qi et al.@footnote 3@ have indented an array of vertically aligned MWCNTs but have not observed force drops indicating these snap-through instabilities. Here, a stiff AFM cantilever with a microsphere tip attached to it is used to indent and compress a film of vertically-aligned MWCNTs with aspect ratio of ~35. These CNTs are grown with dc plasma-enhanced hot filament chemical vapor deposition from an anodized alumina nanopore template.

This is the first use of spherical probe AFM to compress aligned CNTs, though this method has been widely used in indenting biological and polymeric materials. Continuous cycles of loading and unloading to large strains were performed, and both large drops and finer relaxations in the loading portions of the force curves of a collection of MWCNTs were observed with a high degree of reproducibility. The drops are likely signatures of collective kink buckling instabilities seen in individual CNTs. The deformations, while nonlinear, are mostly elastic and reversible, as demonstrated by SEM images of the spherical tip and the sample after many cycles of deformation. We will discuss the implications of these results in the design of composites that take advantage of buckling instabilities for high damping applications. @FootnoteText@ @footnote1@Lakes et al.,Phil.Mag.Lett.,81,95(2001). @footnote2@Waters et al.,Appl.Phys.Lett.,85,1787(2004) @footnote3@Qi et al.,J.Phys.Mech.Sol.,51,2213(2003).

10:40am **NS+SS+TF-WeM9 Measurements and Modeling of Shear Modulus of Multiwalled Tungsten Disulfide Nanotubes***, I. Kaplan-Ashiri,* ***S.R. Cohen****, N. Apter, H.D. Wagner, R. Tenne,* Weizmann Institute of Science, Israel*; G. Seifert,* Technische Universitat Dresden, Germany*; R. Shneck, D. Barlam,* Ben Gurion University, Israel

Recent investigations of the mechanical properties of inorganic fullerene have highlighted their unique properties.@footnote 1@ Although the bending modulus has been measured on single nanotubes, the shear modulus is much smaller and technically more difficult to ascertain. The S-W-S sandwich structure of individual layers of these inorganic nanotubes distinguish them chemically and mechanically from carbon nanotubes. The spacing of 6.18Å between layers is comprised of the tungsten disulfide entity, and a van der Waals gap. Direct measurements of the shear modulus of single tubes could elucidate how the tube mechanics are influenced both by the gap, and the interaction between the adjacent dichalcogenide atomic layers. Measurements were made in a scanning probe microscope (SPM) using a method similar to that described by Wu et al.:@footnote 2@ Nanotubes were dispersed on a grid structure consisting of trenches of depth 200 nm and width 500 nm. Scanning electron microscopy (SEM) was used to locate nanotubes which were appropriately aligned, and suspended over such a trench. These nanotubes were then glued to the substrate at the trench edge with amorphous carbon.@footnote 3@ The SPM was subsequently used to bend the suspended nanotubes from the side with the SPM probe by amounts ranging between 5 and 100 nm, while recording the lateral force. The results were analyzed by applying the bending equation using the known value of the bending modulus to extract shear modes. Results were further compared with both density functional calculations, and finite element analysis modeling, providing insights into mechanical interactions between the layers. @FootnoteText@ @footnote 1@ I. Kaplan-Ashiri, et al, Proc. Nat. Acad. Sci. 103, 523 (2006).@footnote 2@ B. Wu, et al, Nature Mat. 4, 525 (2005).@footnote 3@ Yu et al, Science 287, 147 (2000).

11:00am **NS+SS+TF-WeM10 Deformation Behavior of Low-Density Nanoporous Dielectrics***,* ***S.O. Kucheyev****, P.M. Bythrow, T.F. Baumann, C.A. Cox, Y.M. Wang, T. van Buuren, A.V. Hamza,* Lawrence Livermore National Laboratory*; J.E. Bradby,* The Australian National University

Understanding deformation behavior of nanoporous glasses has recently regained tremendous interest in the community, primarily due to its importance for the development of a new generation of low-k dielectrics. Aerogels are sol-gel-derived nanoporous dielectric materials formed by nanometer size particles randomly interconnected into a solid network with a large degree of porosity and very high surface area. For these materials, the density can be varied from the theoretical maximum density (of a full density solid) to extreme cases of very high porosities (~99 %). Thus, aerogels represent a very attractive model system for studying the deformation mechanisms in nanoporous dielectrics. In this presentation, we discuss the use a combination of sound velocity measurements and nanoindentation with large spherical indenters (1-2 mm diameter) to study the deformation behavior of alumina and tantala aerogels with porosities up to 99%. In particular, we focus on how the deformation behavior is affected by (i) the average density of monoliths, (ii) the morphology and connectivity of nanoligaments, and (iii) the crystallographic phase. Results show that all of the above parameters can strongly affect the mechanical properties of nanoporous solids. Based on our results, we discuss the underlying deformation mechanisms and demonstrate an effective way to control mechanical properties of the nanoporous solids that can be synthesized with ligaments having a quasi-two-dimensional shape, such as platelets, ribbons, or leaflets. Work at LLNL was performed under the auspices of the U.S. DOE by the University of California, LLNL under Contract No. W-7405-Eng-48.

11:20am **NS+SS+TF-WeM11 Nanoporous Au - a 3D Network of Ultra-High Strength Nanowires***,* ***J. Biener****, A.M. Hodge, J.R. Hayes, M. Duchaineau, L.A. Zepeda-Ruiz, A.V. Hamza, F. Abraham,* Lawrence Livermore National Laboratory

Recent mechanical studies on nanoporous gold (np-Au) have revealed that the yield strength of this material is almost one order of magnitude higher than predicted by scaling equations developed for open-cell foams. The higher-than-expected yield strength seems to be linked to the nanoscale morphology of np-Au which can be best described as a three-dimensional network of ultra-high strength Au nanowires. Here, we compare experimental results with molecular dynamics simulations to elucidate the nature of the high yield strength of nanoporous gold. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract of No.W-7405-Eng-48.

11:40am **NS+SS+TF-WeM12 Superconductivity Dependent Friction of Water, Nitrogen and Superheated He Films Adsorbed on Pb(111)***,* ***J. Krim****, M. Highland,* North Carolina State University

The ability to predict sliding friction in adsorbed film systems underlies a vast range of topics in physics and nanotechnology, spanning the origins of static friction to the design of atomic-scale automobiles. One still hotly debated topic in this area is the degree to which electronic effects contribute to friction. In order to explore this issue, we have performed a quartz crystal microbalance study of sliding friction levels in nitrogen, water and superheated helium films adsorbed on Pb(111)@footnote 1@ and also self-affine fractal Pb substrates alternating in and out of the superconducting state. Reductions in friction upon entry into the superconducting state are greater for nitrogen than helium, consistent with a recent theory that linked electronic friction to adsorbate polarizability. Repetitive cycling of the externally applied magnetic field is observed to reduce overall friction levels.@footnote 2@ @FootnoteText@ @footnote 1@ M. Highland and J. Krim, Phys. Rev. Lett., in press (2006)@footnote 2@ Work supported by NSF and AFOSR.

12:00pm **NS+SS+TF-WeM13 In Situ Quantitative TEM Nanoindentation of Individual Nanoparticles and Nanoscale Materials***,* ***Z. Shan****, A.M. Minor,* Lawrence Berkeley National Laboratory*; S.A. Syed Asif, O.L. Warren,* Hysitron Inc.

Monitoring the microstructure evolution while simultaneously measuring the stress and strain information at the nanometer level has been a long standing goal for material scientists. Here we show that by incorporating a miniature capacitive transducer into a TEM holder the load-displacement response (force resolution better than 0.5 ÂµN and displacement resolution better than 1 nm) can be achieved inside a TEM during the in situ nanoindentation process. A wide range of materials have been examined using this technique, such as Al thin films, single crystal Ni and Cu, Au and Cd metallic nanoparticles, and hollow shell-structured nanoparticles. The preliminary results will be reported and the physical insight derived from these results will be discussed. In particular, our results demonstrate unique insight into the initial deformation processes during the nanoindentation of metals and the analysis of elastic moduli and plasticity in nanoparticles.

Plasma Science and Technology
Room 2011 - Session PS2+TF-WeM

Plasma Deposition

Moderator: D. Leonhardt, US Naval Research Laboratory

8:00am **PS2+TF-WeM1 Beam Activation for Atomic Layer Deposition of Ta-Based Barriers on Low-k Dielectric Surfaces***,* ***P.S. Ho,*** The University of Texas at Austin*; J. Liu,* The University of Texas at Austin (presently: Tokyo Electron America Inc.)*; J. Bao, H. Shi,* The University of Texas at Austin **INVITED**

Atomic nitrogen and hydrogen beams were investigated as surface pre-treatment and process enhancement techniques for atomic layer deposition (ALD) of tantalum nitride barrier layer on low k dielectric surfaces. Electron cyclotron resonance (ECR) plasma induced atomic nitrogen and hydrogen species were applied to a methyl silsesquioxane (MSQ) and organic polymer low k surfaces prior to and during ALD growth. In-situ XPS studies of the evolution of the low k surface chemistry revealed

an initial transient growth region controlled mainly by the substrate surface chemistry. For MSQ surfaces, pre-treatment with atomic beams, particularly with nitrogen atoms, was found to enhance significantly the chemisorption of the TaCl5 precursor on the low k surface. The enhancement was attributed to the dissociation of the weakly bonded methyl groups from the MSQ surface followed by nitridation with the atomic nitrogen species. For the organic polymer surface, the initial interaction was manifested by the formation of a charge transfer complex as a result of the interaction between Ta and the aromatic structure. In the subsequent linear growth region, atomic hydrogen species was able to reduce the chlorine content under appropriate temperature and with sufficient purge. The application of beam activation for pore sealing on porous low k surface will also be discussed.

8:40am **PS2+TF-WeM3 PECVD Synthesis and Optimization of High @kappa@ Dielectric Structures***, W. Yang, M. Seman,* ***C.A. Wolden,*** Colorado School of Mines

Alternative dielectrics with high dielectric constants (@kappa@) are required to reduce turn-on voltage and leakage current in conventional as well as thin film transistor technology. The latter application requires processing routes with a low thermal budget. To that end plasma-enhanced chemical vapor deposition processes were developed to fabricate high @kappa@ dielectrics including TiO@sub 2@ and Ta@sub 2@O@sub 5@. The deposition rate was found to be weakly activated, enabling low temperature deposition. The deposition rate was a strong function of the atomic oxygen density, reflecting a competition between plasma-phase oxidation of the precursor and its participation in film growth. Metal-insulator-silicon (MIS) structures were fabricated and characterized using both C-V and I-V measurements. Annealing was found to both enhance @kappa@ and significantly attenuate the leakage current. Under optimized conditions the dielectric performance of MIS devices was superior to that of SiO@sub 2@ control samples with the same equivalent oxide thickness. The leakage current density was correlated to the presence of oxide charge defects in the dielectric, as measured using the flat band voltage shift. By appropriate control of plasma power and oxygen concentration, the flat band voltage shift was minimized and the electrical performance of as-deposited films approached those of annealed samples.

9:00am **PS2+TF-WeM4 Tantalum Oxy-nitride Film Deposition by Electron Cyclotron Resonance Plasma Sputtering for MIM Capacitor***,* ***T. Ono,*** *H. Toyota,* Hirosaki University, Japan*; M. Shimada, Y. Jin,* NTT MI Labs, Japan

A high-k dielectric film is one of the key to realize high performance large scale integrated circuits (LSIs). The deposition characteristics of tantalum oxy-nitride (TaON) films have been investigated by using an electron cyclotron resonance (ECR) plasma sputtering without external substrate heating. A pure tantalum metal target was used as raw material supply combined with gases of oxygen and nitrogen. The electrical characteristics of the deposited films were examined by using MIM capacitor of ruthenium blanket electrodes and aluminum top pad electrodes. The electrical characteristics of the deposited films were changed from metallic conductive states to high-k dielectric states by the mixture ratio of oxygen and nitrogen. For the dielectric films, in high concentrations of oxygen gas, the deposited tantalum oxide (Ta@sub 2@O@sub 5@) films have a refractive index of 2.15 at 632.8 nm wavelength, high dielectric constant of 25, and high breakdown-strength of 5MV/cm. By controlling the oxygen gas concentrations in moderate low region, films of TaON have been stably obtained with the refractive indices of around 2.9 at 632.8 nm wavelength, higher dielectric constants of over 35 and breakdown-strengths of around 1MV/cm. In spite of low substrate temperature without external heating, high quality TaON films have successively obtained. The TaON films deposited by the ECR plasma sputtering can be applicable to the capacitor dielectrics and gate oxides for Si-LSIs, compound MIS-FETs, and the drive circuit devices for LCDs.

9:20am **PS2+TF-WeM5 In Situ Studies of Reaction Mechanisms during Plasma-Assisted Atomic Layer Deposition of Al@sub 2@O@sub 3@***,* ***S.B.S. Heil***[1]*, P. Kudlacek, E. Langereis, R. Engeln, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Extending the atomic layer deposition (ALD) technique with plasma processes (i.e., plasma-assisted ALD or PA-ALD) opens up new routes that are difficult to attain by pure thermal ALD. In particular the ability to deposit high-quality oxide films at low substrate temperatures using an O@sub2@ plasma has recently expanded the interest in ALD from solely semiconductor manufacturing to upcoming fields such as photovoltaics and flexible electronics. However, for PA-ALD the reaction mechanisms leading to film formation have not been extensively studied and especially for the reactions occurring during the plasma step several questions still remain unanswered. In this contribution, we present an in situ study of the PA-ALD process of Al@sub2@O@sub3@ from Al(CH@sub3@)@sub3@ (trimethylaluminum, TMA) and O@sub2@ plasma. Employing a combination of quartz crystal microbalance (QCM), quadrupole mass spectrometry (QMS), and optical emission spectroscopy (OES) an insight into the plasma species, reaction products, and surface chemistry is gained. For example, QMS showed that during the plasma step H@sub2@O and CO@sub2@ are formed from the surface CH@sub3@ groups in a combustion like reaction. This is supported by time-resolved OES in which the consumption of oxygen species and the emission by excited CO molecules were detected until the process reached saturation (<0.5 s). From QCM and QMS measurements it was determined that during the precursor step the TMA reacts mainly bifunctionally with the surface OH groups splitting of ~1.8 CH@sub3@ ligands as CH@sub4@. QCM measurements were correlated with in situ spectroscopic ellipsometry giving more detailed information about film growth during PA-ALD of Al@sub2@O@sub3@. The combustion like reaction occurring in the deposition of Al@sub2@O@sub3@ is expected to be generic for plasma-assisted ALD processes of oxides from metalorganic precursors.

9:40am **PS2+TF-WeM6 XPS Study of Plasma Pretreatment of PEN and Related Polymer Substrates to Enhance Atomic Layer Deposition of Aluminum Oxide***,* ***E.S. Brandt****, J.M. Grace,* Eastman Kodak Company

The role of water plasma pretreatment of polymer substrates to promote atomic layer deposition (ALD) of aluminum oxide from dimethylaluminum isopropoxide (DMAI) is investigated using an in situ ALD deposition chamber that is interfaced directly to the UHV system of an X-ray photoelectron spectrometer. Using X-ray photoelectron spectroscopy (XPS), it is shown that treatment by water plasma incorporates surface hydroxyl functional groups, which enhance the deposition of aluminum oxide by approximately an order of magnitude on poly(ethylene naphthalate) (PEN), and activates an otherwise inert polystyrene (PS) surface to alumina deposition when DMAI and water are used as ALD reactants. By contrast, under our reaction conditions, the intrinsic reactivity of the highly hydroxylated surface of polyvinyl alcohol (PVA) toward repeated DMAI/water ALD cycles is not significantly enhanced by water plasma pretreatment. The data suggest that in the absence of inherently reactive surface functional groups (e.g., hydroxyl groups) to promote chemisorption of the metal-bearing precursor, some polymers, including PS and PEN, require surface functionalization (e.g., water plasma treatment) to initiate ALD growth of metal oxides.

10:40am **PS2+TF-WeM9 The Use of Pulse-Shaped Substrate Bias for Energy-Selective Ion Bombardment During Amorphous Si Deposition***,* ***I.T. Martin,*** *M.A. Blauw, R. Engeln,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

The role of neutrals during expanding thermal plasma (ETP) deposition of a-Si:H has been thoroughly studied in the literature. Less attention has been paid to ions, both because ion flux is low compared to neutral flux, and the remote nature of the plasma source results in low ion energies, <2eV. Ion bombardment effects depend on ion energy as different thresholds exist for enhancing vs. damaging processes. RF-biasing has previously been used to increase ion energy; appropriate substrate voltages resulted in an increase in the photoconductivity of a-Si:H. A disadvantage of rf-biasing is that the resulting ion energy distributions (IEDs) are broad and bimodal. We have applied the pulse-shaped substrate bias technique developed by Wendt and coworkers@footnote 1@ to ETP a-Si:H deposition, which results in narrow IEDs. This improves ion energy control, allowing further optimization of materials properties. Preliminary data demonstrate that the effect of this bias varies for different plasma conditions; materials deposited in plasmas with low ion currents (<3mA) and high deposition rates (~5nm/s) are unaffected by the bias. The setup also allows us to determine ion flux to the substrate. Data show that increasing H@sub 2@ flow results in decreased ion flux, consistent with earlier Langmuir probe measurements. Interestingly, ion flux increases with increasing substrate potential, suggesting the formation of additional plasma in front of the substrate. Materials were deposited with varying Ar:H@sub 2@:SiH@sub 4@ flows, and a range of substrate biases (0 to -140V). Films were characterized using FTIR and photoconductivity measurements; differences in deposition rate, refractive index, hydrogen content and

[1] **PSTD Coburn-Winters Student Award Finalist**

photoconductivity as a function of substrate bias will be discussed. Results are compared to a-Si:H deposited using rf-biasing, and to other materials deposited using a pulse-shaped bias. @FootnoteText@ @footnote 1@S.B. Wang and A.E. Wendt, J. Appl. Phys. 88, 643 (2000).

11:00am **PS2+TF-WeM10 Effects of Clusters and Higher-Order Silane Related Radicals on Stability of a-Si:H Films Deposited by Plasma CVD***, **K. Koga**, H. Miyahara, G. Yuan, A. Genot, S. Iwashita, W.M. Nakamura, M. Shiratani,* Kyushu University, Japan

Light-induced degradation of hydrogenated amorphous silicon (a-Si:H) is one of the most important issues for a-Si:H solar cells.@footnote 1@ Recently, we have succeeded in depositing highly stable a-Si:H films by using a multi-hollow discharge plasma CVD method.@footnote 2@ We can obtain information about species responsible for degrading stability, because stable a-Si:H films are deposited in the upstream region from the discharges while metastable ones are in the downstream region in the multi-hollow discharge plasma CVD reactor. To identify such species, we detected clusters and higher order silane related radicals both in the upstream and downstream region. The amount of amorphous clusters in the upstream region is by more than two orders of magnitude lower than that in the downstream, whereas densities of Si@sub 2@H@sub 6@ and Si@sub 3@H@sub 8@ in the upstream related radicals is 0.3 - 0.7 times as low as those in the downstream even for a high gas velocity of 52 cm/s. Therefore, the multi-hollow discharge plasma CVD method together with a high gas velocity is effective in suppressing volume fraction of clusters incorporated into the films deposited in the upstream region, while such combination has little effects on those of Si@sub 2@H@sub 6@ and Si@sub 3@H@sub 8@ related radicals. These results suggest that amorphous clusters formed in the discharges are one of the species responsible for degrading stability of films, whereas Si@sub 2@H@sub 6@ and Si@sub 3@H@sub 8@ related radicals are not. @FootnoteText@ @footnote 1@R. E. I. Schropp and M. Zeman, "Amorphous and Microcrystalline Silicon Solar Cells", Kluwer Academic Publishers, Boston, 1998, p. 99.@footnote 2@K. Koga, et al., Jpn . J. Appl. Phys., 48 (2005) L1430.

11:20am **PS2+TF-WeM11 Methods of Producing Plasma Enhanced CVD Silicon Nitride Thin Films with High Compressive and Tensile Stress***, **M.P. Belyansky**, N. Klymko, A. Madan, M. Chace, S. Molis, P.A. Ronsheim, J. Kempisty, A. Mallikarjunan, Y. Li,* IBM Microelectronics

High stress plasma enhanced chemical vapor deposition (PECVD) films are becoming an integral part of the state-of the-art metal oxide semiconductor field effect transistor (MOSFET) technology. Generation of a uniaxial strain in a silicon channel is shown to substantially increase device speed, which is achieved by an application of high stress tensile or compressive silicon nitride (SiN) films leading to either electron or hole mobility enhancement respectively. Various methods of generating high stress in thin PECVD SiN films are discussed. Besides the mainstream variation of plasma power and other process parameters, novel techniques of stress build-up in thin films like creation of specific types of interfaces and multilayer structures by PECVD or exposure of SiN films to ultraviolet (UV) radiation are reported. Thin PECVD SiN films (about 50nm) have been analyzed by a variety of analytical techniques including Fourier Transform Infrared Spectroscopy (FTIR), X-ray reflectivity (XRR), Secondary Ion Mass Spectrometry (SIMS) and Rutherford backscattering (RBS) to collect data on bonding, density and chemical composition. Mechanisms of stress formation in both compressive and tensile SiN thin films are discussed. Level of bonded hydrogen as well as film density has been found to correlate with film stress. Interface formation and creation of a multilayer structure helps to build up more stress compared to a standard single layer film deposition. Both the density and number of interfaces in a film, characterized by XRR, affect the stress. Exposure of multilayer SiN films to elevated temperature results in a loss of a well-defined interface structure and leads to the predictable increase in tension and degradation in compressive stress. Interface composition and barrier properties of multilayer films are discussed. Effect of UV radiation exposure on PECVD SiN and the resulting increase in film tensile stress is also delineated.

11:40am **PS2+TF-WeM12 Analyses of CH4/H2 RF Plasma and Iron Catalysts for Control of Carbon Nanotube Growth***, A. Okita, **Y. Suda**, A. Ozeki,* Hokkaido University, Japan*; A. Oda,* Nagoya Institute of Technology, Japan*; J. Nakamura,* Tsukuba University, Japan*; K. Bhattacharyya, H. Sugawara, Y. Sakai,* Hokkaido University, Japan

We have studied CH@sub 4@/H@sub 2@ gas mixture RF plasma by one-dimensional fluid modeling and iron catalysts by X-ray photoelectron spectroscopy (XPS) for controlling carbon nanotube (CNT) growth in plasma-enhanced CVD (PECVD).@footnote 1,2@ To control CNT growth in terms of length, diameter, number density and orientation, understanding the behavior of hydrocarbon (C@sub x@H@sub y@) radicals and ions onto metal-catalyzed substrate becomes important. So far, we have shown that the carbon amount evaluated from the fluxes of C@sub x@H@sub y@ radicals and ions by the modeling is reasonably consistent with that in CNTs grown by PECVD.@footnote 1@ The PECVD setup sustains the CH@sub 4@/H@sub 2@ or H@sub 2@ plasma in a pressure range of 1-10 Torr. The substrate temperature is kept at 550°C for reduction and 650°C for growth. Length, diameter and number density of the CNTs grown are analyzed. The carbon atom density in a graphene sheet (3.81X10@super 15@ atoms/cm@super 2@) is used to evaluate the amount of carbon in CNTs. One-dimensional fluid modeling analyzes the densities and fluxes of C@sub x@H@sub y@ radicals and ions between powered and grounded electrodes. Assuming the sticking probability of C@sub x@H@sub y@ radicals on substrate: CH, 0.025; CH@sub 2@, 0.025; CH@sub 3@, 0.01; C@sub 2@H@sub 5@, 0.01; H, 0.01,@footnote 3@, we predict the amount of carbon which are supplied from the plasma and incorporated into CNTs. Very recently, we have shown that the content of iron oxide in the catalyst analyzed by XPS correlates with CNT growth.@footnote 2@ In this presentation, we discuss the growth speed of CNTs by both the PECVD and modeling and the CNT growth duration by XPS analysis. @FootnoteText@@footnote 1@A. Okita, et al., J. Appl. Phys., 99 (2006) 014302 @footnote 2@A. Okita, et al, Jpn. J. Appl. Phys. (accepted) @footnote 3@I. B. Denysenko, et al., J. Appl. Phys. 95, 2713 (2004).

12:00pm **PS2+TF-WeM13 Increase of O(@super 1@D) Metastables by Rare-Gas Diluted O@sub 2@ Plasma and Application to the Oxide Growth***, **T. Kitajima**,* National Defense Academy of Japan, Japan*; T. Nakano,* National Defense Academy of Japan*; T. Makabe,* Keio University, Japan

Rare gas diluted O@sub 2@ plasmas are gaining interests for application to high quality SiO@sub 2@ film formation. Especially, metastable O(@super 1@D) atoms produced in rare gas diluted O@sub 2@ plasma is believed to promote higher production rate of the oxide films. We have found the increase of O(@super 1@D) atoms in rare gas diluted O@sub 2@ RF plasma measured by VUV absorption spectroscopy.@footnote 1@ The increase of the O(@super 1@D) density is due to the increase of rare gas metastables that selectively produce O(@super 1@D) atoms via dissociative excitation of O@sub 2@. Among rare gas species, Krypton dilution enables highest O(@super 1@D) density. Then we applied the increased O(@super 1@D) flux of the Kr diluted O@sub 2@ plasma to the formation of SiO@sub 2@ films. Silicon substrate is flashed in the vacuum by direct current heating to form bare Si(001) surface. The surface is exposed to the Inductive coupled plasma operated at 70 MHz in O@sub 2@(3%)/Kr at 0.1 Torr for oxidation. After the oxidation, the sample is introduced to the UHV chamber which have a contact mode AFM for film evaluation. The topography and breakdown voltage of the SiO@sub 2@ films are measured by the biased AFM tip. The topographic images and breakdown current map shows the uniform oxide formation of the rare-gas diluted O@sub 2@ plasma. The breakdown voltage of the film is nearly same to the one of pure O@sub 2@ plasma case. Regarding the increase and the decrease of the O(@super 1@D) and the ground state O(@super 3@P) flux to the surface during oxidation, O(@super 1@D) atom has an order higher oxidation rate of Si(001) than O(@super 3@P). The results show the enhancement of oxidation rate of silicon with using increased O(@super 1@D) selectively produced in rare-gas diluted O@sub 2@ plasma. @FootnoteText@ @footnote 1@ T.Kitajima, T.Nakano, and T.Makabe, Appl. Phys. Lett. 88, 091501 (2006).

Thin Film
Room 2022 - Session TF-WeM
Thin Films for Photovoltaics and Energy Applications

Moderator: J. Lewis, RTI

8:00am **TF-WeM1 Preparation of Transparent Conducting B-doped ZnO Films by Vacuum Arc Plasma Evaporation***, **T. Miyata**, Y. Honma, T. Minami,* Kanazawa Institute of Technology, Japan

Recently, a newly developed vacuum arc plasma evaporation (VAPE) method providing high-rate film depositions on large area substrates has attracted much attention for transparent conducting oxide film depositions. In this paper, we describe highly transparent and conductive B-doped ZnO (BZO) thin films prepared by the VAPE method using sintered BZO fragments. It was found that the obtained electrical and optical

properties of deposited BZO thin films were considerably affected by the B content doped into films as well as the preparation condition of the BZO fragments used. Fragments suitable for preparing low resistivity BZO films were obtained by breaking previously sintered disks into small pieces; a mixture of ZnO and B@sub 2@O@sub 3@ powders was pressed and then sintered at a temperature above about 900@super o@C in a pure Ar gas atmosphere to produce the disks. In particular, the B content doped into deposited BZO thin films could be controlled by varying the B content of the BZO fragments used. The lowest resistivity was obtained with a B content (B/(B+Zn) atomic ratio) of approximately 1 at.%. To obtain high transmittance, it was necessary to introduce O@sub 2@ gas during film preparation on low temperature substrates that were below approximately 150@super o@C. Low resistivities of 7.9X10@super â?"4@ and 5.1X10@super â?"4@@ohm@cm and a high average transmittance above 85% in the visible region were obtained in BZO thin films prepared with a high deposition rate at glass substrate temperatures of 100 and 200@super o@C, respectively.

8:20am **TF-WeM2 Photonic Band Edge Engineering through Nano Coating of Cu Thin Film on 3D Photonic Crystals*, D.-X. Ye*,** *Z.-P. Yang, J. Bur, S.Y. Lin, T.-M. Lu,* Rensselaer Polytechnic Institute

Photonic crystals have extraordinary applications in illuminations, solar cells, and photovoltaic devices by redistributing the energy. At the edge of a photonic band gap, the photon group velocity approaches zero giving the coherent photon localization. Therefore, spontaneous emission near the photonic band edge can be totally suppressed. For energy applications, interesting photonic crystals are those with a band edge close to visible wavelengths. However, the band edge on this side is limited both by the fabrication methods and by the nature of the dielectric materials used. Here we present our strategy of breaking these limitations by conformal coating of Cu films using chemical vapor deposition (CVD). First, on pre-fabricated Si and W woodpile structures, 70 nm thick Cu was coated by CVD. Optical measurements showed that the photonic band edge is pushed from ~1500 nm to ~700 nm in these structures. Another class of photonic crystals is constructed using arrays of square nanosprings by oblique angle deposition technique. This technique was first used to fabricate the Si spring photonic crystals by M. J. Brett et al. However, the dimensions of the nanosprings cannot be maintained due to the fan-out growth. We designed a substrate rotation method to overcome this difficulty which is referred as swinging technique. In swinging technique, the substrate is rotated azimuthally back-and-forth within an angular range with a constant rotation speed. Uniform Si photonic structure can be fabricated without fan-out problem now. On the other hand, the other limitation of this technique prevents the geometry of the nanosprings to be optimized to achieve a large band gap. We solved this problem again by further Cu coating on Si nanosprings. The overall photonic crystal shows a complete band gap in the near infrared region. In summary, Cu coating on photonic crystals provides an easy path to modify the properties of photonic crystals.

8:40am **TF-WeM3 Thin-Film Superlattice Thermoelectric Energy Conversion Materials and Devices*, R. Venkatasubramanian,*** RTI International **INVITED**

The increasing cost of energy produced from fossil fuels has further renewed the emphasis on issues such as energy efficiency, alternative fuels and so-called sustainable technologies. Nearly 60% of the world' energy, today, is wasted as heat. A prime example is the internal combustion engine - where almost 70% of the fuel's calorific value is lost as heat through the exhaust and radiator. Thermoelectric devices can convert this waste heat to much-needed electric power. Thermoelectrics is also relevant for solid-state, noise-free, CFC-free, refrigeration and air-conditioning. These applications have been limited in the past, mainly due to the efficiency of materials, low power density, as well as scalability. Using thin-film nanoscale materials, which allow unique physics such as thermal conductivity reduction without deterioration of electronic conduction, we have been able to achieve a significant improvement in materials performance (Nature 2001). The thin-film nature has enabled devices with high specific power (in Watts/cc) and cooling densities (in Watts/square cm); the former is attractive for portable power while the latter is highly relevant for high-perforamance electronics cooling. In addition to these applications, our long-term vision is to contribute to energy eficiency, by harnessing untapped heat sources. We will describe our early efforts in the applcation of this technology for automotive waste-heat recovery. We will also compare the advantges offered by thin-film thermoelectrics for solar-thermal-to-electric power versus convenional photovoltaics.

9:20am **TF-WeM5 Synthesis of CuO and Cu2O by a Process Combining Sputtering and Rapid Thermal Annealing*, J.H. Hsieh,*** Mingchi University of Tech., Taiwan

Cu2O and CuO thin films were first deposited using magnetron sputtering, then, annealed by a rapid thermal annealing system at various temperatures and oxygen partial pressure. After processing, the films were characterized using UV-VIS photometer, four point probe, and Hall measurement system. The electro-optical properties of these films were compared with those prepared by direct sputtering.

9:40am **TF-WeM6 Microcrystalline Silicon Deposition Efficiency Optimization*, B. Strahm,*** *A.A. Howling, L. Sansonnens, Ch. Hollenstein,* Ecole Polytechnique Fédérale de Lausanne, Switzerland

Microcrystalline silicon is widely used in solar cells, because of its better performances and stability compared to the standard amorphous silicon. However, the low light absorption of microcrystalline silicon implies that thick layers have to be deposited. Therefore high deposition rates (> 1 nm/s) have to be achieved in order to allow a cost-effective mass production of solar cells. An analytical plasma chemistry model has been used to determine the amorphous/microcrystalline silicon microstructure transition and the gas utilization efficiency as a function of plasma parameters. Modeling results show that high gas utilization efficiency is not incompatible with microcrystalline silicon deposition. In situ deposition rate and infra-red absorption measurements in a large area RF-PECVD capacitive reactor have been used to determine the gas utilization efficiency and the silane depletion. Ex situ Raman spectroscopy was used to measure the crystallinity of the deposited layers. Experimental data have validated the analytical plasma chemistry model and the results were used to build up a new experimental approach to optimize microcrystalline silicon deposition efficiency. Starting with appropriate plasma parameters (RF input power, excitation frequency and silane flow rate and concentration) and by varying only hydrogen flow rate and pressure, the gas utilization efficiency can be increased to values higher than 80 %. This high efficiency has not only the advantage of high deposition rate, but also reduces raw material consumption and powder formation.

10:40am **TF-WeM9 Chemical-Kinetics Analysis of In-Vacuum Cu@sub 2@Te Thermal Decomposition and Comparison to Equilibrium Vapor-Pressure Measurements*, G. Teeter,*** National Renewable Energy Laboratory

Auger electron spectroscopy measurements of polycrystalline Cu-foil substrates exposed to elemental Te vapor at substrate temperatures below 373 K indicate that copper-telluride films are formed at the substrate surface that have a 2:1 Cu-to-Te ratio, as predicted by the Cu-Te phase diagram for a system in equilibrium. When these films are annealed above about 700 K in vacuum, Te desorbs from the substrate with zero-order kinetics. An analysis of Te desorption traces that assumes the reaction Cu@sub 2@Te(s) --> 2Cu(s) + @alpha@Te(v) + 1/2(1-@alpha@)Te@sub 2@(v) finds a thermal-decomposition activation energy of 217 ± 3 kJ/mol. These Te-desorption data are compared to the Te impingement rate calculated from Cu@sub 2@Te equilibrium vapor-pressure data@footnote 1@ from the literature and found to be in excellent agreement. This abstract is subject to government rights. This work was performed with the support of U.S. Department of Energy Contract DE-AC36-99-GO10337. @FootnoteText@ @footnote 1@B. Brunetti, V. Piacente, P. Vassallo, and A. R. Villani, Mater. Chem. Phys. 70, 263-267 (2001).

11:00am **TF-WeM10 B doped Be Coatings for NIF Target Development*, H. Xu*,** *K. Moreno, K. Youngblood, A. Nikroo,* General Atomics*; J. Cooley,* Los Alamos National Laboratory*; C. Alford, S. Letts, A.V. Hamza, T. van Buuren,* Lawrence Livermore National Laboratory

Sputtered beryllium and copper-doped beryllium coatings as thick as 170 µm have been deposited on spherical substrates to produce hollow shells that are required as targets for inertial fusion experiments.@footnote 1@ Be coatings by magnetron sputtering have achieved ~93-95 percent bulk density consistently up to 170 µm in thickness. Coatings on the spherical substrates exhibit columnar structure through the entire thickness. Transmission Electron Microscopy (TEM) indicates the presence of sub-micron voids mainly aggregated along the columnar structure and grain boundaries as well as some intra-granular voids. Ultra Small Angle X-ray Scattering (USAXS) was used to determine the size and distribution of pores within the coatings, which correlated well with the TEM data. Holes drilled in beryllium shells produced in this manner allow filling with the fusion fuel. Gas retention of these shells has been examined using mass spectrometry. It appears that a fraction of the pores in the coatings are interconnected, which leads to leakage in the hollow shells. Boron-doped Be layers at concentrations of ~5-20 atomic percent near the eutectic

phase have been added to the Be shells. The addition of these layers has led to a significant improvement in D@sub 2@ gas retention of shells. However there remains a considerable scatter in the measured leakage. @FootnoteText@ @footnote 1@S. Haan et al., Phys. Plasma 2 (1995) 2480.

11:20am **TF-WeM11 Morphological Changes in CIGS2 Upon Thickness Reduction of Absorber Layer and its Correlation with Device Performance***, **P. Vasekar**, N.G. Dhere,* Florida Solar Energy Center

Chalcopyrites are important contenders among thin film solar cells due to direct band gap and higher absorption coefficient. Copper-Indium-Gallium Sulfide (CIGS2) is a chalcopyrite material with a near-optimum band gap of 1.5 eV. At FSEC PV Materials Laboratory, record efficiency of 11.99 % has been achieved on a 2.7 µm CIGS2 film prepared by sulfurization. Copper indium sulfide modules are being commercialized by Sulfurcell in Germany. The availability and cost of Indium can be a limiting factor. The required amounts of metals can be lowered by using thinner films. Efforts are being made to reduce the thickness while maintaining the comparable performance. At NREL, 17.16 % efficiency has been obtained with 1 µm copper-indium-gallium selenide absorber layer. Thickness reduction up to 0.75 µm seems plausible. It has been estimated that thickness can be reduced even to 0.5 microns without light trapping. We have already obtained about 6.4 % efficiency for CIGS2 with thickness of 1 µm. Initially small size grains are formed during the film growth. With continuing growth to large thicknesses, more favorably oriented grains grow faster and coalesce to form compactly packed large-grain morphology. Solar cell performance in smaller grain chalcopyrite absorber deteriorates due to larger fraction of grain boundaries. It is essential to hasten the grain growth through coalescence to retain quality even in thinner films. This work presents a study of morphology of CIGS2 absorber layers of decreasing thicknesses and the assessment of the efficacy of various techniques in improving morphology and thus the device performance and yield even at thicknesses below 1 µm.

11:40am **TF-WeM12 Thermoelectric Properties of Compositionally Graded Co-Doped TiO@sub 2@ Thin Films***, **N. Nguyen**,* University of Washington*; D. Kukuruznyak,* National Institute for Materials Science, Japan*; A. Yamamoto,* Advanced Industrial Science and Technology Institute, Japan*; T. Chikyow,* National Institute for Materials Science, Japan*; F.S. Ohuchi,* University of Washington

There has been a recent interest in improving thermoelectric performance using segmented thermoelectric elements. Concentration gradient of dopants in the material can be regarded as a continuously segmented component composed of a single parent material. In terms of material processing, concentration gradient is more advantageous, and may result in better compatibility for device applications, especially for thin film structures. The compositionally graded Co-doped TiO@sub 2@ thin films were grown on (001) LaAlO@sub 3@ substrates by a pulsed laser deposition. Spatial distribution of the electrical resistance and thermopower mapping of the samples were mapped using a custom-designed scanning conducting probe. The Seebeck coefficients were varied from -10 µV/K to -30 µV/K, whereas the resistivity changed from 1 @Ohm@cm to 150 @Ohm@cm. The I-V characteristics under the presence of the temperature gradient were then measured by applying a current source in such a way that the thermopower current was suppressed by applying the current in the opposite direction. Power factors (S@super 2@@sigma@) were then evaluated as a function of temperature, where those for Co-doped TiO@sub 2@ were increased as compared to non-doped TiO@sub 2@ by a factor of multiple times. A part of the reason for enhancement of the power factor may relate to a spin entropy effect induced by Co doping to TiO@sub 2@. Since the maximum power factor occurs at certain temperature and/or range for given concentration of the Co-doping, the concentration graded films have an advantage to broaden the temperature range for operation with the peak performance occurring continuously over the wide temperatures of interest.

12:00pm **TF-WeM13 Procedure for Performance Monitoring of Thin-Film Photovoltaic Modules***, **N.G. Dhere**, A. Kaul, B. Kumar, S. Khatri,* Florida Solar Energy Center

Thin film PV modules from all five leading US PV manufacturers are being tested at Florida solar energy center. Grid-connected photovoltaic systems are usually subjected to harsh environmental conditions and high voltage bias. Hence a study is undertaken for understanding key reliability issues and exploring avenues for improving manufacturing technology. Array output voltage, current, and back-of-module temperatures along with meteorological parameters namely; solar irradiance, UV, relative humidity, ambient temperature, wind speed, etc, are being monitored continuously. Error analysis of statistical data and PV system performance monitoring to Performance Test Conditions (PTC) is carried out using regression. Current-Voltage Characteristics (I-V) of the module arrays taken on quarterly basis, serve as a supplement to the continuous data monitoring. I-V measurements provide characteristic data of PV arrays, such as open circuit voltage, short circuit current, peak power, fill factor etc. The PTC power calculated for each month supported by quarterly I-V measurements are used to assess the degradation rate, if any, for each module array over a period of several months. This paper presents procedure of data acquisition and analysis for verification of possible degradation of thin-film PV modules.

Thin Film
Room 2022 - Session TF-WeA

Thin Films for Energy Applications in Photovoltaics, Fuel Cells, Hydrogen Storage & Batteries

Moderator: R. Carter, Advanced Micro Devices

2:00pm **TF-WeA1 Na Doped V@sub 2@O@sub 5@ Thin Films for the Thermoelectric Device Applications***, **S. Iwanaga**, M. Marciniak, R.B. Darling, F.S. Ohuchi,* University of Washington

The thermoelectric properties of bronze-like V@sub 2@O@sub 5@ thin films were investigated above room temperatures. The potential utilization of these materials for thin film based thermoelectric devices were considered. The original motivation for this research came from the fact that V@sub 2@O@sub 5@ exhibits an unusually high Seebeck coefficient of about -550 µV/K; however, low electrical conductivity (@sigma@ ~ 1E-4 @OMEGA@cm) hinders its usage as a thermoelectric material in practical applications. Systematic doping of Na into the V@sub 2@O@sub 5@ host lattice was investigated in an attempt to find the conditions that maximize a power factor described by @sigma@S@super 2@, where @sigma@ and S are the electrical conductivity and Seebeck coefficient, respectively. The Na doped V@sub 2@O@sub 5@ solutions were made by the melt-quench method, which provides very stable solutions that lasts for months. The solution was then coated on quartz substrates. It was experimentally shown that proper annealing of Na doped V@sub 2@O@sub 5@ thin films dominantly produce @beta@-Na@sub 0.33@V@sub 2@O@sub 5@. The electrical conductivity was increased by a factor of about 1000, while the Seebeck coefficient decreased to ~40 % of the original value, resulting in an improvement of the power factor by a factor of about 160. These improved thermoelectric properties were further studied by current-voltage (I-V) measurements. The I-V measurements were performed while applying a temperature gradient to the film by applying a current source in such a way that the thermopower current was suppressed by applying the current in the opposite direction. The I-V characteristics at different applied @DELTA@T were thus obtained, from which the output power was calculated from the I-V data. The Na@sub 0.33@V@sub 2@O@sub 5@ thin films were used in a sensor application and their performance was evaluated.

2:20pm **TF-WeA2 Effect of Na Quantity on the Morphology of the Absorber Layer in the CIGSS/CdS Thin Film Solar Cell***, **V.V. Hadagali**, S.A. Pethe, N.G. Dhere,* Florida Solar Energy Center, University of Central Florida

The highest efficiencies of CIGS thin-film solar cells have been obtained by using soda lime glass as substrate material. Soda lime glass contains significant amounts of sodium in the form of NaO2. The presence of Na during growth of the CIGS absorber layer is beneficial. Na promotes increase in grain size and preferred (112) orientation of CIGS films. The overall effect of Na incorporation during grain growth is an increase in efficiency by enhancements of fill factor and open circuit voltage. This paper presents the effect of the Na quantity on the morphology of CIGSS thin film solar cells. Among the available sodium containing precursor, NaF is non-hygroscopic, stable in air and evaporates stoichiometrically. NaF of various thicknesses ranging from 30-120 Å is deposited by thermal evaporation on a Mo coated glass. The CIGSS is grown in a two stage process. The Cu-In and Ga are deposited by sputtering and the selenization / sulfurization process in a conventional furnace. The absorber layer was deposited on the substrates with various NaF quantities in the same process. Various morphological effects such as hillocks and valleys have been observed due to the presence of Na. The area density of hillocks and valleys varied with the quantity of NaF. Selenization of the film containing Na results in the formation of NaSex compounds. In some cases, absorber layer peeled immediately after deposition or during chemical bath deposition of CdS heterojunction layer. The peeling effect could be attributed to the non-optimum sodium and selenium contents. SEM, AES and Optical microscopy techniques were used to understand morphology.

2:40pm **TF-WeA3 Properties of Grain Boundaries in Cu(In,Ga)Se2***, **D. Hebert**, A. Hall, A. Aquino, C.H. Lei, I.M. Robertson, A. Rockett,* University of Illinois, Urbana-Champaign

CuInSe@sub 2@ (CIS) 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. One of the primary questions concerning the nature of these devices is the optoelectronic behavior of grain boundaries in the material. We have grown epitaxial bicrystals of these materials on polished GaAs bicrystalline substrates and have studied the grain boundaries by a variety of methods including atomic force microscopy, Kelvin probe force microscopy, position-dependent photoluminescence, cathodoluminescence, transmission electron microscopy, Hall effect and other methods. The bicrystals show distinct differences in the two grains, one of which has a nearly (100) surface orientation while the other has a nearly (110) orientation. The latter is highly faceted. The grain boundary is fully dense. The (110) grains show a lower energy luminescence characteristic of subgap emission from deep defect states, while the (100) grain show higher energy luminescence. No distinct behavior directly connected with the grain boundary is evident in any of the measurements. Furthermore, there is no measurable chemical change in the CIS chemistry at the grain boundary that might account for surface state passivation. Although this negative result is surprising, it is consistent with the observation that grain boundaries are inactive in the devices. This confirms the evidence that grain boundaries are surprisingly innocuous in this material.

3:00pm **TF-WeA4 Growth and Characterization of In@sub x@Ga@sub 1-x@N (0 @<=@ x @<=@ 1) Thin Films Grown by MOCVD for Photovoltaic Applications***, **J. Mangum**, O. Kryliouk,* University of Florida*; A. Davydov,* National Institute of Standards and Technology*; T.J. Anderson,* University of Florida

Recently the electronic band gap of indium nitride (InN) has been revealed to be 0.7 eV in marked contrast to the previously accepted value of ~2.1 eV. By varying the band gap of InN with the incorporation of gallium to form In@sub x@Ga@sub 1-x@N, the optimal band gap energy for either a single cell or tandem cell combination is possible. Furthermore, the high absorption coefficient and radiation hardness make InN and In@sub x@Ga@sub 1-x@N attractive materials for photovoltaics. In@sub x@Ga@sub 1-x@N films on Si (111) and Al@sub 2@O@sub 3@ (0001) substrates were grown by metal organic chemical vapor deposition (MOCVD) at low temperatures (T < 600 @super o@C) over the entire compositional range (0 @<=@ x @<=@ 1). The lattice parameter was determined from XRD measurements of the as-grown films. The films were also characterized by PL, SEM, and Hall measurements. An In@sub x@Ga@sub 1-x@N based solar cell device structure is proposed that is assessed by device modeling as well! as quantum efficiency measurements.

3:20pm **TF-WeA5 Thin Film Deposition Technologies Enabling a New Generation of 3-D Integrated All-Solid-State Batteries***, **P. Notten**,* Philips Research and Eindhoven University of Technology, The Netherlands*; R.A.H. Niessen, J.H.G. Op het Veld,* Philips Research Laboratories, The Netherlands **INVITED**

It is anticipated by the electronic industry that smart Autonomous Devices, enabling future Ambient Intelligence inside offices and houses, will play a dominant role in our future life. Characteristic of these Autonomous Devices is that these should operate independently, meaning that the energy supply must be guaranteed wirelessly. This implies that both energy scavenging and electrochemical energy storage are of crucial importance for these devices. It has been reported that all-solid-state Li-based rechargeable batteries can be frequently charged and discharged. These thin-film batteries were, however, planar structured and include a dynamic metallic lithium anode. The thin film geometries were grown, by making use of physical deposition techniques. However, the geometric energy density of these devices is unfortunately relatively low due to its planar structure. Interestingly, it has recently been discovered that the amount of Li which could be reversibly intercalated and de-intercalated in thin film Silicon electrodes is about 10 times higher than in conventional graphite electrodes, making these anodes much more energy dense and, compared to metallic Li, mechanically more robust. Silicon is a well-known substrate material nowadays widely applied in the electronic IC-industry, allowing a high degree of component integration. One of the latest developments is the integration of capacitors into Si wafers; 3-D structured high surface area substrates are obtained by either physical or wet-chemical etching, enabling the beneficial deposition of high surface area electrode structures. Based on the various above-mentioned developments a new battery concept is proposed to come to fully 3-D integrated, all-solid-state, rechargeable batteries, revealing a high energy density. This concept will be based on the Li-intercalation chemistry of Silicon and LiMeOx. In the present presentation the details of this challenging 3-D integrated battery concept will be disclosed and the electrochemistry of Li-intercalation in Silicon will be reported

4:00pm **TF-WeA7 Fabrication and Fuel Cell Performance of Ultra-Thin Yttrium-Doped Barium Zirconate Films*, J.H. Shim,*** *T.M. Gür, F.B. Prinz,* Stanford University

Acceptor-doped perovskites such as yttrium or gadolinium-doped barium cerate (BaCeO@sub 3@), strontium cerate (SrCeO@sub 3@) and barium zirconate (BaZrO@sub 3@) have been intensively studied as potential proton conducting electrolytes for fuel cells due to their high ionic conductivity for protons.@footnote 1@ However, instability in acidic gas environment such as carbon dioxide has limited practical usage of most of the doped cerates. Only yttrium doped barium zirconate (Y:BaZrO@sub 3@) has shown high proton conductivity combined with sufficient chemical stability.@footnote 2@ However, Y:BaZrO@sub 3@ is difficult to be densified using conventional sintering processes. This adversely affects their conductivity and mechanical strength.@footnote 3@ Furthermore, most Y:BaZrO@sub 3@ membranes that have been reported in the literature have been fabricated at thicknesses exceeding few tens of microns, which limits their use in low temperature applications because of its high area specific resistance (ASR). In this work, we report fabrication of nano-scale Y:BaZrO@sub 3@ films using an optimally-conditioned pulsed laser deposition technique. The thin films are prepared on single crystal magnesium oxide substrates or silicon nitride-buffered single crystal silicon wafers. Structural qualities of the film including crystallinity, density, and film composition are investigated using the X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and reflection (XRR) measurements. With the ultra-thin Y:BaZrO@sub 3@ membrane, we have fabricated fuel cells and measured the performance in terms of voltage-current relations. @FootnoteText@ @footnote 1@ Iguchi, S. et al., 2004 Fuel Cell seminar, Nov. 1-5, San Antonio, TX, USA (2004)@footnote 2@ Kreuer, K. D. Annual Review of Materials Research 33, 333-359 (2003)@footnote 3@ P. Babilo & S. M. Haile, J. Amer. Cer. Soc. 88, 2362-2368 (2005).

4:20pm **TF-WeA8 Growth and Electrochemical Properties of Li-Ni-Co-Al Oxide Films*, C.V. Ramana,*** University of Michigan*; K. Zaghib,* Institut de Recherches d'Hydro-Quebec*; C.M. Julien,* Universite Pierre et Marie Curie

There is a constantly increasing demand for miniaturized high energy density batteries to power microsystems such as microsensors, smart cards, implantable medical devices, intelligent labels, and so on. From this view point, there has been particular interest in solid-state lithium batteries fabricated by thin-film technology. The present work deals with the growth and electrochemical properties of the Li(Ni,Co,Al)O@sub 2@ films grown using pulsed laser deposition (PLD). The investigations revealed that the the growth and microstructure of the films is highly dependent on the substrate material, the growth temperature, and the gas pressure during ablation. The charge-discharge process conducted in Li-microcells demonstrates that effective high specific capacities can be obtained with films 1.35 Âµm thick. Stable capacities of 83 and 92 ÂµAh/cm@sub 2@Âµm are available in the potential range 4.2-2.5 V for LiNi@sub 0.8@Co@sub 0.2@O@sub 2@ and LiNi@sub 0.8@Co@sub 0.15@Al@sub 0.05@O@sub 2@ films, respectively. A comparison of the electrochemical performance of microcells using films deposited on Si and Ni is also made. The results obtained will be presented and discussed.

Thin Film
Room 2022 - Session TF-ThM
Fundamentals in Thin Film Deposition

Moderator: M.C.M. Van De Sanden, Eindhoven University of Technology, The Netherlands

8:00am **TF-ThM1 Tilted Fiber Texture in Aluminum Nitride Thin Films**, *J.M.E. Harper,* University of New Hampshire, US*; **D. Deniz**,* University of New Hampshire*; J.W. Hoehn, F. Chen,* Seagate Technology Inc.

We report a strong dependence of fiber texture tilt angle on the angle of deposition and gas composition in aluminum nitride (AlN) thin films prepared by reactive magnetron sputtering in N@sub 2@/Ar mixtures. Texture distributions were measured using x-ray pole figures. For fully nitrided films, deposited with N@sub 2@ flow of 15% of the total flow, the AlN c-axis fiber tilt angle increases steadily with deposition angle, with the c-axis approximately aligned with the deposition direction. At a deposition angle of 64@sup o@ from normal, a second population of grains appears with c-axis perpendicular to the main population, corresponding to a-axis alignment with the deposition direction, as reported by Rodriguez-Navarro et al.@footnote 1@ We measured the c-axis AlN tilt angle as a function of N@sub 2@ flow ratio for a deposition angle of 42@sup o@ from normal, and found that the c-axis remains perpendicular to the substrate for a N@sub 2@ flow ratio up to 12%, and then abruptly shifts towards the deposition direction for a N@sub 2@ flow ratio above 12%. We also identified a range of deposition parameters at lower N@sub 2@ flow in which an amorphous phase of AlN is formed. We attribute the tilted fiber texture to the energetic atom flux causing less damage and resputtering in grains oriented with open channeling directions, compared with non-channeling directions in AlN. The abrupt change in fiber tilt angle vs. gas composition is attributed to adatom mobility being quenched above 12% N@sub 2@ flow. @FootnoteText@ @footnote 1@A. Rodriguez-Navarro, W. Otano-Rivera, J.M. Garcia-Ruiz, R. Messier, and L.J. Pilione, J. Mater. Res., Vol. 12, No. 7, 1689 (1997).

8:20am **TF-ThM2 CVD of Titanium Diboride using Single Source Precursor***, **N. Kumar**, Y. Yang, W. Noh, G. Girolami, J. Abelson,* University of Illinois Urbana-Champaign

TiB@sub 2@ is a mechanically hard, metallic ceramic with a bulk melting temperature of 3220 °C and electrical resistivity of 10 @micro@@ohm@-cm. Thin films of TiB@sub 2@ have been used as wear resistant protective coatings in magnetic storage media and other applications. TiB@sub 2@ has also been investigated as a possible liner material and/or contact electrode in microelectronics. CVD growth of TiB@sub 2@ can be accomplished using halide based precursors, but this process is inherently corrosive and requires substrate temperatures in excess of 600°C. Girolami et al. previously synthesized the halogen free, single source precursor Ti(BH@sub 4@)@sub 3@dme. This talk will focus on the CVD of TiB@sub 2@ films using this precursor, including the deposition kinetics, film microstructure, diffusion barrier properties and conformality on trench shaped substrates. Films were grown at substrate temperatures ranging from 170 to 800 °C. Films grown at lower temperatures are X-ray amorphous whereas films grown at 800°C are polycrystalline. Film growth starts at temperatures as low as 170 °C on SiO@sub 2@ substrates. The growth rate is 2 nm/min below 200°C, 4 nm/min for intermediate temperatures, and 2.5 nm/min at 800 °C. There is no nucleation delay as measured by in situ ellipsometry, even at the lowest growth temperatures. For the lowest and highest growth temperatures, the films are nearly stoichiometric and have C and O contents lower than 5 at. % as measured by AES. In the intermediate temperature range the films have B/Ti ratio < 2 and the C and O contents are > 10 at. %. Low temperature films have a dense columnar microstructure as evaluated by SEM. For a 40 nm thick film, the RMS roughness by tapping mode AFM is 1.5 nm. The electrical resistivity is 265 @micro@@ohm@-cm. The film also performed well as a diffusion barrier to prevent Cu diffusion into Si for temperatures as high as 600 °C.

8:40am **TF-ThM3 Fundamentals in Thin Film Pulsed Laser Deposition: Growth Control at an Atomic Level***, **D.H.A. Blank**,* University of Twente and MESA+ Institute for Nanotechnology, The Netherlands **INVITED**

Pulsed Laser Deposition (PLD) is attractive for research on complex oxides because it is fast and one can easily investigate a wide range of different materials and compositions. Currently, a major issue in the growth of oxide materials with PLD is the control of the surface morphology. For most materials it is necessary to control the thickness and roughness of the thin films down to an atomic scale. Such well-controlled growth can also be used to manufacture artificially layered structures of, e.g., ferroelectric materials. In this way it is possible to create a whole new class of materials. It would be possible to create materials tailor-made to applications. Such materials are also ideal for the purpose of understanding the physics and the search for materials with even yet not-known properties. Much effort is put in the deposition of excellent textured layers without grain boundaries. In general the properties of highly oriented films approximate the properties of single crystals. Single or multi-layer structures require a well-conditioned process technique. The deposited layers must have a large homogeneity with well-defined material properties, smooth surfaces, and, in the case of oxides, the correct oxygen stoichiometry. Growth monitoring became possible even at relative high deposition pressures using ellipsometry and so-called high pressure Reflecting High Energy Electron Diffraction (RHEED). These developments have helped to make PLD a grown-up technique to fabricate complex materials and structures. With our development of HP RHEED PLD we are able to control the growth of these materials and to introduce new growth manipulations, like pulsed laser interval deposition. At present, extremely sharp and homogeneous interfaces can be realized and this is, for example, yet utilized in SrTiO@sub 3@-LaAlO@sub 3@ interfaces and artificial ferroelectric structures. In this presentation I like to show these unique techniques and the obtained results to design complex materials 'on demand'.

9:20am **TF-ThM5 Solvation Effects in the Kinetics of Supercritical CO@sub 2@ Based Deposition of Metal Oxide Thin Films***, **Q. Peng**, K.J. Park, D. Hojo, D. Barua, G.N. Parsons,* North Carolina State University

Supercritical CO@sub 2@ (scCO@sub 2@) offers unique solvent properties for metal-organic deposition, such as high solubility, high diffusion rate, zero surface tension, and high penetration ability. In our work, supercritical carbon dioxide process has been successfully used to deposit a variety of metal oxides including Ga@sub 2@O@sub 3@, Al@sub 2@O@sub 3@, ZrO@sub 2@, FeO@sub x@, Cr@sub 2@O@sub 3@, Co@sub 3@O@sub 4@, and WO@sub x@ thin films on native oxide silicon wafer from direct pyrolysis of organometallics. Conformal and reflective metal oxide films with good adhesion have been obtained. The kinetics of Al@sub 2@O@sub 3@ and Ga@sub 2@O@sub 3@ deposition has been studied to show the mechanism of scCO@sub 2@ based deposition process. For example, for Al@sub 2@O@sub 3@ deposition from Al(acac)@sub 3@, the deposition rate at 200°C is observed to be 10nm/min, compared to <1nm/min for typical vacuum based CVD from the same precursor. Similar results were observed for Ga@sub 2@O@sub 3@ thin film from Ga(acac)@sub 3@. Moreover, an overall activation energy of 60-70 kJ/mol and 80-85 kJ/mol were observed for pyrolysis of Al(acac)@sub 3@ and Ga(acac)@sub 3@ in scCO@sub 2@ phase, respectively, which are less than typical values obtained in vacuum CVD. Solvation energy of stabilization of the reaction transition state is suggested as the main reason for the enhanced surface reaction rates. The reduced kinetic barrier will be discussed in terms of relative polarity of the solvent and transition state structure. The solvation effect of scCO@sub 2@ can enable lower process temperature to enable material processing on temperature-sensitive surfaces.

9:40am **TF-ThM6 Formation of c-Si/a-Si:H Interfaces Studied by Real-Time Second-Harmonic Generation, Spectroscopic Ellipsometry, and Infrared Spectroscopy***, **J.J.H. Gielis**, P.J. van den Oever, B. Hoex, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

The properties of crystalline silicon / amorphous silicon (c-Si/a-Si:H) interfaces are of key importance for new developments in solar cell research, e.g. to obtain high efficiency silicon heterojunction (SHJ) solar cells or diffused emitter solar cells with an excellent level of surface passivation. We have studied the interface formation between H-terminated Si(100) and a-Si:H in a hot-wire chemical vapor deposition process (HWCVD). The interface formation has been studied in real-time for films between 5 and 70 nm using three different optical diagnostics simultaneously. Spectroscopic ellipsometry (SE) has been used to determine the optical properties of the a-Si:H, the film thickness and the surface roughness evolution and gives insight into the nucleation phase of film growth. Information on the hydrogen bonding modes and hydrogen depth profile in the film has been obtained by attenuated total reflection (ATR) infrared spectroscopy. Second-harmonic generation (SHG), a nonlinear optical technique sensitive to surface and interface states, has been used both in real-time and spectroscopically in the fundamental photon energy range of 1.33-1.75 eV. In this range the SHG signal is governed by two-photon resonances related to modified Si-Si bonds in the

surface and interface regions of the c-Si and a-Si:H. The spectral width of the resonances provides a distinction between c-Si and a-Si:H. The spectra indicate that the SHG signal is generated mainly at the c-Si/a-Si:H interface. From the real-time experiments detailed information into the c-Si/a-Si:H interface formation is obtained, such as: the nucleation of a-Si:H islands on the c-Si along with SiH@sub x@ surface species, the occurrence of film 'closure', and the appearance of bulk SiH@sub x@ together with a correlation with the SHG signal. On the basis of these observations key aspects of the c-Si/a-Si:H interface formation will be discussed.

10:00am **TF-ThM7 Kinetic Pathways Leading to Layer-By-Layer Growth: A Multibllion Time-Step Molecular Dynamics Study***, **V. Chirita**, D. Adamovic, E.P. Münger, L. Hultman,* Linköping University, Sweden*; J.E. Greene,* University of Illinois, Urbana

We employ multibillion time-step embedded-atom method molecular dynamics simulations to study homoepitaxial growth of Pt(111) during low-energy (5 - 50 ev) Pt irradiation at 5 eV intervals. We deposit 5 monolayers at 1000K and with fluxes corresponding to deposition rates of 5x10@super 5@ µm/min and 5x10@super 4@ µm/min, i.e. only 3, respectively 2, orders of magnitude higher than experimental rates used in electron beam-physical vapor deposition (EB-PVD). To analyze the results we calculate normalized anti-phase intensities, as measured in reflection high-energy electron diffraction (RHEED), and detect a 3-dimensional (3D) growth mode for energies of up to 20 eV. However, for E = 20 eV and higher, the RHEED intensities signal the transition to layer-by-layer growth mode. In order to determine the mechanism responsible for the observed change in the growth mode we isolate, with unprecedented accuracy, the effects of irradiation-induced processes from thermally activated mass transport during deposition. We find that for all energies irradiation events are completed within 10 ps following impacts while thermal migration is not affected by the deposition energy. We provide direct evidence that the energy threshold observed at 20 eV (and observed in many experimental studies) is entirely due to the atomic processes induced by the irradiation process, in the first 10 ps following the arrival of energetic species. Adatom scattering, surface channeling, dimer formation and cluster disruption are identified as primary mechanisms responsible for 2-fold and 5-fold increases in intra-, respectively interlayer, mass transport rates as irradiation energy is increased from 10 to 20 eV. The same kinetic pathways, leading to an even more clear transition from 3D to layer-by-layer growth, are identified in µs-long (multibillion time step) MD simulations carried out at fluxes approaching experimental conditions. Our results should apply to most fcc (111) metallic planes and have added significance in the low-temperature regime, where thermal processes are exponentially depressed, as it will be discussed.

10:20am **TF-ThM8 Interpretation of the Roughness in Au(111) Polycrystalline Films***, **E. Rodriguez-Canas,*** Instituto de Ciencia de Materiales de Madrid (CSIC), Spain*; J.A. Aznarez,* Instituto de Fisica Aplicada (CSIC), Spain*; E. Vasco, J.L. Sacedon,* Instituto de Ciencia de Materiales de Madrid (CSIC), Spain

Recently, the surface morphology of columnar polycrystalline Au(111) films grown by thermal evaporation on native SiO@sub x@-covered Si(100) has been investigated by scanning tunneling microscopy (STM). The STM images reveal that the surface can be broken down into columnar-assembled paraboloidal-like elements. The analysis method based on the surface decomposition into single elements introduces a complete set of statistical parameters related to the elements shapes and allows to quantitatively characterize the Au(111) growth front. The height distribution curves of the imaged surfaces are described by means of an explicit expression of these shape parameters, which are connected with phenomena that control the columnar growth and the growth front evolution.@footnote 1@ After summarizing these results, we will show that the usual roughness or interface width can be decomposed as an algebraic expression of the statistical set of parameters. This expression allows to decompose the roughness into components with well-defined meanings. The roughness expression is applied to analyze the scaling laws of the roughness with deposition time in the Au(111) films and it is successfully compared with the experimental results. We extend the roughness analysis method proposed here to surface morphologies formed from elements with other shapes (e.g., conical- or spheroidal cap-like elements). The application of the method is suitable for columnar as well as for growth fronts composed by mounds. The relation of the components of the roughness with the various kinds of growth models is discussed. @FootnoteText@ @footnote 1@ J. L. SacedÃ³n, E. RodrÃguez-CaÃ±as, C. Munuera, A. I. Oliva, and J. A. AznÃ¡rez, Phys. Rev. B 72, 195413 (2005).

Surface Science
Room 2004 - Session SS2+NS+TF-ThA

Tribology

Moderator: J. Krim, North Carolina State University

2:00pm **SS2+NS+TF-ThA1 Investigation of the Tribology of Diamondlike Carbon and SAMs using Molecular Dynamics***, **J. Harrison**, P. Mikulski, G. Gao, J. Schall,* United States Naval Academy **INVITED**

Examination of the Tribology of DLC and SAMs using Molecular Dynamics@footnote 1@ The development of micron-sized devices, such as microelectromechanical devices, for terrestrial and space applications has prompted the need for protection of the surfaces of these devices. Amorphous carbon films, diamondlike carbon, and self-assembled monolayers (SAMs) are all possible candidates for the passivation and lubrication of these devices. The fundamental problem associated with controlling friction is a lack of understanding of the underlying atomic-scale processes that govern both friction and wear. Over the past several years, we have performed extensive molecular dynamics simulations using the REBO@footnote 2@ and the AIREBO@footnote 3@ potentials aimed at understanding the atomic-scale mechanisms of friction in hydrocarbon systems. We have examined the contact forces present at the interface of a nominally flat, DLC tip and model alkane SAMs during sliding. We have also examined the effects of tip roughness on the contact friction. In addition, we have done simulations that have analyzed the tribological, mechanical, and transport properties of amorphous carbon films and diamondlike carbon films with various compositions. Some of our recent results will be discussed. @FootnoteText@ @footnote 1@ This work was supported by The Air Force Office of Scientific Research under contracts F1ATA04295G001 and F1ATA04295G002 (The Extreme Friction MURI) and by The Office of Naval Research (N00014-06-WX-20205).@footnote 2@ D. W. Brenner, Shenderova, O. A., Harrison, J. A., Stuart, S. J., Ni, B., and Sinnott, S. B., J. Phys. C. 14, 783 (2002).@footnote 3@ S. J. Stuart, Tutein, A. B., and Harrison, J. A., J. Chem. Phys. 112, 6472 (2000). .

2:40pm **SS2+NS+TF-ThA3 Interfacial Force Microscopy of Viscous Water on Hydrophilic Surfaces***, **M.P. Goertz**, R.C. Major, X.-Y. Zhu,* University of Minnesota*; J.E. Houston,* Sandia National Laboratories

The hydration of surfaces is important to many fields and its effect on system behavior has been studied for decades, yet the detailed origins of the forces involved are still under debate. We use interfacial force microscope (IFM) to measure the viscosity of water thin films with nanometer thickness on hydrophilic surfaces, including silica and carboxylic acid terminated alkanethiol self-assembled monolayers. We obtain the viscosity from this interfacial water from three different measurements: shear force measurement for a water meniscus formed between a tip and the hydrophilic surface under ambient conditions; shear force measurement for the interfaces under water; and repulsive, draining-force measurements of the two approaching interfaces immersed in water. In all three types of measurements, we obtain effective viscosities more than 10@super 6@ times greater than that of bulk water for interfacial separations on the nanometer scale. The experiments clearly show that the extent of the interphase layer and its level of viscosity depend sensitively on the strength of hydrophilic interaction, gradual degrading after the surfaces have been in water for a couple of hours. Thus, it is clear that a strong water/surface interaction gives rise to an increases in water-water bonding near the two surfaces and it is this increased level of bonding that is disturbed by the lateral tip motion resulting in the observed viscosity increase.

3:00pm **SS2+NS+TF-ThA4 Design of Environmentally Friendly Lubrication Systems through Surface Grafting of Ultrahydrophilic High-density Polymer Brushes***, **A. Takahara**, M. Kobayashi,* Kyushu University, Japan*; K. Ishihara,* The University of Tokyo, Japan*; A. Suzuki, M. Kaido,* Toyota Motor Co., Ltd., Japan

The hydrophilic polymer brushes of poly(2,3-dihydroxypropyl methacrylate) (poly(2)) and poly(2-methacryloyloxyethyl phosphorylcholine) (poly(3)) were prepared by surface-initiated atom transfer radical polymerization of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (1) and (3) on the initiator- immobilized silicon wafer. A large water contact angle hysteresis was observed for poly(2). Extremely low water contact angle and low contact angle hysteresis of poly(3) against water were observed. Neutron reflectivity measurements at water/poly(3) brush interface reveled that the poly(3) is highly stretched to the bulk water phase. Frictional properties of the poly(2) and (3) brushes were characterized by sliding a glass ball probe on the polymer brush surfaces in various solvents under the load of 0.49 N at a sliding velocity of 90 mm/min. Friction coefficient of poly(3) brush was lower than that of poly(2) in water. This can be ascribed to the presence of phosphorylcholine in poly(3). Further low friction coefficient was observed, even in air, by sliding a poly(3) brush immobilized glass ball against poly(3)-immobilized silicon wafer.

3:20pm **SS2+NS+TF-ThA5 Mechanical Properties of Alkanethiol Monolayers on Gold: A Force Spectroscopy Approach***, **G. Oncins**, C. Vericat, F. Sanz,* University of Barcelona, Spain

Since the discovery of the self-assembling process of alkanethiol molecules on gold, these monolayers have been a matter of increasing interest not only from the point of view of basic surface science, but also due to their many applications in nanotechnology.@footnote 1@ Their mechanical properties have been widely studied by several techniques, especially by scanning probe microscopy.@footnote 2@ The growth mechanism of these monolayers on gold in vacuum has been followed by in situ Scanning Tunnelling Microscopy (STM).@footnote 3@ Atomic Force Microscopy (AFM) has proved to be suitable to study the topography and mechanical properties of alkanethiol monolayers under compression.@footnote 4@ In this contribution, we used Force Spectroscopy to study the behavior of alkanethiol monolayers deposited on a (111) monocrystalline gold surface in an electrolyte aqueous solution. The analysis of the force curves shows that the tip indents the monolayer in a stepped way and that the force at which these stepped events have place depends on the compactness of the monolayer. Thanks to newly developed models to calculate the mechanical constants of monolayers on hard substrates,@footnote 5@ we were able to calculate the different values of Young's modulus for alkanethiol monolayers of different compactness and chain length. @FootnoteText@ @footnote 1@J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, Chem. Rev., 2005, 105, 1103.@footnote 2@R.W. Carpick, M. Salmeron, Chem. Rev., 1997, 97, 1163.@footnote 3@G.E. Poirier, Langmuir, 1999, 15, 1167.@footnote 4@E. Barrena, C. Ocal, M. Salmeron, J. Chem. Phys., 2000, 113(6), 2413.@footnote 5@E.K. Dimitriadis, F. Horkay, J. Maresca, B. Kachar, R.S. Chadwick, Biophys. J., 2002, 82(5), 2798.

3:40pm **SS2+NS+TF-ThA6 Observations of Microslip in Realistic Microscopic Contacts with Combined Nanoindentation and Quartz Microbalance***, **B. Borovsky**,* St. Olaf College*; A. Booth,* Grinnell College

For emerging technologies such as micromachined devices, it is increasingly important to understand the frictional properties of microscale sliding contacts and how these may be optimized with ultrathin lubricant films. While high sliding speeds and multiple contact points characterize realistic systems of interest, most theoretical and experimental studies of small contacts do not access this physical regime. We have therefore used a combined indenter probe and quartz crystal microbalance (QCM) to study the contact between a sapphire sphere and a polycrystalline gold electrode undergoing transverse shear at speeds near 1 m/s. The contacts were lubricated with monolayer octadecanethiol films. We find that both the elastic and dissipative components of the interaction are best described by the microslip model for reciprocating interfaces. We directly observe a 60% reduction in the tangential stiffness as the interface undergoes a spontaneous transition from stuck to slipping. For a mostly-slipping interface, the frequency and bandwidth shifts of the QCM are proportional to each other and track changes in the contact radius, as derived from the normal contact stiffness. Furthermore, we observe shear loss tangents over 0.4, more than 100 times larger than expected for no-slip conditions. We will show that our results are consistent with force-equilibrium microslip theory@footnote 1,2@ by proposing a simplified dynamic model of hysteresis effects in microslip, based on the driven harmonic oscillator. Research supported by NSF, Research Corporation, and Hysitron, Inc. @FootnoteText@ @footnote 1@R. D. Mindlin, W. P. Mason, T. F. Osmer, and H. Deresiewicz, Proceedings of the First U. S. National Congress of Applied Mechanics, 1951, pp. 203-208.@footnote 2@K. L. Johnson, Contact Mechanics, Cambridge University Press, NY, 1985, pp. 216-230.

4:20pm **SS2+NS+TF-ThA8 The Effect of Filling and Temperature on the Mechanical Responses of Carbon Nanotubes***, **S.-J. Heo**, S.B. Sinnott,* University of Florida

It is well known that carbon nanotubes (CNTs) have fascinating electrical, optical, chemical, and mechanical properties that differ from the properties of macroscale carbon materials such as graphite or diamond. As a result of these properties, CNTs are being considered as candidate materials for MicroElectoMechanical System (MEMS)/NanoElectroMechanical System

(NEMS) components. It is therefore worthwhile to study the mechanical behavior of CNTs to better understand how they might fit in with the mechanical property requirements of MEMS/NEMS. To facilitate this better understanding, we have explored two different mechanical responses of CNTs, to bending and compression, using classical molecular dynamics simulations. The second generation reactive bond order potential is used to model the short-range covalent interactions and a Lennard-Jones potential is used to model the long- range van der Waals interactions. In particular, we have modeled a three-point bend test to explore the mechanical responses of the single walls CNTs, single-walled CNTs filled with C60, double-walled CNTs, and triple-walled CNTs. A compression test has also been done on these same systems. Filling the single-walled CNTs, or increasing the number of inner shells in the case of multi-walled CNTs, is predicted to increase both the bending strength and the maximum buckling force. We have also investigated the effect of temperature on the mechanical responses of the CNTs. On the whole, higher temperatures are predicted to lower the bending strength of the CNTs. This work is supported by the National Science Foundation funded Network for Computational Nanotechnology (EEC-02288390).

4:40pm **SS2+NS+TF-ThA9 Assessing nanomechanical properties and nanoscratch resistance of Me-ZrN and ZrN thin films using Atomic Force Microscope***, **D.M. Mihut**, J. Li, S.R. Kirkpatrick,* University of Nebraska-Lincoln*; S. Aouadi,* Southern Illinois University*; S.L. Rohde,* University of Nebraska-Lincoln

The present study aims at getting a better understanding of the correlation between nanomechanical properties (nanohardness (H), elastic modulus (E), H/E and H3/E2 ratio) and nanotribological properties (resulting from nanoscratch measurements) for three groups of Me-ZrN thin films (Inconel-ZrN, Cr-ZrN and Nb-ZrN) and ZrN thin films. Nanomechanical and nanotribological properties for Me-ZrN and ZrN thin films deposited by DC unbalanced magnetron sputtering were investigated using atomic force microscope (AFM) interfaced with a Hysitron Triboscope. The elastic recovery of thin films under a normal load applied during nanoindentation was evaluated and correlated with elastic recovery of thin films under a dynamic load applied during nanoscratch measurements and with other mechanical properties in order to predict the thin film composition that will better serve for wear resistant applications.

Thin Film
Room 2020 - Session TF1-ThA
Field Emission

Moderator: B. Holloway, Luna Nanoworks

2:00pm **TF1-ThA1 Field Emitter Arrays: Issues and Opportunities***, **J. Shaw**,* Naval Research Laboratory **INVITED**

An electron source technology compatible with micro-fabricated structures would enable many new devices ranging from x-ray sources to a new generation of high frequency vacuum electron devices. One well-known candidate source is the field emitter array. Field emission allows electrons to be removed from solids without first raising their energy (eg by heat or radiation), making them very convenient to use. The non-linear I-V characteristic allows row-column addressing. Local emission current densities over 10@super 8@ A/cm@super 2@ are possible, limited by space charge. Field emitter arrays, multiple field emission structures together with local electrodes used to produce the extraction field, can be fabricated using a number of standard and exotic patterning methods. Individual cells in an array typically have dimensions on the order of 1 micron. Transit through the high field region takes less than 1 pS, potentially allowing THz emission modulation. Average current densities over 10@super 3@ A/cm@super 2@ and total currents over 100 mA have been demonstrated. However, producing these outstanding results is not easy. One might assume that N field emitters in parallel might produce N times the current that can be produced by a single tip. But variations among emitters typically allow only a small fraction of the emission sites to produce current, and the fraction tends to decline with the number of emission sites. The total current is typically no more than 10@super 3@ times the maximum current from a single emitter, even when 10@super 5@ or 10@super 6@ emitters are present. The poor uniformity is not surprising, given that the field emission current is sensitive to both the shape of the emitter and the density and energy of electrons at the surface. I will discuss some strategies for improving the total emission current.

2:40pm **TF1-ThA3 Field Emission Performance in Various Vacuum Conditions and Multistage Field Enhancement Effect of Tungsten Oxide Nanowires***, **R. Seelaboyina**, J. Huang,* Florida International University*; D. Kang, J. Park,* Samsung Advanced Institute of Technology, Korea*; W.B. Choi,* Florida International University

We report on the field emission properties of tungsten oxide nanowires grown on a tungsten tip and its emission performance in various vacuum conditions. Tungsten oxide (W@sub 18@O@sub 49@) nanowires were grown by thermal chemical vapor deposition in a mixture of CH@sub 4@ and H@sub 2@ on an electrochemically sharpened tungsten tip. The field emission measurements showed a low turn-on field of ~0.9 V/µm, high emission current of 170 mA and a large field enhancement factor of ~19800. The high field emission current is attributed to the multi stage field enhancement of the two-stage emitter geometry. High emission current of a few µA was also observed in relatively poor vacuum of 3x10 @super -3@ Torr, and the emission properties were recovered at 1x10 @super -6@ Torr after measurements under poor vacuum.

3:20pm **TF1-ThA5 Digital Electrostatic Electron-Beam Array Lithography (DEAL) Prototype Improvements***, **R.B. Rucker**,* University of Tennessee*; S.J. Randolph,* Oak Ridge National Laboratory and University of Tennessee*; L.R. Baylor, W.L. Gardner,* Oak Ridge National Laboratory*; K.L. Klein,* Oak Ridge National Laboratory and University of Tennessee*; M.A. Guillorn,* IBM*; S. Islam, Y. Guan, T. Rahman, S.A. Eliza, T. Grundman, R. Vijayaraghavan,* University of Tennessee*; D.C. Joy, P.D. Rack,* Oak Ridge National Laboratory and University of Tennessee*; D.K. Hensley, R.J. Kasica, D.K. Thomas, T. Bigelow,* Oak Ridge National Laboratory

The Digital Electrostatic electron beam Array Lithography (DEAL) design is presently under development at Oak Ridge National Laboratory.@footnote 1@ The device is designed for massively parallel electron beam lithography that encompasses an array of individually addressable field emitters (FE) and an electrostatic focusing grid. The device design has shifted from utilizing carbon nanofiber (CNF)-based cathodes to tungsten (W) nanofibers deposited by electron-beam-induced deposition (EBID), which has considerably improved the quality and placement of the emitter. The tungsten nanofibers provide performance improvements from the localization of emission sites and a reduction of chromatic aberration. In an effort to increase the depth of focus and lower beam divergence, as well as to function as a focusing electrode, a 500-nm diameter beam- forming aperture has been developed. Fabrication and operation details will be covered, which demonstrates further improved performance of the device design. @FootnoteText@ @footnote 1@This research was sponsored by the Defense Advanced Research Projects Agency (DARPA) under contract No. DARPA-MIPR-97-1357 with ORNL. The research was carried out at ORNL and the University of Tennessee, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract No. DE-AC05-00OR22725. 2 L. R. Baylor, D. H. Lowndes, M. L. Simpson, C. E. Thomas, M. A. Guillorn, V. I. Merkulov, J. H. Whealton, E. D. Ellis, D. K. Hensley, and A. V. Melechko, J. Vac. Sci. Technol. B 20, 2646 (2002).

Thin Film
Room 2022 - Session TF2-ThA
Pulsed Laser Deposition of Thin Films

Moderator: S.L. Jones, Norfolk State University

2:00pm **TF2-ThA1 Cathodoluminescence Degradation of Y@sub 2@SiO@sub 5@:Ce Thin Films***, E. Coetsee, **J.J. Terblans**, H.C. Swart,* University of the Free State, South Africa

The cathodoluminescence (CL) intensity of cerium-doped yttrium silicate (Y@sub 2@SiO@sub 5@:Ce) phosphor thin films, grown by pulsed laser deposition (PLD), were investigated for possible applications in low voltage field emission displays (FEDs). A thin layer of tin oxide (SnO@sub 2@) was ablated on the surface of some of the films in order to investigate the effect, of the coated layer, on the degradation of the CL intensity. Auger electron spectroscopy (AES), X-ray photo electron spectroscopy (XPS) and CL spectroscopy were used to monitor changes in the surface chemical composition and luminous efficiency of the thin films. AES and CL spectroscopy were done with 2 keV energy electrons and beam current densities between 26.3 mA.cm@super -2@ and 52.6 mA.cm@super -2@, in high vacuum and in oxygen pressures of 1x10@super -8@, 1x10@super -7@ and 1x10@super -6@ Torr. Residual gas mass analysis (RGA) showed that the adventitious C was removed from the surface as volatile gas species which is consistent with the electron stimulated surface chemical reaction (ESSCR) model. Tin oxide (SnO@sub 2@) coated thin films resulted

in a lower but more stable CL intensity than the uncoated thin films with light emission from the rare earth, Ce@super 3+@, due to the 5d - 4f transition resulting in the characteristic double shoulder peak of Y@sub 2@SiO@sub 5@:Ce between 400 and 500 nm (blue light).

2:20pm **TF2-ThA2 Computational Study of the Initial Stage of Pulsed Laser Deposition of SrTiO@sub 3@ Thin Films***, **J.M. McKillip**, R.K. Behera, S.R. Phillpot, S.B. Sinnott,* University of Florida

Thin film deposition of SrTiO@sub 3@ is currently a popular area of research due to its widespread use in electronic applications and the motivation to shrink electronic components. Pulsed laser deposition (PLD) is an effective deposition process yielding dense, homogeneous thin films. Here, classical molecular dynamics simulations are used to delve into the initial processes occurring in PLD. The simulations show that collisions between the incident particles and the substrate can induce chemical bonding. This study considers the deposition of SrO and TiO@sub 2@ molecules assigned a kinetic energy of 0.1, 0.5 and 1.0 eV/atom on a (001) surface of SrTiO@sub 3@. The effects of impact energy and surface termination layer (SrO vs. TiO@sub 2@) are examined. The main surface phenomenon of interest is chemical changes that occur at the metal-oxide surface due to the incident particles and structural features of the deposited film. The simulation results are compared to experimental data, where available.

2:40pm **TF2-ThA3 Dynamics of Ultrafast Laser Generated Ablation from Metals and Semiconductors Close to the Ablation Threshold***, **S.M. Yalisove**, J.P. McDonald,* University of Michigan **INVITED**

The evolution of ultrafast laser generated material ejection close to the ablation threshold can studied with a variety of methods. Ultrafast microscopy has been used to study the expulsion of a thin (~40nm) layer of molten material from metals and semiconductors when irradiated with laser pulses of duration less than ~600 femtoseconds and intensity close to the ablation threshold. These methods use pump-probe techniques to construct a series of time resolved images with resolution limited by the duration of the ultrafast laser pulse. We will present results from Si surfaces with a variety of thermal oxide thicknesses that are irradiated with 780 nm laser pulses of duration 150 femtoseconds at normal incidence. The intensities we have studied range from 1-20 times the ablation threshold. Intensities below 10 times of the ablation threshold generally do not produce optically emitting plasmas. We will show that ablation in this regime is fundamentally different that at higher intensities. Three different pump-probe imaging methods will be presented; Newton's ring analysis at normal incidence, side view imaging at grazing incidence, and a new method using a delayed pulse to excite optical emission of the ejected material. While many physical processes occur on the sub picosecond time scale, ejection of material typically occurs about 1-10 picoseconds after ultrafast laser irradiation. The images in this study are acquired every 50 picoseconds up to about 12 nanoseconds after irradiation. Movies made from these images will be shown. Analysis of the results from these studies will be presented including momentum transfer and efficiency of these processes, a physical model to explain phenomena observed with varying oxide thickness and laser fluence, and the different dimensionalities of Sedov-Taylor scaling that are observed. The impact of these studies on ultrafast pulsed laser deposition will be discussed.

3:20pm **TF2-ThA5 Electrical Conduction in Pulsed-Laser Deposited As- and Ga-doped ZnO Films***, **A.K. Pradhan**, K. Lord, D. Hunter, T.M. Williams, S. Cherry, S.L. Jones,* Norfolk State University

The increasing demand for transparent conducting oxides and p-n junction based-short wavelength light emitting diodes has created a lot of research interest. We report the synthesis of epitaxial As-doped ZnO and Mn-doped (ZnAs)O films by pulsed-laser deposition (PLD) technique. The grain size in (ZnAs)O films decreases from 40 nm to less than 10 nm upon Mn doping, illustrating that Mn acts a potential catalyst creating nanosize grains. Temperature dependent electrical resistance shows metal-insulator (MIT) and metal-semiconductor transitions (MST) at 165 and 115K, respectively, in (ZnAs)O, although Mn-doping suppresses MST completely. Both ionization efficiency of oxygen vacancies and percolation of charge carriers may be responsible for such transitions. In addition, electrical conduction is these films show strong ageing effects related to the conductivity instability in the film. We have also synthesized highly epitaxial conducting Ga-doped ZnO system by the PLD techniques. The films show transmittance more than 85% in the visible region. The films show very high electrical conductivity. The temperature dependent resistivity measurements of these highly conducting and transparent films show several transitions. The extensive results will be presented.

3:40pm **TF2-ThA6 Nanoscale Laser Processing and Micromachining of Biomaterials and Biological Components***, **D.B. Chrisey**,* Rensselaer Polytechnic Institute **INVITED**

Lasers are increasingly proving to be an enabling approach to process biomaterials and biological components on the nanometer length scale. While nanotechnology encompasses an array of enabling technologies that utilize the fact that matter at length scales less than 100 nanometers have distinctly different physical and chemical properties than the same matter at larger length scales, biology and biological components are a special subset since the fundamental building blocks are almost all less than 100 nanometers in size, i.e., biological molecules are constantly being used in a directed self-assembly manner to communicate and build new materials. There are already several successful examples of nanotechnology starting from the somewhat mundane sharper scalpels and protective sunscreens, to more effective drug delivery, and even biomolecular motors, gene therapeutics, tissue engineering and improved medical diagnostics. The unique capabilities of laser processing for these applications is based on tuning the laser-material interaction to create novel structures, i.e., the laser wavelength, pulse width and power can be varied over a wide range as can the composition and state of the material. This presentation will summarize several successful examples of the laser processing of biomaterials and biological components.

4:20pm **TF2-ThA8 Laser Desorption from Polytetrafluoroethylene at 157 nm -- A Possible Reactant Source for Thin Film Growth***, **S. John**, S.C. Langford, J.T. Dickinson,* Washington State University

Thin film growth of a number of polymers, including polytetrafluoroethylene (PTFE -- Teflon), has been achieved using pulsed laser deposition (PLD). Past studies have also shown that 157 nm Excimer (nanosecond) pulsed laser irradiation is uniquely clean and efficient in etching PTFE. We characterize the resulting neutral and charged products accompanying this exposure using time resolved mass spectroscopy as a function of laser fluence. We find that photochemical release of neutral species of the form (CF@sub 2@)@sub n@, where n = 1,2,3, and possibly 4 occurs with non-thermal kinetic energies (~0.8 eV). A slow component is also observed attributed to an un-zipping reaction with a lifetime of 180 µs. We also observe both positive and negative ions with kinetic energies of a few eV. Mechanisms for the formation of these ions is under study; electrons emitted during the laser pulse are likely involved in the formation of negative ions. We examine possible scenerios to maximize PTFE film growth in light of our measurements.

Thin Film
Room 3rd Floor Lobby - Session TF-ThP
Thin Film Poster Session

TF-ThP1 Electrochromic Smart Windows Based On Titanium Doped WO@sub 3@ Thin Films*, **A. Karuppasamy**, A. Subrahmanyam,* Indian Institute of Technology Madras, India

Smart windows are electrochromic glass window panes that can change their transparency value in response to an applied voltage pulse. In the present study, we have developed the proton based and lithium based monolithic electrochromic structures consisting of five thin film layers; Glass/ITO/Ti:WO@sub 3@/Ta@sub 2@O@sub 5@/NiO/ITO and Glass/ITO/Ti:WO@sub 3@/LiAlF@sub 4@/NiO/ITO respectively. The Ionic conductor (Ta@sub 2@O@sub 5@) and ion storage layer (NiO) were deposited by electron beam evaporation and the active electrochromic (EC) layer (Ti:WO@sub 3@) was deposited by reactive pulsed dc magnetron sputtering. Pure Titanium and Tungsten metal targets were co-sputtered in argon and oxygen atmospheres keeping the sputtering power constant. The smart window performance of the EC film was systematically studied in three steps. First, the material properties of the EC film were investigated by XRD, AFM, UV-Vis spectrophotometer and Kelvin probe. The thickness and the optical constants were estimated from the reflectance measurements. Secondly, the electrochromic behaviour of the EC film was characterized by cyclic voltammetry (CV). The CV measurements were performed using a potentiostat with a standard three-electrode configuration consisting of the sample as the working electrode.1.0 MLiClO@sub 4@ in PC and 1.0 MHCL were used as electrolytes. Finally, the smart window comprising of five layers were devoloped and tested. The optical modulation (@DELTA@OD), coloration effiiency(CE) and switching time(@tau@@sub s@) for the proton based device was found to be better with typical values; @DELTA@OD = 60%, CE = 80 cm@super 2@/C (at@lambda@=550nm) and @tau@@subs@~1s (for 1cm x 1cm device).

TF-ThP2 Effect of Substrate Temperature on PMMA Nanocomposite Thin Films Grown by Laser Assisted Deposition*, A.T. Sellinger, E.M. Leveugle, K. Gogick, L. Zhigilei, **J.M. Fitz-Gerald**,* University of Virginia

Nanocomposite thin films of poly (methyl methacrylate) (PMMA) infused with carbon nanotubes (CNT) were grown using matrix assisted pulsed laser evaporation (MAPLE) and pulsed laser deposition (PLD). MAPLE targets were formed from frozen solutions of PMMA dissolved in toluene with CNTs in suspension. Significant surface morphology was observed in films deposited at room temperature. The origin of surface feature formation was probed using scanning electron microscopy (SEM), time-gated imaging and molecular dynamics simulations. Both experimental and computational findings suggest that micron sized matrix-polymer clusters are ejected from the irradiated target and are subsequently deposited onto the substrate. In flight, a polymer rich membrane is formed around the exterior of the cluster, encapsulating the solvent within. The remaining toluene vapor eventually escapes from the cluster, leaving only a polymer "sack". In an effort to decrease the observed morphology, substrate temperature was varied between 10 and 152 °C during subsequent depositions. Significant improvements in film morphology were observed as the substrate temperature was increased. Polymer degradation in films grown at several substrate temperatures was characterized using Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC).

TF-ThP3 Characterization of ZnO-In@sub 2@O@sub 3@/ZnO Laminated Thin Films Prepared by Pulsed Laser Deposition*, **T. Moriga**, K. Ishida, A. Taki, H. Ohno, Y. Sakakibara, K. Murai,* The University of Tokushima, Japan*; M. Mikawa,* Takuma National College of Technology, Japan*; K. Tominaga,* The University of Tokushima, Japan

It is well-known that zinc oxide thin film is easy to be deposited as a crystalline wurtzite-type structure. However, heavy doping of indium in zinc oxide (~10%) led the films to be poor crystallized. When single-crystalline sapphire substrates were used instead of glass substrates, the significant reduction of resistivity and improvement of crystallinity were observed in the zinc-rich ZnO- In@sub 2@O@sub 3@ films. In this study, we deposited the zinc-rich ZnO- In@sub 2@O@sub 3@ film over crystalline ZnO film on a glass substrate, that is, ZnO-In@sub 2@O@sub 3@/ZnO laminated thin film on a glass substrate, to improve the electrical properties. Thin films were deposited on a Corning 1737 glass substrate by pulsed laser deposition using a KrF excimer laser beam with a laser fluence of 2J/cm@super 2@. The targets were pellets of a mixture composed of ZnO and In@sub 2@O@sub 3@ powder, which were sintered at 1000°C for 1 hour. The base pressure in the chamber was of the order of 10@super -6@ Torr, and pure oxygen gas was introduced into the chamber with a flow rate of 30ccm during the deposition. The shot numbers for depositions were 10000 for a buffer film and 30000 for a major film on the buffer. At the substrate temperature of 380°C, we could deposit the ZnO-In@sub 2@O@sub 3@ layer over ZnO layer as a buffer layer on the glass substrate. When the composition reached x=0.90 in xZnO-(1-x) In@sub 2@O@sub 3@, the overall resistivity of the 0.90ZnO-0.10 In@sub 2@O@sub 3@/ZnO bilayer film was remarkably improved by one order magnitude, compared with that of the single 0.90ZnO-0.10 In@sub 2@O@sub 3@ film on the glass substrate. Simultaneously, the diffraction intensity assigned to the 0.90ZnO-0.10 In@sub 2@O@sub 3@ phase in the bilayer film increased significantly, resulting from improvement of crystallinity of the phase.

TF-ThP4 The Effect of Additive Oxide Material to the MgO Protecting Layer on the XPS Spectra and the Electrical Properties in AC-PDP*, **S.H. Moon**, T.W. Heo, S.Y. Park, J.H. Kim, H.J. Kim,* Seoul National University, South Korea

A MgO layer reduces the discharging voltage of AC-PDP (Alternating current â?" Plasma Display Panel) due to its high secondary electron emission coefficient and protects the dielectric layer from the ion bombardments during the discharge.@footnote 1-2@ The mechanism of secondary electron emission from MgO is basically understood by Auger neutralization and resonance neutralization.@footnote 3-4@ Considering to the mechanism, it is a key factor to control the work function or the summation of band gap and electron affinity.@footnote 5@ This report focused on the effect of additive oxide material to the MgO protecting layer on the XPS spectra and the electrical properties. Some kinds of materials, which have a lower work function than MgO, were chosen for adding. The pellets for the source of e-beam evaporation were fabricated by mixing the additive oxide powder with the MgO powder. Then, the mixed powder was pressed and sintered. To evaluate the discharging property, 2-inch test panels were fabricated. The characteristics of the films were evaluated by SEM, XRD and XPS. In case of adding Gd@sub 2@O@sub 3@, the firing voltage was lower than that of the conventional MgO films by about 17 eV. Also, the firing voltage was reduced by about 19 eV for adding (Ba,Sr,Ca)CO@sub 3@. The interesting results were that the firing voltage had a correlation with the XPS valence band spectra. The firing voltage was reduced as the valence band edge was shifted to lower binding state. It means that the secondary electrons can be ejected more easily and the ejected electrons have more energy. Consequently, the discharging property was improved. @FootnoteText@ @footnote 1@H. Uchiike et al., IEEE Trans. Elec. Dev., ED-23 1211 (1976). @footnote 2@Yasushi Motoyama et al., J. Appl. Phys., 95 (12), 8419 (2004). @footnote 3@ H. D. Hagstrum, Physical Review, 122 (1), 83 (1961) @footnote 4@M. O. Aboelfotoh et al., J. Appl. Phys., 48 (11), 4754 (1977). @footnote 5@T. J. Vink et al., Appl. Phy. Lett., 80 (12), 2216 (2002).

TF-ThP6 Real Time Monitoring of Plasma-less Vacuum Process using Self - Plasma Optical Emission Spectroscopy (SP-OES)*, **S.-H. Han**, D. Lee, S.W. Hwang, Y. Kim, C. Shin, C.-J. Kang, H. Cho, J.-T. Moon,* Samsung Electronic Co. Ltd., Korea

As the semiconductor devices shrink, degradation of device characteristics caused by plasma damage, such as charge-up and UV exposure becomes more severe. To dissolve this kind of process damage issue, a plasma-less process in a process chamber has been recently introduced for semiconductor fabrication. On the purpose of monitoring this kind of plasma-less processes, there has been studied self plasma optical emission spectroscopy (SP-OES), which is installed at pumping line and generates plasma using a small discharge cell. The emission spectra from the cell discharge plasma are analyzed to give the information on the process change in the plasma-less vacuum process chamber. By using SP-OES, it was possible to monitor the change of process behavior such as a reaction mechanism and end point detection (EPD) for which, till lately, there were no proper real-time monitoring tools for plasma-less process. Additionally, we have confirmed a possibility of monitoring process drift over wafer to wafer as a function of fault detection and classification (FDC) tool.

TF-ThP8 Leakage Current and Dielectric Loss of BLT Thin Film Capacitors Fabricated by Chemical Mechanical Polishing (CMP) with Changes of Polishing Pressure*, **P.-G. Jung**, N.H. Kim, W.-S. Lee,* Chosun University, Korea

PZT thin films, which are the representative ferroelectric materials in ferroelectric random access memory (FRAM), have some serious problem

such as the imprint, retention and fatigue which ferroelectric properties are degraded by repetitive polarization. BLT thin films have many advantages such as highly fatigue resistant characteristic, low processing temperature, and large remanent polarization. BLT thin film capacitors were fabricated by plasma etching, however, the plasma etching of BLT thin film was known to be very difficult. In our previous study, the ferroelectric materials such as PZT and BLT were patterned by chemical mechanical polishing (CMP) using damascene process to top electrode/ferroelectric material/bottom electrode. It is also possible to pattern the BLT thin film capacitors by CMP, however, the CMP damage was not considered in the experiments. The properties of BLT thin films were changed by the change of polishing pressure although the removal rate was directly proportional to the polishing pressure in CMP process. The structural property of BLT thin films after CMP with the change of the polishing pressure and then the behaviors of leakage current and dielectric loss were compared with the structural property. In view of the results so far achieved, the removal rate and the leakage current must be considered simultaneously when the polishing pressure of CMP process parameter were decided. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2004-005-D00007).

TF-ThP9 High-Performance Pentacene Thin-Film Transistors with PEDOT:PSS S/D Electrodes and Polymer Gate-Insulators, ***J.-M. Kim**, H.-J. Her, J. Kim, Y.J. Choi, C.J. Kang,* Myongji University, Korea*; D. Jeon,* Seoul National University, Korea*; Y.-S. Kim,* Myongji University, Korea

Organic thin-film transistors (OTFTs) have been studied with much interests over the last decade, due to their attractive features such as low cost, low temperature processing and mechanical flexibility. Among the various organic semiconductors, pentacene-based TFTs show the best results in terms of the electrical performance, if the OTFTs are fabricated using inorganic gate-insulators, metal electrodes and silicon substrates. The device performance of OTFTs made only from organic materials, which are ideal for low cost, flexible and large-area electronic applications, has yet to be improved. The fully organic OTFTs implies organic gate insulators, conducting polymer electrodes and flexible substrates. We have fabricated pentacene TFTs in which the conventional inorganic gate-insulators, S/D metal electrodes and substrates are replaced by organic material, Poly (3, 4-ethylenedioxythiophene)-Polystyrene Sulfonate (PEDOT:PSS) and plastic substrates, respectively. The PEDOT:PSS S/D electrodes are deposited by inkjet printing technique for low cost and simple process. We also fabricated pentacene TFTs with several kinds of polymers as gate insulators. The physical and electrical properties of the polymer gate insulator are measured by atomic force microscope (AFM) and I-V measurement. In this work, fully organic pentacene TFTs with PEDOT:PSS S/D electrodes and polymer gate insulators are successfully demonstrated by simple process on the plastic substrate and their electrical properties are compared with conventional pentacene-based organic TFTs with inorganic electrodes and/or inorganic gate insulators.

TF-ThP10 Pb(Zr,Ti)O3 Thin Film Capacitors by Damascene Process : Fabrication and Characterization, ***P.J. Ko**, N.H. Kim, W.-S. Lee,* Chosun University, Korea

The ferroelectric materials of the PZT, SBT and BLT attracted much attention for application to ferroelectric random access memory (FRAM) devices. Through the last decade, the lead zirconate titanate (PZT) is one of the most attractive perovskite-type materials for the ferroelectric products due to its higher remanant polarization and the ability to withstand higher coercive fields. FRAM has been currently receiving increasing attention for one of future memory devices due to its ideal memory properties such as non-volatility, high charge storage, and faster switching operations. In this study, we first applied the damascene process using chemical mechanical polishing (CMP) to the fabricate the PZT thin film capacitor in order to solve the problems of plasma etching such as low etching profile and ion charging. The structural characteristics were compared with specimens before and after CMP process of PZT films. The P-E characteristics of PZT capacitors were examined at various voltages and room temperature. The properties of PZT capacitor were Current-voltage characteristics (I-V) and capacitance-voltage (C-V) measured with RT66A. The densification by the vertical sidewall patterning and charging-free ferroelectric capacitor could be obtained by the damascene process without remarkable difference of the characteristics. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2004-005-D00007).

TF-ThP12 Formation of Magnetic Iron Oxide Films from Decomposition of Ferric Acetylacetonate on Cold Substrates, ***S. De Dea**, D. Graziani, D.R. Miller, R.E. Continetti,* University of California, San Diego

Ferric acetylacetonate Fe(acac)@sub 3@ is known to undergo thermal decomposition to form either Fe@sub 3@O@sub 4@ or @alpha@-Fe@sub 2@O@sub 3@ magnetically ordered materials when heated above 180°C. We have recently observed that magnetically ordered Fe@sub 3@O@sub 4@ and @alpha@-Fe@sub 2@O@sub 3@ can be formed near room temperature conditions in an inert atmosphere when a supercritical solution of Fe(acac)@sub 3@ in CO@sub 2@ is sprayed in a supersonic free-jet onto a cold Si substrate. This process is referred to as Rapid Expansion of Supercritical Solutions (RESS), and we originally anticipated the need to grow the thin cluster films on a heated substrate in an oxygen environment. We have now grown films in background pressures from vacuum to atmosphere and in both air and inert gases. The resulting cluster films have particles in the range from 50 nm to 800 nm, depending on experimental conditions, and have been analyzed by SEM, SQUID, and Mossbauer spectroscopy. The measured coercivities for the thin films range from 50 Oe to 100 Oe. These data suggest that we have grown Fe@sub 3@O@sub 4@ and @alpha@-Fe@sub 2@O@sub 3@, even on cold substrates in both inert and oxidizing gas backgrounds. We were able to identify @alpha@-Fe@sub 2@O@sub 3@ on the basis of the Morin transition and we are currently performing additional measurements to confirm that the other magnetically ordered phase is Fe@sub 3@O@sub 4@ . In order to better understand the mechanism for the decomposition, we are in the process of introducing a time-of-flight mass spectrometer probe of the jet conditions before the solution impacts the substrate. To remove the effects of the free-jet expansion, which can provide considerable translational energy to the impinging Fe(acac)@sub 3@ molecules and clusters, we are also preparing to use the supercritical solution in a batch experiment in a closed cell.

TF-ThP13 Surface Modification of Porous Nanocrystalline TiO2 Films for Dye-Sensitized Solar Cell Application by Various Gas Plasma, ***Y.-S. Kim**, K.-J. Kim,* Korea University*; Y.H. Lee,* KIST, Korea

Dye-sensitized solar cells (DSSCs) have been attracting much attention because solar cells are clean, renewable and of low-cost. Many research groups make an effort to enhance photocurrent by using the modification of dye, electrolyte, and TiO@sub2@ films. In this study, cold plasma treatment was used in order to modify TiO@sub2@ films. Cold plasma treatment is a very effective technology in the surface modification for a variety of materials because the surface can be modified without affecting the bulk properties of the materials. The influence of plasma treatment of TiO@sub2@ film on the photoelectric performance of DSSC was investigated. Treatment parameters include kinds of gases, plasma power, and gas pressure. In order to modify TiO@sub2@ surface, we used different ion species such as O@sub2@, N@sub2@, Ar, H@sub2@ and CF@sub4@. After various gas plasma treatment, stoichiomertric changes of TiO@sub2@ films were observed. Short-circuit photocurrent (Jsc), open-circuit voltage (Voc) and the amount of adsorbed dye for DSSCs were measured. As a result, the solar-to-electricity conversion efficiency of the O@sub2@ and N@sub2@ treated cell increased by 10-15% in comparison with untreated cell. On the other hand, solar energy conversion efficiency of CF@sub4@ plasma treated cell decreased drastically. The increased amount of adsorbed dye on the TiO@sub2@ film was measured by UV/Vis absorption spectroscopy. Modified TiO@sub2@ surfaces by plasma treatment were characterized using analytical instruments such as X-ray photoelectron spectroscopy (XPS), Near-edge X-ray absorption fine structure (NEXAFS) and Raman spectroscopy. The improved performance of DSSCs by plasma treated TiO@sub2@ film was attributed to the removal of carbon contaminants, reduction of oxygen vacancies, and the enhancement of bond strength between TiO@sub2@ film and dye.

TF-ThP14 Oxide-Nitride-Oxide (ONO) Deposition Mechanism and Modelling Study in a Batch Furnace for Sub-Micron Technology, ***E. Chiu**, A. Kolessov, J. Bailey,* Aviza Technology, Inc.

A highly uniform oxide-nitride-oxide (ONO) dielectric film deposition is required to achieve reliable flash memory device performance in the sub-micron manufacturing realm. A vertical furnace was used to investigate the effects of thin thermal oxide (<17Å), oxy-nitride and high temperature oxide (HTO) on film formation; uniform film control and low particle performance were achieved in the entire ONO film stack. In a batch reactor, various chamber and gas injection geometries were found to have moderate impact on within-wafer uniformity (WiW), while controlled temperature zone gradient significantly impacted wafer-to-wafer uniformity (WtW) across the load. Thermal oxide growth in oxygen and

oxy-nitride deposition with DCS, NH@sub3@ and N@sub2@O provided excellent WiW and WtW uniformities in the optimized chamber configuration from these reaction rate controlled processes. From the HTO process experiments, high chamber pressure and low N@sub2@O/DCS gas ratio were found to be the contributing factors in improving WiW uniformity. A computer model and deposition reaction mechanism were developed to simulate flow, gas-phase and surface reactions to provide further understanding of the effects of HTO deposition with DCS and N@sub2@O. Results demonstrated that both the reaction and diffusion rates of gas species play an important role in determining the deposition efficiency. In the model, process temperature and reactant concentration mostly determined the WiW and WtW uniformities. As the simulation showed, the current chamber hardware could be further adjusted to improve the process performance. With optimized control of temperature zone gradient and reactant concentration, high quality films were deposited to meet and exceed the requirements for WiW and WtW ONO stack uniformities.

TF-ThP16 Characterization of TFT-LCD and OLEDs Devices by Phase Modulated Spectroscopic Ellipsometry for Display Applications*, E. Teboul,* ***Y. Ji,*** HORIBA Jobin Yvon Inc*; N. Nabatova-Gabain,* HORIBA Ltd.

Accurate and reliable optical characterization of polymers, liquid crystals (LCs) and organic light emitting diodes (OLEDs) is a crucial step in the manufacturing process of flat panel display. Different methods for measuring the optical constants and multiple film thickness of solid materials are available. One of the most sensitive and accurate method that measure simultaneously optical constants and film thickness is the well established technique called Spectroscopic Ellipsometry. Beside the fact that only few optical data are available for LCs and OLEDs, these devices are formed by complex structure such as multi-layer stacks including anisotropy, absorbing and graded materials. Therefore, the correct use of spectroscopic ellipsometry to characterize complex materials such as the ones found in LCs and OLEDs, require a combination of the proper choice of hardware and the appropriate ellipsometric model to analyze the data. Compare to conventional ellipsometers technique, Phase Modulated Spectroscopic Ellipsometry (PMSE) provide significant advantages for display applications. Its technology is most suitable for accurate thin film measurements on transparent substrate. In this work, we presents ellipsometric results obtained by a commercially available phase modulated spectroscopic ellipsometer on full TFT-LCD structure characterized from UV to NIR. As expected, strong anisotropy and inhomogeneous optical properties were found respectively on LCs and ITO materials. We also introduce the results on OLEDs devices previously published by Tsuboi et al (IEICE Transact. Electronics, E87-C, No.12 (2004) 2039-2044). In this case, it was found that film thickness and optical constants of a single layer differs significantly from the measurements of the same materials in a multiple layer configuration.

Electronic Materials and Processing
Room 2003 - Session EM+TF-FrM

High-k Dielectric & Multi-Functional Oxide Growth & Processing

Moderator: R.L. Opila, University of Delaware

8:00am **EM+TF-FrM1 Chemical Analyses and Electrical Studies of HfO@sub 2@/Y@sub 2@O@sub 3@, Y@sub 2@O@sub 3@/HFO@sub 2@ Bilayered and Y@sub x@Hf@sub y@O@sub z@ Intermixed Dielectric Materials for MIM Capacitors***, M. Kahn,* *C. Vallee, C. Dubourdieu, M. Bonvalot, J.R. Plaussu, J. Ducote, T. Baron, O. Joubert,* LTM/CNRS, France

Improving the capacitance density of MIM devices constitutes a real challenge to satisfy scaling rules for next IC generations and to reduce the cost as well. Silicon dioxide and nitride have been commonly used up to date as dielectrics in conventional MIM capacitors. However, they cannot provide capacitance values larger than 2fF/µm@super 2@. With further scaling going on at an active pace, high-@kappa@ dielectric materials offer a viable alternative to provide both high capacitance density and low leakage currents. This dielectric material of a MIM device has to meet several requirements such as a high capacitance density, low leakage currents and minimum variation of capacitance values with voltage bias. In a previous work, we studied TiN/Y@sub 2@O@sub 3@/Au capacitors and showed that Y@sub 2@O@sub 3@ exhibits appropriate electrical properties with low leakage currents and a capacitance density of 5 fF/µm@super 2@ @foonote 1@. However, we observed that the capacitance density cannot be further increased without a substantial increase in the leakage current, which in turn exceeds ITRS requirements. The aim of the present work is to overpass this capacitance limitation thanks to the introduction of a bilaminate dielectric material. Studies of MIM capacitors based on HfO@sub 2@/Y@sub 2@O@sub 3@, Y@sub 2@O@sub 3@/HFO@sub 2@ bilaminate and intermixed Y@sub x@Hf@sub y@O@sub z@ dielectric materials will be presented. These high @kappa@ dielectric layers are prepared by pulsed injection MOCVD on WSi@sub x@ bottom electrodes and the gold top electrode is realized by evaporation. 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 SIMS), with special attention devoted to metal/oxide and oxide/oxide interface investigations. In particular, the observation of a non symmetrical C(V) curve will be highlighted with respect to the bilaminate stack HfO@sub 2@/Y@sub 2@O@sub 3@ and Y@sub 2@O@sub 3@/HFO@sub 2@ of dielectric materials. @FootnoteText@ @footnote1@ C. Durand, C. Vallee, C. Dubourdieu, M. Kahn, M. Derivaz, S. Blonkowski, D. Jalabert, P. Holliger, Q. Fang, I.W. Boyd ; J. Vac. Sci. Technol to be published (May/June 2006).

8:20am **EM+TF-FrM2 Process-Dependent Interface States at Mo/Hafnium Oxide/Si Interfaces***, S. Walsh, L. Fang,* The Ohio State University*; J.K. Schaeffer, E. Weisbrod,* Freescale Semiconductor, Inc.*; L.J. Brillson,* The Ohio State University

A major challenge for Hafnium Oxide (HFO) and other high-K dielectric materials is the control of their interface state and trapped charge densities. Among the chief electronic and chemical requirements for their development is the identification of post-growth processes to optimize oxide bonding within the thin dielectric films and at their interfaces. This requires characterization techniques that are nondestructive, that can measure electrically-active defects that correlate with electrical device features, and that can spatially isolate these defects within ultra-thin films to help identify their physical origins. We have used low energy electron-excited nanoscale-depth-resolved (DRCLS) spectroscopy to probe the bulk and interface defect states of ultra-thin Mo/HFO/Si with 8 different process sequences. After atomic layer deposition (ALD) of 4 nm HfO@sub 2@ on Si and an O@sub 2@ post treatment, we deposited 10 nm Mo using either plasma vapor or electron beam deposition, with or without a subsequent 1000@super O@C N@sub 2@ anneal, and with or without a forming gas anneal. DRCLS revealed pronounced gap state emissions within the ultrathin films and their interfaces with Mo and Si. There are multiple deep level emissions below the 5.5 eV band gap, including 3 peak emissions at 3.4, 3.5 eV, and 3.9-4.3 eV that can be associated with HFO oxygen vacancies in different charge states predicted theoretically.[1] In addition, states at 2 -2.6 eV that resemble known SiO@sub 2@-related nonbonding oxygen hole centers (NBOHC) and E' (positively charged O vacancy) native defects increase with depth within the 4 nm HFO film suggesting the formation of a Hf silicate at the HFO/Si interface. Furthermore, different process steps produce large changes in these states and for at least one sequence, a dramatic decrease in both types of defects. The differences between process sequences can be understood in terms of known reactions at HFO-Si interfaces.

8:40am **EM+TF-FrM3 Materials Challenges for High Permittivity Gate Dielectrics and Metal Gate Electrodes***, J.K. Schaeffer, D. Gilmer, S. Samavedam, M. Raymond, D.H. Triyoso, R.I. Hegde, M. Stoker, S. Kalpat, C. Capasso, B. Taylor, P.J. Tobin, B.E. White,* Freescale Semiconductor, Inc.*; S. Walsh, L. Fang, L.J. Brillson,* The Ohio State University **INVITED**

This talk will review recent advances and remaining challenges associated with high-k gate dielectrics and metal gate electrodes with a specific focus on the fundamental materials properties responsible for critical device characteristics. Recent reports have shown that alloying ZrO@sub 2@ into HfO@sub 2@ improves device reliability and effective oxide thickness (EOT) scaling. This talk will review the structural and electrical properties of Hf@sub x@Zr@sub 1-x@O@sub 2@ films that impact EOT and device reliability. Next, to better understand the nature of the metal/HfO@sub 2@ interface, the previously established empirical relationship between the mean electronegativity and effective work function developed for Schottky contacts has been applied to multi-element electrode materials on hafnium dioxide gate dielectrics. Our data show good agreement with the pre-existing framework established for metal/insulator contacts, and illustrates the important role that sub-lattice elements such as N and C can have on effective work-function. This understanding helped lead to the development of tantalum carbide as a thermally stable NMOS gate electrode candidate. Finally, many device properties result from the electrical and chemical interactions between the various gate stack layers which can lead to differences in EOT growth, increased dielectric leakage, fixed charge, and changes in effective work function. The selection of the gate metal can have a pronounced impact on these properties. Such interactions are likely responsible for the difficulty in manufacturing devices with low PMOS device threshold voltages and scaled EOT on silicon substrates. Recent experiments are now providing new insights into the origins of this problem.

9:20am **EM+TF-FrM5 Molecular Beam Epitaxy of Multifunctional Materials Using a Chloride Refractory Metal Chemistry***, W.A. Doolittle, A.G. Carver, W. Henderson, W. Laws Calley, S.-S. Kim,* Georgia Institute of Technology **INVITED**

Multifunctional materials, materials that interact with their environment via differing force mechanisms, including but not limited to electrostatic, magnetic, acoustic, photonic, and chemical, are of great interest for future sensor and actuator applications. Lithium metal oxide multifunctional materials, including LiNbO@sub 2@, LiNbO@sub 3@, LiTaO@sub 2@ and LiTaO@sub 3@ are presented as a promising but challenging materials for multifunctional devices. Example proposed applications will be presented. A chloride based chemistry that bypasses many of the traditional pitfalls of Lithium Niobate (LN) epitaxy including the need for electron beam evaporation of refractory metals, and use of complex metal organic precursors prone to pre-reaction is described. Methods of dealing with the normally corrosive chloride based chemistry in a Molecular Beam Epitaxy (MBE) chamber are detailed. The present state of homoepitaxy and heteroepitaxy of LN on semiconductors is presented. It is shown that LiNbO@sub 2@ is preferentially grown over LiNbO@sub 3@ in the oxygen deficient MBE vacuum environment. However, LiNbO@sub 2@ is shown to be converted to LiNbO@sub 3@ by an ex-situ oxygen anneal. Dramatic changes in optical properties and crystalline lattice structure result and will be detailed. A limited stoichiometry control is demonstrated via use of ion filters on an oxygen plasma source including the ability to partially select between various valences of niobium oxides, NbO, NbO@sub 2@ and Nb@sub 2@O@sub 5@. While the demonstrated metal chloride based epitaxy is shown as a viable candidate for MBE of multifunctional refractory metal oxides, particularly for electronic applications, the possibility for thicker films, and thus impact on optical devices, is currently limited by the available Li source. Efforts to circumvent this difficulty, including a large volume valved Li source, will be described.

10:00am **EM+TF-FrM7 Magnesium Oxide Thin Film 'Bridge' on Hexagonal Silicon Carbide for Integration of Functional Oxides***, T.L. Goodrich, Z. Cai,* ***K.S. Ziemer,*** Northeastern University

Single crystalline MgO (111) films, 15 to 100 Å thick, have been grown on hexagonal silicon carbide (6H-SiC) in order to integrate complex oxides, such as lead zirconate titanate [PZT], with SiC high-power, high-

temperature, high-frequency devices with multiple functionalities. 6H-SiC substrates (0001)@sub Si@ and (000I)@sub C@ were cleaned to create atomic steps hundreds of nanometers wide and 1.5 nm high, and reduce oxygen contamination from 12% to 8% for the (0001)@sub Si@ surface and from 8% to 3% for the (000I)@sub C@ surface, as measured by x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy. The residual oxygen concentration was determined by reflection high energy electron diffraction (RHEED) to be incorporated into a @sr@3x@sr@3 R30° silicate adlayer reconstruction. MgO films were grown using a remote oxygen plasma source to produce a constant chamber oxygen pressure (5x10@super -6@ Torr) and a solid source Mg effusion cell at various Mg fluxes but constant Mg fluence. The (000I)@sub C@ surface and the (0001)@sub Si@ surface of the SiC produce differently structured films, as measured by RHEED and atomic force microscopy (AFM), under the same molecular beam epitaxy growth conditions. All films are roughly stoichiometric as measured by XPS, with some suggestions of Mg metallic bonding near the substrate. MgO thin films grown on (0001)@sub Si@ oriented SiC substrates were three-dimensional and crystalline at low Mg flux but became more conformal and improved single crystalline as the Mg flux was increased. The opposite was observed for (000I)@sub C@ oriented SiC. At Mg fluxes than 1x10@super 14@ atoms/cm@super 2@s, the films were conformal but highly polycrystalline. As the Mg flux was increased, the crystalline MgO thin films became less polycrystalline but exhibited more 3-D morphology. Current studies will compare the deposition of BaTiO and PZT on the MgO thin films to those deposited directly on the cleaned SiC substrates.

10:20am **EM+TF-FrM8 Zirconium Dioxide Formation on Silicon Surfaces by Metal-Organic Chemical Vapor Deposition in UHV**, ***A. Sandell**, P.G. Karlsson, J.H. Richter,* Uppsala University, Sweden*; J. Blomquist, P. Uvdal,* Lund University, Sweden*; T.M. Grehk,* Hogskolan Dalarna, Sweden

Previous work has shown that deposition of zirconium tetra-tert-butoxide at elevated temperatures leads to the formation of a ZrO2 film. The previous studies also reveal the presence of an interfacial region between the Si substrate and the ZrO2 film. However, up to date, the evolution of the interface has not been comprehensively addressed using surface science techniques. In this contribution, a detailed study of the growth and interface formation on Si(100) and Si(111) in UHV is presented. Core level photoelectron spectra provide information on the growth rate, atomic oxidation state and the chemical composition of the interface, including the fate of the butoxy ligands. X-ray absorption spectra give valuable complementary information on the local geometric structure of the Zr-O units and the Zr-O electronic interaction. In addition, STM images of the first stages of nucleation are shown. These suggest that it is possible to distinguish between precursors induced defects on the Si(100) surface related to oxidation and reaction with carbonaceous fragments, respectively.

10:40am **EM+TF-FrM9 Controlling Interfacial Reactions between HfO@sub 2@and Si using Ultra-Thin Diffusion Barriers**, ***R.R. Katamreddy,*** University of Illinois at Chicago*; R. Inman, G. Jursich, A. Soulet,* American Air Liquide*; C.G. Takoudis,* University of Illinois at Chicago

Hafnium oxide has gained considerable interest in recent years as a potential high-k dielectric material for future fabrication of complementary metal oxide semiconductor devices. One of the problems with HfO@sub 2@ is its interfacial reactivity with Si at the high temperature necessary for post deposition annealing. Our previous studies have shown that HfO@sub 2@ films on Si form silicates and silicides at the interface as low as 600 °C and this is not suitable for CMOS process integration. In this study we examine the effectiveness of ultra-thin Al@sub 2@O@sub 3@ as a HfO@sub 2@-Si diffusion barrier up to 1000 °C. Al@sub 2@O@sub 3@ has superior interface stability with Si but it also has a lower dielectric constant than HfO@sub 2@. So, to minimize reduction in overall dielectric constant of the film with this barrier layer, there is a need to understand how thin the Al@sub 2@O@sub 3@ layer can be in this system and yet still maintain its effectiveness as a barrier. Our studies have shown 0.5 nm of alumina was sufficient to prevent formation of silicates and silicides of hafnium at temperatures below 1000 °C, while thicker alumina films were required to prevent the same at 1000 °C. The ultra-thin dual layer films are prepared by sequential atomic layer deposition of Al@sub 2@O@sub 3@ and HfO@sub 2@ using tetrakis(diethylamino)hafnium and tris(diethylamino)alane as the metal oxide precursors and water vapor as the oxidizer. Nitrides and oxynitrides of silicon are some other promising diffusion barriers. Silicon nitride and oxynitride are also investigated as potential barrier layers for HfO@sub 2@-Si. After deposition, the films are subjected to high temperature annealing up to 1000 °C and the extent of interfacial reactivity is examined using Fourier transformed infrared spectroscopy, x-ray photoelectron spectroscopy, and scanning transmission electron microscopy/electron energy loss spectroscopy. An explanation of the observed behavior is also proposed for these systems.

11:00am **EM+TF-FrM10 Comparison of the Calculated Electronic Structure of Oxygen and Nitrogen Adsorption onto Ge(100)**, ***S.R. Bishop**, T.J. Grassman, A.C. Kummel,* University of California, San Diego

For high-k dielectrics on Ge(100), a germanium oxynitride (GeON) interface leads to superior C-V characteristics compared to GeO@sub 2@ passivation layers. Experimental studies show GeON is both a better diffusion barrier and surface passivant than GeO@sub 2@. To understand why GeON is an effective passivating layer, it is necessary to first determine the oxygen and nitrogen binding sites independently. STM studies have shown that the initial stage of O and N adsorption is insertion into the backbonds and into the 2x1 surface dimers, while the final stage is Ge displacement by O and N. The clean Ge(100) surface, oxygen adsorption sites, and nitrogen adsorption sites were modeled using density functional theory (DFT). The DFT calculations show that all oxygen insertion and displacement sites leave the near-Fermi level density of states essentially unchanged compared to the clean surface. This is consistent with O atom insertion and displacement creating no new unfilled dangling bonds. In contrast, the insertion and adsorption sites for nitrogen all create new electronic states in the near-Fermi level region, consistent with nitrogen atoms making two bonds to the surface, but retaining a half-filled dangling bond. However, the Ge-N bonds were found to be stronger than the Ge-O bonds, consistent with GeON being more effective than GeO@sub 2@ as a diffusion barrier. Since the efficiency of GeON as an electronically passivating layer is not intrinsic to its chemisorption states on Ge(100), it may be related to the nitrogens' ability to be electronically passivated by hydrogen. The DFT calculations show that even though N atom displacement of Ge creates states near the Fermi level, hydrogen passivation greatly reduces or eliminates the density of those states.

11:20am **EM+TF-FrM11 Thermal Stability of High-k Dielectrics on Ge(001)**, *F.S. Aguirre-Tostado, M.J. Kim,* ***R.M. Wallace,*** University of Texas at Dallas*; R. Sreenivasan, K.-I. Seo, C.O. Chui, K.C. Saraswat, P.C. McIntyre,* Stanford University*; F.A. Stevie, R. Garcia, Z. Zhu, D.P. Griffis,* North Carolina State University

The use of high-mobility channel materials, such as SiGe and Ge has attracted substantial interest as a means to maintain integrated circuit scaling and performance. A necessary requirement for a MOSFET application is a stable gate dielectric which can be integrated into an appropriate CMOS process flow. High-k dielectrics, such as ZrO@sub 2@ and HfO@sub 2@ have been previously reported for this application with promising electrical results.@footnote 1,2,3@ This paper will describe thermal stability studies of these high-k dielectrics on Ge(001) using in-situ ARXPS and SPM analysis in conjunction with backside SIMS@footnote 4@ and HRTEM analysis. The extent of Zr, Hf and Ge interdiffusion is examined with oxide or oxynitride interfacial layers. Corresponding electrical characterization of the associated devices will also be described in view of the thermal budget where the maximum process temperature is ~500°C. @FootnoteText@@footnote 1@K.I. Seo, P.C. McIntyre, S. Sun, D.I. Lee, P. Pianetta, K.C. Saraswat, Appl. Phys. Lett. 87 (2005) 042902. @footnote 2@D. Chi, C.O. Chui, K.C. Saraswat, B.B. Triplett, P.C. McIntyre, J. Appl. Phys. 96 (2004) 813. @footnote 3@C.O. Chui, H. Kim, P.C. McIntyre, K.C. Saraswat , IEEE Elec. Dev. Lett. 25 (2004) 274. @footnote 4@C. Gu, et. al., J. Vac. Sci. Technol. B22, 350 (2004).

11:40am **EM+TF-FrM12 Oxidation Properties of Al-nanostructures on Si Surfaces**, ***P. Morgen,*** University of Southern Denmark, Denmark*; C. Janfelt,* University of Copenhagen, Denmark*; K. Pedersen,* University of Aalborg, Denmark*; Z.S. Li,* University of Aarhus, Denmark

We have explored the oxidation properties of different nanostructures of Al formed by deposition of Al on Si surfaces with surface sensitive techniques to reveal the differences in reactivity between differently organized nanostructures of Al on these surfaces. In a parallel effort some of these reactions have been modeled with surface electronic structure calculations simulating STM and photoemission spectra, based on the DFT method. Recently several theorists have looked at the initial phases of oxide formed during exposure of Al to oxygen, and found these to differ from bulk Al-oxide. Here we discuss the results for the oxidation of Al on Si (111) and Si (100) in quantities of less than a monolayer as deposited and after annealing of these systems. For the un-annealed systems we discover a route to control the formation of Al-oxide on top of Si with a sharp unmixed interface, while the reactions of the annealed systems show

mixing and enhanced reactivity of the Si surface to oxygen. Ultrathin films of Al on top of Si oxidize at room temperature and at elevated temperatures as a self limiting process, like Si itself. The structure of this oxide includes Al with a coordination number of four.

Thin Film
Room 2022 - Session TF+EM-FrM
In-Situ/Ex-Situ & Real-Time Monitoring and Characterization

Moderator: C. Stoessel, Southwall Technologies

8:00am **TF+EM-FrM1 Parameter Uncertainties and Higher-Order Effects in the Analytic First-Order Solution for the Complex Refractive Index and Thickness of a Thin Film on a Substrate***, **I.K. Kim**, D.E. Aspnes,* North Carolina State University

We recently reported a solution in the thin-film limit of the general problem of determining the complex refractive index ñ = n+i@kappa@ and thickness d of an isotropic film on an isotropic substrate from the changes induced in polarimetric data by deposition or removal. Here, we consider uncertainties in n, @kappa@, and d in terms of uncertainties in the measured Fourier coefficients of the intensity. Taking advantage of the fact that the uncertainty @delta@(@DELTA@R/R) in the reflectance is much higher than the uncertainty @delta@(@DELTA@@rho@/@rho@) in the relative complex reflectance ratio, we obtain an analytic expression that gives the uncertainties of n, @kappa@, and d in both relative and absolute terms. The expression can be used to establish conditions where one or the other is determined with maximum accuracy. In contrast to expectations from ellipsometry, the relative uncertainties @delta@n/n and @delta@d/d can be significantly different. By adding noise to simulated data, we investigate the range of linearity and higher-order nonlinearities. Symmetric fluctuations of the Fourier coefficients about their average values can yield highly asymmetric fluctuations about the parameter values corresponding to the coefficient averages, particularly d. We describe a procedure for correcting the results for these asymmetries. Finally, we confirm all results with polarimetric data obtained by cyclically physisorbing and desorbing a monolayer of H@sub 2@O on oxidized GaAs.

8:20am **TF+EM-FrM2 Optical and Morphological Studies on SiO@sub 2@-like Films Deposited by Means of Ion Bombardment- Assisted Expanding Thermal Plasma CVD***, **A. Milella**, M. Creatore, M.A. Blauw, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

The role of ion bombardment in the growth of plasma-deposited thin films has been often investigated in literature as a route towards film matrix densification at low temperature, this latter being a requirement when thermally sensitive substrates, such as polymers, are studied. In the present paper we report our latest results on the densification of SiO@sub 2@-like films by applying an external rf bias to the substrate holder during film deposition by means of an Ar-fed expanding thermal plasma, in which hexamethyldisiloxane and oxygen are injected downstream. A comprehensive study of the optical properties of the deposited films, as determined by Spectroscopic Ellipsometry, with increasing dc bias voltage will be presented. In particular, it will be shown that ion bombardment can effectively improve film density when parameters such as the energy of the ions impinging the surface of the growing film and the ion-to-depositing radical flux ratio, are carefully controlled. Densification of film network by ion bombardment can be furthermore assessed by Fourier Transform IR spectroscopy, following changes in SiOSi asymmetric stretching absorption band with dc bias voltage. Film porosity increases with increasing deposition rate which results in a different absorption band shape. Surface morphology evolution of SiO@sub 2@-like films deposited under increasing dc bias voltage conditions as determined by Atomic Force Microscopy will be presented. In absence of ion bombardment, films display growth of spherical nodules distributed uniformly across the surface, with heights and lateral dimensions depending on the process parameters selected. Quantitative analysis shows that both RMS roughness and mean peak-to-valley distance decrease almost exponentially with increasing dc bias voltage. These results correlate with refractive index trends as determined from spectroscopic ellipsometry.

8:40am **TF+EM-FrM3 Real-Time X-ray Studies of Surface and Thin-Film Processes***, **K. Ludwig**, Y. Wang, A. Özcan, G. Ozaydin, C. Sanborn, A. Bhattacharyya, R. Chandrasekaran, T.D. Moustakas,* Boston University*; R. Headrick, H. Zhou,* University of Vermont **INVITED**

A new facility for the time-resolved x-ray study of surface and thin film processes is now in use at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory. To promote flexibility, the base spectrometer is designed so that modest-sized processing/vacuum chambers can be rolled onto it. This design allows multiple specialized chambers to be constructed, optimized for experimentation, and then moved onto the diffractometer for real-time x-ray studies. Here results from studies of wide-bandgap group III-nitride growth on sapphire by plasma assisted molecular beam epitaxy (PA-MBE) will be discussed. These experiments have examined migration-enhanced epitaxy, the early stage kinetics of sapphire surface nitridation, and Ga droplet formation with subsequent nitridation to form GaN nanodots. Studies examining the spontaneous nanopatterning and smoothening of surfaces by ion bombardment will also be presented. This research is partially supported by DOE DE-FG02-03ER46037 and by NSF DMR-0507351.

9:20am **TF+EM-FrM5 Novel Annealing Treatments Applied to Binary Alloy Thin Films***, **J.R. Skuza**, R.A. Lukaszew,* The University of Toledo*; E.M. Dufresne,* Argonne National Lab*; C. Cionca, R. Clarke,* University of Michigan, Ann Arbor*; A. Cebollada,* Instituto de Microelectronica de Madrid, Spain

Rapid thermal annealing (RTA) is widely used for electronic materials processing, from the activation of dopants to the healing of lattice defects caused by ion implantation. Here, we describe an innovative application of x-ray undulator radiation to simultaneously anneal and probe the structural evolution that occurs during annealing in real-time. X-ray Rapid Thermal Annealing (XRTA) is similar to laser annealing, but there is a unique advantage in that the x-ray energy can be tuned to the absorption edge of a particular element, thereby permitting efficient annealing of buried layers and nanostructures. In our studies at the MHATT/XOR (Sector 7) beam line at the Advanced Photon Source, we have used XRTA to enhance the degree of chemical order in epitaxial and equiatomic FePt thin films. We have chosen this particular binary alloy system because it exhibits an interesting fcc-fct phase transformation. This phase transformation allows for the real-time tracking of the degree of chemical ordering achieved due to the appearance of a forbidden reflection in fcc structures [(001) peak] and the doubling of the fundamental reflection [(002) peak]. These results will be compared to the ones obtained with traditional resistive annealing. We will demonstrate that undulator radiation offers unique possibilities for materials processing AND real-time structural probing. @FootnoteText@ This work was partially supported by the National Science Foundation (DMR Grant #0355171), the American Chemical Society (PRF Grant #41319-AC), and the Research Corporation Cottrell Scholar Award. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

9:40am **TF+EM-FrM6 In-Situ Studies of Stress Evolution during the Heteroepitaxial Growth of Group III-Nitrides***, **J.M. Redwing**, S. Raghavan, X. Weng, J.D. Acord, E.C. Dickey,* Penn State University **INVITED**

The group III-nitrides (GaN, AlN, InN and related alloys) are an important class of III-V semiconductors that form the basis for commercial high brightness blue/green light emitting diodes, laser diodes and high power microwave electronics for military and communication applications. Due to difficulties associated with the bulk crystal growth of GaN, group-III nitride thin films are grown heteroepitaxially on substrates such as sapphire, silicon carbide and silicon. These substrates have significantly different lattice constants and coefficients of thermal expansion than GaN, which can result in thin film stress, dislocation formation and film cracking. In addition to the epitaxial and thermal mismatch stresses, which are well known, growth-related stresses due to developing film morphology also play an important role, but are not as well understood for the GaN materials system. In this study, we have utilized in-situ wafer curvature measurements to study the magnitude and evolution of growth stress during the metalorganic chemical vapor deposition of group III-nitride thin films. Specific examples will be presented including the case of GaN growth on silicon and AlGaN growth on silicon carbide. By combining the in-situ measurements with post-growth atomic force microscopy and cross-sectional transmission electron microscopy, we correlate the growth stress to microstructural changes in the film arising from island coalescence and dislocation bending and demonstrate that dislocation density reduction in AlGaN films primarily occurs when the film is growing under a compressive

stress. Methods to mitigate stress and reduce film cracking including the use of compositionally graded buffer layers will also be discussed.

10:20am **TF+EM-FrM8 In Situ ATR - FTIR Spectroscopy of Hf (IV) Tert Butoxide and Tetrakis Ethyl Methyl Amino Hf Adsorption on Si (100), Si (111) and Ge***, K. Li, S. Dubey, T.M. Klein,* The University of Alabama

Hafnium oxide ultra thin films on Si are being developed to replace thermally grown SiO2 gates in CMOS devices. In this work, a specially designed attenuated total reflectance - fourier transform infra-red spectroscopy (ATR-FTIR) reaction cell has been developed to observe chemisorption of hafnium (IV) t-butoxide (HtB) and tetrakis ethyl methyl amino hafnium (TEMAH), onto a Si (100), Si (111) and Ge ATR crystals heated up to 250Â°C and under 1 torr of vacuum allowing the observation of initial reaction pathways in real time. Chemisorption spectra were compared to spectra of the liquid precursor and to spectra generated by density functional theory (DFT) calculations of liquid, monodentate and bidentate adsorbed precursors. Asymmetric stretching modes located at 1017 cm-1 and 1250cm-1 present in the chemisorbed spectra but not in the liquid spectra of HtB indicate that the adsorbed hafnium containing group is prevalent as a bidentate ligand on Si (111). Surface concentration of the chemisorbed species was dependant on the substrate temperature and precursor partial pressure allowing for determination of heats of adsorption of the t-butyl groups, which is 26.5 kJ/mol for HtB on Si (111).

10:40am **TF+EM-FrM9 In Situ Defect Spectroscopy: Probing Dangling Bonds during a-Si:H Film Growth by Subgap Absorption***, I.M.P. Aarts, A.C.R. Pipino,* ***M.C.M. Van De Sanden,*** Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Detecting ultralow defect concentrations in a-Si:H thin films is of great importance for improving the efficiency of a-Si:H-based solar cells. Likewise, from a more fundamental point of view, it is essential to obtain understanding of the role of surface defect states during the growth process. Yet, a paucity of experimental techniques capable of detecting these surface and or bulk defect states is readily available. Using the technique of evanescent-wave cavity ringdown spectroscopy, we have realized a unique and absolute absorption technique capable of detecting defect states such as dangling bonds with an unprecedented sensitivity that can be applied in situ and during film growth as we will demonstrate for hotwire chemical vapor deposited a-Si:H. We deposited a thin a-Si:H film (from 0 up to 800 nm thickness), onto a total-internal reflection surface of a ultralow-loss monolithic folded optical resonator. Subgap absorption spectra between wavelengths of 1170 and 1245 nm are obtained and show the typical broad absorption feature due to dangling bonds defect states present in the bulk and at the interfaces. The minimal detectable absorption of the technique is 3 10@super -8@ optical loss, which is equivalent to 3 10@super 8@ dangling bonds/cm@super 2@. Furthermore, from the real time experiments the defect distribution in the film could be established and showed that the highest defect concentration was present at the interface of the a-Si:H with the substrate while the surface defect density was approximately ten times smaller. Moreover, changes in surface dangling bond concentration (formation- and decay-curves) could be monitored in real-time under various growth conditions.

11:00am **TF+EM-FrM10 In Situ Monitoring of Hafnium Oxide Atomic Layer Deposition***,* ***J.E. Maslar****, W.S. Hurst, D.R. Burgess, W.A. Kimes, N.V. Nguyen,* NIST

In situ monitoring of atomic layer deposition processes has the potential to yield insights that will enable efficiencies in film growth, in the development of deposition recipes, and in the design and qualification of reactors. However, demonstrations of in situ monitoring of actual atomic layer deposition processes are limited. In this work, the species present in the gas phase during atomic layer deposition of hafnium oxide were investigated in an attempt to gain insight into the chemistry of this system and evaluate potential in situ gas phase optical monitors. Hafnium oxide was deposited on a silicon substrate using tetrakis(ethylmethylamino) hafnium and water as the hafnium and oxygen sources, respectively. In situ Raman and infrared absorption spectroscopy measurements were performed in a research-grade, horizontal-flow reactor under a range of deposition conditions. Density functional theory quantum calculations of vibrational frequencies of expected species were used to facilitate identification of observed spectral features. Gas phase measurements performed at the wafer surface were compared to measurements performed at the chamber exhaust to investigate the utility of exhaust-based optical measurements for deposition monitoring. Results of in situ gas-phase measurements were compared with results of ex situ hafnium oxide film characterization, vacuum ultraviolet spectroscopic ellipsometry and infrared absorption spectroscopy, in an effort to correlate observed gas phase species with deposited film properties.

11:20am **TF+EM-FrM11 In-situ and Real-Time Spectroscopic Ellipsometry on Organic Semiconductors during Growth***, U. Heinemeyer,* Universit@um a@t T@um u@bingen, Germany*; S.M. Kowarik,* Oxford University, UK, Germany*; A. Gerlach,* ***F. Schreiber,*** Universit@um a@t T@um u@bingen, Germany*; G. Humphreys, R. Jacobs,* Oxford University, UK

We demonstrate the use of in-situ and real-time spectroscopic ellipsometry as a non-invasive technique for following the growth of organic semiconductor thin films of diindenoperylene and pentacene. It is possible to take spectra in the spectral range between 1.25eV and 5 eV sufficiently fast (~ 1 sec) to follow organic molecular beam deposition in detail. We show how this technique can be used to detect spectral changes occurring during growth of these complex materials. From the vibrational progression of the HOMO-LUMO transition we analyze the time/thickness evolution of the exciton-phonon (Huang-Rhys) parameter S. We discuss our results and their implications for organic device fabrication in the context of a recent real-time structural study which found structural and orientational transitions during growth.@footnote 1@ @FootnoteText@ @footnote 1@S. Kowarik et al., Phys. Rev. Lett. 96, 125504 (2006).

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