Monday Morning, November 15, 2004

Materials Solutions for Cooling Technology Topical Conference
Room 303B - Session CT+TF-MoM
Thermal Transport in Thin Films and Nanostructured Materials

Moderator: D. Cahill, University of Illinois, Urbana-Champaign

8:20am **CT+TF-MoM1 Impact of Electron-Phonon Coupling on Thermal Boundary Resistance by Molecular-Dynamics Simulation***, **R.J. Stevens**, P.M. Norris,* University of Virginia

With the growing interest in ULSI circuits and superlattices, an increasing need to understand thermal transport mechanisms across interfaces has become necessary. As the density of interfaces rapidly increases, device level thermal management is no longer dominated by the thermal properties of the individual layers but rather the thermal boundary resistances (TBR). Unfortunately, our current understanding of room temperature TBR is not adequate for proper thermal design of interface dense devices. Most TBR theoretical work has been an extension of the acoustic mismatch theories and has been limited to phonon elastic scattering processes for perfect interfaces. Other transport mechanisms have been considered such as electron-phonon (e-p) scattering and inelastic phonon scattering. There has been very little effort to systematically measure room temperature TBR and verify the proposed theories. Unfortunately, measuring TBR is quite difficult, although there has been some success using ultrafast spectroscopy techniques. Alas, it is problematical to systematically fabricate and fully characterize a series of interfaces and validate the proposed models. Molecular-dynamics simulations (MDS) can enhance existing experimental work by allowing analysis of controlled and well-defined interfaces. MDS enable the ability to alter material properties and atomic-level structure of the interface, so the mechanisms of TBR can better be understood. In this work, we perform MDS of the energy transport through an interface of a Si â?" metal system described by semi-empirical potentials (Stillinger-Weber and Embedded Atom Method). The electronic heat conduction in the metal film and e-p coupling are included by using a recently developed model that combines MD with a continuum description of the evolution of the electron temperature. The electron scattering contribution to TBR is determined by altering the e-p coupling strength in the bulk and at the interface.

8:40am **CT+TF-MoM2 Thin Film SiGe Superlattice Micro Refrigerators Flip-Chip Bonded with IC Chips***, **Y. Zhang**, A. Shakouri,* University of California, Santa Cruz*; G. Zeng,* University of California, Santa Barbara*; P. Wang, A. Bar-cohen,* University of Maryland

Thin film SiGe-based superlattice micro refrigerators, with device sizes ranging from 40-150 micron in diameter, have demonstrated cooling by 4.5C at ambient temperature and cooling power density exceeding 500W/cm2. In this talk we present theoretical and experimental study of these thin film refrigerators flip-chip bonded underneath 50 micron thick silicon substrate. The idea is to evaluate the effectiveness of these refrigerators to eliminate hot spots in IC chips without modifying the IC processing steps. Even though the 50 micron thick silicon has relatively high thermal conductivity and the cooling of micro refrigerators is spread over larger areas, theoretical studies show that localized cooling by 1-2C with cooling power density exceeding 100W/cm2 should be possible. Experimentally three micron thick gold-to-gold bonding is used to attach the two wafers. Cooling on top of the silicon heat load wafer is measured using microthermocouples. Thin film resistor heaters are used to evaluate the cooling power density. We have achieved cooling power density ~40W/cm2. It is interesting to note that even though bare microrefrigerators have an optimum size for maximum cooling on the order of 70 microns in diameter and largest cooling power density is obtained with the smallest devices, in the two-chip bonded configuration, the biggest coolers have the largest cooling and the cooling power density is not a strong function of the size. 3D electrothermal simualtions are used to explain the measured results and to evaluate maximum cooling performance under various ideal and non-ideal conditions.

9:00am **CT+TF-MoM3 Interfaces, Functionalization and Heat Flow in Nanoscale Materials.***, **S. Shenogin**, A. Bodapati, L. Xue, P. Keblinski,* Rensselaer Polytechnic Institute

The influence of the interface resistance on heat exchange between carbon nanotubes (CNs), fullerenes and embedding soft material medium was studied by means of molecular dynamics simulation. Due to a weak coupling between thermal vibrations of stiff carbon nanostuctures and soft organic matrix, the inclusion-matrix interface has high thermal resistance (Kapitza resistance). Recent experiments and simulations showed that the resistance of such interfaces is equivalent to the matrix layer with thickness 5 to 20 nm@footnote 1@,@footnote 2@. High boundary resistance considerably reduces thermal conductivity of the nanotube-based polymer composites and limits potential heat management applications. Our simulation shows that chemical functionalization of the nanoparticles with short organic chains reduces the interface thermal resistance by enhancing interactions between nanoparticels and the matrix. Detail dynamical analysis demonstrates that functionalization widens the overlap between the vibrational spectra of carbon nanostructures and the matrix. Remarkably, in the case of fullerenes, functionalization with a single chain reduces interfacial resistance by a factor of ~ 5. In the case of CN the interface resistance is reduced 4 times when 7 or more % of carbon atoms are functionalized. However, the functionalization decreases the intrinsic high thermal conductivity along the nanotube. The selection of the optimal side group length and concentration will be discussed. @FootnoteText@ @footnote 1@ S.T Huxtable et. al., Nature Materials, 2, 731 (2003).@footnote 2@ S.Shenogin et. al, J.Appl.Phys 95 (12), (2004).

9:20am **CT+TF-MoM4 Thermal Transport in Nanostructured Materials***, **D. Cahill**,* University of Illinois, Urbana-Champaign **INVITED**

The thermal conductance of interfaces is a key factor in controlling the thermal conductivity of materials with high densities of internal interfaces, e.g., nanocomposites, nanocrystalline ceramics, and short-period multilayer films and superlattices. Low interface conductance puts a lower limit on the size of nanoparticles that can be used as fillers in thermal interface materials and limits the increases in the the thermal conductivity that can be achieved in carbon nanotubes composites. We study these effects using high-precision measurements of thermal conductivity using the 3-omega method and psec transient absorption measurements of the thermal decay time of carbon-nanotubes suspended in micelles in water. We have also recently advanced the state-of-the-art of time-domain-thermoreflectance (TDTR) measurements of thermal transport and are using TDTR to study heat transport across individual interfaces and the thermal conductivity of sputtered multilayers. The thermal conductance of epitaxial interfaces between similar materials approaches the high values predicted by simple theory. Nanolaminates of dissimilar materials show remarkable reductions in thermal conductivity when the layer thickness is a few nm; this approach provides a novel materials with ultra-low thermal conductivity without sacrificing strength or environmental protection.

10:00am **CT+TF-MoM6 Thin Film Micro Refrigerators for on Chip Thermal Management***, **A. Shakouri**,* University of California at Santa Cruz **INVITED**

In this talk, we review design considerations for high cooling power density thermoelectric/thermionic coolers. Conventional bismuth telluride-based thermoelectric modules have a maximum cooling of about 70° C, however the cooling power density is low, on the order of 1-10 W/cm2. The micro and nanoscale electronic devices can generate thousands of watts per centimeter square heating, which is far beyond the capability of current TE modules. The maximum cooling power density of a TE module is inversely proportional to the length of its elements (distance between hot and cold junctions). Thus it is possible to increase the cooling power density with the use of thin film material. 100 micron thick Peltier modules with cooling power density exceeding 100W/cm2 have been demonstrated. Further increase requires significant improvement in metal-semiconductor contact resistance and in heat sink thermal resistance. An alternative solution is to use the thermoelectric properties of silicon or III-V substrate material. Heat and current spreading in 3D electrode configuration, allow removal of hot spots in IC chips. Furthermore, addition of a 1-5 micron thick superlattice can improve the cooling performance by increasing the selection between hot and cold carrier transport via thermionic emission and by reducing thermal resistance between hot and cold junctions. Several III-V and silicon heterostructure integrated thermionic (HIT) microcoolers have been fabricated and characterized. They have achieved cooling, on the order of 4.5° C at room temperature and 12° C at 200° C ambient temperature. Cooling power density was also characterized and values ranging from 100-680W/cm2 were measured. Finally, an optical technique based on thermoreflectance imaging was used to obtain temperature distributions on top of devices with sub micron spatial resolution and <0.1° C temperature resolution.@footnote 1@ @Footnotetext@ @footnote 1@ Work supported by DARPA and ONR MURI.

10:40am **CT+TF-MoM8 Micro- and Nanoscale Thermal Phenomena in Magnetic Recording Heads*, Y.S. Ju,*** UCLA **INVITED**

Advances in magnetic recording heads are critical in enabling continued growth in areal densities of magnetic data storage. In the present talk we review studies of thermal characteristics of recording heads at micro- and nanoscales, which strongly affect their performance and reliability. Geometric scaling of GMR (giant magnetoresistance) and TMR (tunneling magnetoresistance) sensors leads to significant increase in temperature rise per unit power, which limits maximum permissible bias current and increases electrostatic discharge (ESD) susceptibility. This motivates fundamental studies of thin film thermal conductivity, thermal interface resistance, and heat generation due to electron tunneling. Reliability of magnetic recording heads is also compromised by thermal protrusion and thermal creep flow induced by Joule heating in write heads. Spatial distribution of eddy current heating in magnetic yoke structures and heat transfer across air bearing are important factors influencing thermomechanical behavior of recording heads and reliability of head-disk interface. Fundamental understanding of thermal phenomena in magnetic recording heads will also play an important role in the development of thermally-assisted recording, which is a promising approach to extending magnetic recording beyond the superparamagnetic limit of conventional recording media.

11:20am **CT+TF-MoM10 Transport and Mechanics in Hard and Soft Nanomaterials*, A. Majumdar,*** University of California, Berkeley **INVITED**

Hard and soft materials are characterized by the ratio of their respective binding energies (Eb) with respect to thermal fluctuations that are characterized by kT. Mechanics and dynamics of hard materials (Eb >> kT) are generally unaffected by kT, except when undergoing irreversible processes such as transport phenomena or inelastic deformations. On the other hand, fluctuations dominate the behavior of soft materials (Eb ~ kT) such as liquids and biomolecules, where entropic forces are critical in their mechanics. As part of this lecture, I will focus on two topics, both of which relate to the interplay between entropic and elastic forces: (i) Transport of heat and fluid in solid nanostructures such as nanotubes and nanowires. I will share some of our recent discoveries of how heat and charge transport in such nanostructures can be manipulated by size confinement and interface engineering; (ii) Actuation of mechanical devices such as cantilever beams using reactions of biomolecules (eg. DNA hybridization, antigen-antibody binding). I will also discuss the implications of our work on energy conversion and biomedical technologies.

MEMS and NEMS
Room 213C - Session MN-MoM
Processing and Characterization for MEMS and NEMS

Moderator: S.L. Firebaugh, United States Naval Academy

8:20am **MN-MoM1 Porous Thin Films for MEMS and Nano Applications*, C.J. Kim,*** University of California, Los Angeles **INVITED**

The talk will summarize various porous thin-films developed at the UCLA Micro and Nano Manufacturing Laboratory over the past several years. (1) Micromachining of aerogel-like thin film has been developed, including photolithographic steps and surface micromachining procedures for silica and alumina. Mechanical properties have been measured by direct bending tests with such fabricated free-standing aerogel microbeams. (2) Polysilicon thin film on silicon dioxide, which represents a typical surface micromachining process, has been converted permeable by post-deposition electrochemical etching, allowing on-chip vacuum encapsulation of micro and nano structures finally practical. (3) Silicon wafer with high-aspect-ratio pores serves as a mold in developing three-dimensional nanobatteries. Although most projects start from development of pore formation processing steps, the main goals for all are to explore specific new applications that take advantage of the unique property of the materials or the processing procedures.

9:00am **MN-MoM3 Nanotribological Characterization of Perfluoropolymer Thin Films for BioMEMS Applications*, K. Lee,*** *B. Bhushan, D. Hansford,* The Ohio State University

The undesired adhesion of micro-organisms and biomolecules to surfaces and biofilm development called biofouling may cause detrimental effects to the performance of most biomedical microelectromechanical system (BioMEMS) devices. A vapor phase deposition technique to modify surfaces with perfluoropolymer and silane thin films was developed to reduce or prevent protein or cell interactions, critical for their use. The surface properties of these devices and therefore the surface modifications become increasingly important for BioMEMS applications as the channel dimensions decrease within these systems. Compared to dip coating or spin coating, the vapor phase deposition is more effective for smaller channels, especially at the nanoscale. Since nanotribological behaviors such as surface topography, adhesive and frictional properties and mechanical stability of these films play a very important role in forming uniform, conformal and ultra thin films on the surface and reducing protein or cell interactions, coating effects of these films were characterized extensively using an atomic force microscopy in this study.

9:20am **MN-MoM4 Multi-scale Friction Experiments Using Atomic Force Microscopy and Surface Micromachined Interfaces*, E.E. Flater,*** *M.D. Street,* University of Wisconsin-Madison*; A.D. Corwin, M.P. de Boer,* Sandia National Laboratories*; R.W. Carpick,* University of Wisconsin-Madison

Friction and wear are major limiting factors for the development and commercial implementation of devices fabricated by surface micromachining techniques. We use atomic force microscopy (AFM) to determine the constitutive relation for friction for a single asperity nanoscale contact on micromachined surfaces. Friction is measured using AFM SiO@sub2@- and alkyl-monolayer terminated tips sliding on alkyl-terminated single crystal silicon. The alkyl monolayer coatings include octadecyltrichrolosilane (OTS), octadecene, and fluorinated monolayers (FOTAS). Frictional information at the nanoscale is then used to predict tribological properties of a polycrystalline silicon nanotractor device interface. This microscale friction and wear test device provides abundant, quantitative information about friction and wear at an actual microelectromechanical system (MEMS) interface. This in-situ approach to measuring tribological properties of MEMS, combined with high-resolution atomic force microscope images of device wear, provides insight into the effects of wear and prescriptions for avoiding it.

9:40am **MN-MoM5 Deposition and Characterization of Nitrogen-Doped Polycrystalline SiC Films for MEMS Applications**, *J. Trevino, X.-A. Fu, S. Rajgopal, M. Mehregany,* ***C.A. Zorman,*** Case Western Reserve University

This presentation reports on the development of processes to deposit undoped and nitrogen-doped, polycrystalline silicon carbide (poly-SiC) films on large-area substrates in a high-throughput, low pressure chemical vapor deposition (LPCVD) reactor using SiH2Cl2, C2H2 and NH3 precursor gases. The films were deposited in a customized deposition system constructed around a resistively-heated, horizontal furnace similar in design to a conventional polysilicon furnace and capable of holding up to 100, 150 mm-diameter substrates. To the best of our knowledge, this is the largest furnace designed specifically for the production of poly-SiC films for MEMS. Depositions were performed on 100 mm-diameter Si and SiO2-coated Si wafers using a SiH2Cl2 flow rate of 35 sccm, a C2H2 (5% in H2) flow rate of 180 sccm and NH3 (5% in H2) flow rates ranging from 10 to 90 sccm. The furnace temperature was held at 900C while the deposition pressures ranged from 2.5 to 4 Torr. Stoichiometric poly-SiC films were deposited over this entire range. The films exhibit a strong (111) 3C-SiC texture regardless of pressure. Films having a thickness of up to 2 microns are uniform, with less than a 5% variation across both the wafers and the boat. Four-point probe measurements indicate that the highest conductivities are achieved at a NH3 flow rate of 90 sccm. Wafer-scale residual stresses were measured using an optical curvature measurement technique. The residual stresses in the heavily-doped films are tensile with values decreasing to around 100 MPa in films deposited at 4 Torr. Single-layer, surface mechanical properties test structures, such as cantilever beams, stress pointers and lateral resonators were fabricated, successfully released and used to characterize the films. Likewise, bulk micromachined membranes were fabricated and tested using a load-deflection technique. Stress measurements from these micromachined structures confirm the wafer-scale residual stress measurements.

10:00am **MN-MoM6 Characterization of Nanotribological Properties and Surface Chemistry of Advanced Nanostructured Carbon Materials for MEMS and NEMS Applications*, A.V. Sumant,*** *D.S. Grierson,* University of Wisconsin-Madison*; J.E. Gerbi,* Argonne National Laboratory*; J.P. Birrell,* Argonne National Laboratory, U.S.*; J.A. Carlisle, O.H. Auciello,* Argonne National Laboratory*; T. Friedmann, J.P. Sullivan,* Sandia National Laboratories*; R.W. Carpick,* University of Wisconsin-Madison

Despite rapid advances in micro- and nanofabrication technologies, the implementation of reliable, high endurance devices that involve sliding contacts remains elusive. At small length scales, device properties are dominated by surface chemistry rather than bulk properties, and therefore materials with superior tribological properties and optimized surface chemistry are needed. Ultrananocrystalline diamond (UNCD) and tetrahedra amorphous carbon (taC) thin films have exceptional physical, chemical and tribological properties at the macroscale (nearly equivalent to those of single crystal diamond) and are being considered promising materials for the fabrication of high performance MEMS devices. However, little is known about the surface chemistry of these materials, and how it affects their nano- and micro-scale tribological performance. We have developed detailed methodologies to characterize nanotribological properties and surface chemistry of UNCD and taC at the tribologically relevant interface by using a combination of near-edge X-ray absorption fine structure spectroscopy (NEXAFS), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). We show that the surface chemistry, sp2-sp3 ratio, and nanoscale friction and adhesion can be different on the etched underside of the film (the side which becomes exposed and makes tribological contact after a MEMS release process) as compared with the top side of the film. We also discuss the effect of hydrogen plasma treatment, which in the case of UNCD renders the surface extremely inert and chemically pure, and reduces nano-scale friction and adhesion dramatically. Adhesion, as measured with tungsten carbide AFM probes, is reduced to the van der Waals limit indicating full saturation of dangling surface bonds and elimination of surface contaminants.

10:40am **MN-MoM8 Critical Issues in Epitaxial Growth of Pulse Laser Deposited AlN Films for MEMS and NEMS based RF Resonators*, S. Hullavarad*,** *R. Vispute, T. Venkatesan,* University of Maryland*; A. Wickenden, L. Currano, M. Dubey, T. Takacs, J. Pulskamp,* U.S. Army Research Laboratory

AlN exhibits strong piezo-electric properties suitable for RF resonator applications. In this work we report the growth of highly oriented AlN films for MEMS and NEMS resonator devices. A multiple flexural structure of Pt/SiO2/Si is used as a substrate and films are grown by Pulse Laser Deposition (PLD) technique at a pulse energy of ~2J/cme2 with a repetition rate of 10 Hz. The process is optimized for the growth of AlN on different thicknesses of underlying SiO2. The films are characterized by XRD, RBS and techniques for crystalline quality and stoichiometry respectively. The interface analysis of underlying structures is analyzed in detail by RBS and oxygen content in the film is monitored by Resonant Oxygen Scattering technique. The morphology of AlN films is studied by scanning electron and atomic force microscopies. We have obtained highest Q factors for PLD grown AlN MEMS resonator beams of Q = 8,000 at fo = 2.5 MHz and Q = 17,400 at fo = 0.44 MHz We also address in this work critical issues related to (1) thickness of SiO2 (2) method of growth of SiO2 in fabricating MEMS and NEMS devices. These factors are very essential for the growth of high quality AlN films. However, SiO2 provides a amorphous underlayer for the growth of AlN leading to non in plane aligned AlN with respect to substrate. A lattice matching, epitaxial oxide layer like Y2O3 in place of SiO2 is going to be a unique solution for eventual epitaxial growth of AlN. We address the epitaxial issues of AlN and underlying oxide for improving the resonator properties of AlN based MEMS and NEMS devices.

11:00am **MN-MoM9 Vapor Phase Uptake of Mobile Organophosphates for MEMS Lubrication Purposes*, D.A. Hook*,** *W. Neeyakorn, C. Jaye, J. Krim,* North Carolina State University

MEMS devices are highly susceptible to surface forces that can cause suspended members to deflect towards the substrate, collapse and/or adhere permanently to the substrate. A number of surface treatments have met with varying degrees of success for alleviation of MEMS-related stiction/adhesion problems, but friction and wear remain problematic. We report here the results of a quartz crystal microbalance (QCM) study of the nanodynamics and uptake characteristics of organophosphate (tricresylphosphate and t-butyl phenyl phosphate) layers adsorbed from the vapor phase onto silicon and silane treated silicon surfaces. Silanes applied from the liquid phase as self-assembled monolayers are in common use as anti-stiction treatments for silicon MEMS devices, but degrade at elevated temperatures. Organophosphates are highly stable at temperatures in excess of 600ï,°C, act as antioxidants, and have well-documented tribological performance for certain materials combinations. We observe that organophosphates adsorb readily onto selected silanes. The silane +organophosphate combinations moreover exhibit interfacial slippage and/or viscoelasticity in response to the oscillatory motion of the QCM. Such effects have previously been linked to beneficial tribological performance.[1] Work is in progress to assess the tribological performance of these materials on actual MEMS devices. Work supported by AFOSR and NSF. @FootnoteText@ @footnote 1@M. Abdelmaksoud, J.Bender and J. Krim, Phys. Rev. Lett. 92, 176101 (2004).

11:20am **MN-MoM10 Mechanical and Electrochemical Characterization of Gold Membranes on a Drug Delivery MEMS Device*, Y. Li*,** *M.J. Cima,* Massachusetts Institute of Technology

Our drug delivery MEMS device was designed to release multiple substances with complex profiles in order to maximize the efficacy of drug therapies. The device consists of arrays of microreservoirs etched into a silicon substrate to contain different types and doses of drug. The release of drug is achieved through the electrochemical dissolution of the gold membranes that seal individual reservoirs. The mechanical and electrochemical properties of the gold membranes are important parameters in evaluating the reliability of device performance. A bulge test apparatus was constructed to measure the mechanical properties of the gold membranes. The apparatus is pressurized, and the resutling deflection of the membranes is measured using interferometry. The biaxial modulus of elasticity and residual stress in the membranes extracted from the bulge test were 126-168 GPa and ~100 MPa (tensile) respectively for membranes with in-plane sizes ranging from 20 to 200 mm. An in situ experimental set up was constructed to observe the electrochemical disintegration process of the gold membranes when voltage was applied. The bulge test was used to evaluate the mechanical integrity of gold membranes corroded for different duration of time. The decrease in the membrane burst pressure with longer corrosion time under the bulge test confirmed a gradual loss of mechanical integrity of the gold membranes due to corrosion. Observation of the membrane morphology with an optical profiler indicated an abrupt transition in the membrane stress state from slightly tensile to highly compressive after five seconds of corrosion. This suggests that the gold membrane disintegration occurs by a combination of thinning through active dissolution and accumulation of compressive stress.

11:40am **MN-MoM11 Microfabrication and Nanomechanical Characterization of Polymer MEMS for Biological Applications*, G. Wei*,** *B. Bhushan, N. Ferrell, D. Hansford,* The Ohio State University

Polymer Microelectromechanical System (MEMS) devices are promising for biological applications such as development of biosensors and biomechanical devices. The relatively low stiffness and improved biological interface between cells and polymeric materials make polymer cantilever and beam structures attractive as highly sensitive force sensors for measuring cellular and biomolecular nanomechanics. In order to develop polymer Bio-MEMS, novel polymer microfabrication techniques are required, and the nanomechanics studies including measurement of the mechanical properties of the polymer materials in the nano scale must be carried out. This paper presents the development of soft lithography based polymer Bio-MEMS microfabrication techniques and systematic studies on the nanomechanical characterization of the polymer materials, polymer beams and polymer cantilevers. Poly (methyl methacrylate) (PMMA) and poly (propyl methacrylate) (PPMA) are used to make the polymer beams and cantilevers, which are 5 µm wide, 10-30 µm long and 200 nm-5 µm thick, for MEMS integration. The hardness, creep behavior and scratch resistance of the PMMA and PPMA microstructures were measured using nanoindentation/nanoscratch technique with a Nano Indenter II system, and the nanomechanical properties are compared with the bulk values. The elastic modulus of the polymer beam was obtained from the bending tests performed by nanoindentation, and the nano scale fatigue of the polymer cantilever was measured using the nanoindentation Continuous Stiffness Measurement (CSM) technique. To simulate the working environment of the polymer Bio-MEMS, PMMA and PPMA beams and cantilevers were also placed in an aqueous solution (saline, DI water, etc.), and nanoindentation experiments were performed on such samples. The results are discussed along with the dry condition values.

Thin Films

Room 303C - Session TF-MoM

ALD and Applications

Moderator: S.M. George, University of Colorado

8:20am **TF-MoM1 Atomic Layer Deposited Barriers for Copper Interconnects*, J. Schuhmacher*,** *A. Martin, D. Ernur, Zs. Tökei, Y. Travaly, C. Bruynseraede, A. Satta, C.M. Whelan, D. Shamiryan, G. Beyer,* IMEC, Belgium*; T. Abell,* Intel affiliate at IMEC, Belgium*; V. Sutcliffe,* Texas Instruments affiliate at IMEC, Belgium*; M. Schaekers, K. Maex,* IMEC, Belgium **INVITED**

Development and properties of a WNC atomic layer deposited (ALD) barrier film in terms of requirements and performance for damascene BEOL process flows are discussed. Damascene type substrates comprise various surfaces. The interaction of a surface with the ALD precursors controls the growth of ALD films. The effects of the substrate are reflected by the characteristics of the transient, non-linear growth period. Examples show the importance of characterizing the nature of the substrate / ALD interaction. Surface preparation before or during the ALD process is a useful tool for improving ALD film quality. An example for the challenges set by the introduction of a new material in an existing process flow is given with the interaction of ALD WNC to the chemical mechanical planarization (CMP) process. Film reliability will be discussed on damascene test structures with ALD WNC in the range of 2 to 10 nm.

9:00am **TF-MoM3 Effects of Surface Chemistry on ALD Ta(N) Barrier Formation on Low k Dielectrics***, **J. Liu**, J. Bao,* University of Texas at Austin*; M. Scharnberg,* Technische Fakultat der Christian-Albrechts-Universitat, Germany*; P.S. Ho,* University of Texas at Austin

For atomic layer deposition (ALD) of ultra-thin Cu barrier layers, the initial chemisorption at the substrate surface is important in controlling the barrier uniformity and morphology. It is particularly important for organosilicate (OSG) low k dielectrics generally characterized by inactive surface bonds which have to be properly activated for sufficient ALD nucleation. In-situ x-ray photoelectron spectroscopy (XPS) was employed to study the effects of the surface chemistry on ALD Ta(N) barrier formation on two main types of low k surfaces, OSG and SiLK. The initial chemisorption was confirmed to be through formation of Ta-O bonding on OSG films and charge transfer complexes on the aromatic SiLK films. The evolution of the low k surface chemistry revealed an initial transient growth region controlled mainly by the substrate surface chemistry. Pre-treatment of the OSG low k surfaces with nitrogen and hydrogen radical beams, particularly with nitrogen radicals, was observed to enhance significantly the chemisorption of the TaCl@sub 5@ precursor on the OSG surfaces. The enhancement was attributed to the dissociation of the weakly bonded methyl groups from the low k surface followed by surface nitrogen enrichment. The improvement of the growth rate observed in this study illustrates the criticality of the surface coverage at saturation for a successful ALD process. In the subsequent linear growth region, atomic hydrogen species was able to reduce the chlorine content under appropriate temperature and with sufficient purge. The role of the atomic hydrogen in this process enhancement is discussed. In addition, precursor penetration was observed to be suppressed as a result of surface activation on the mesoporous OSG, suggesting a possible approach to pore sealing of porous OSG with halide ALD chemistry.

9:20am **TF-MoM4 Evaluation of Plasma Enhanced Atomic Layer Deposition TaN for Metal Gate Electrode Application***, **H. Kim**,* IBM Thomas J. Watson Research Center*; D.-G. Park, P. Ronsheim,* IBM Semiconductor Research and Development Center*; S.M. Rossnagel,* IBM Thomas J. Watson Research Center

TaN has been one of the most attractive materials as a diffusion barrier for Cu interconnect technology due to its good diffusion barrier properties, good adhesion to dielectrics, and high thermal stability. More recently, TaN has been considered as a strong candidate for a direct metal gate material due to its proper work function (~4.3eV) as n-type conductivity. As for the deposition technique of metal gate electrode, previous study on TiN metal gate demonstrated that atomic layer deposition (ALD) has benefits including negligible defect generation and improved device reliability compared to other deposition method. Previously, we have reported that PE-ALD from TaCl@sub 5@ and N@sub 2@/H@sub 2@ plasma produced low resistivity cubic TaN films with various N/Ta ratios with excellent barrier properties for Cu metallization. In this study, PE-ALD TaN was evaluated as a gate electrode for metal-oxide-semiconductor (MOS) capacitors composed of TaN/SiO@sub 2@/p-Si with nanoscale thick (1.8-5.5 nm) SiO@sub 2@ dielectric. For as-patterned MOS structure, the leakage current characteristics were strong functions of N/Ta ratio and plasma power. A dramatic decrease of leakage current with two orders of magnitude was observed with decrease of the plasma power from 500W to 200W. For PE-ALD TaN electrode with stoichiometric N/Ta ratio, we observed a severe damage at SiO@sub 2@/Si interface as observed by a distorted capacitance-voltage (C-V) curve shape near the valence band edge of Si band gap. While the interface damages were partially disappeared after forming gas anneal, the gate leakage current level was remained high. However, the reduction of leakage current was more prominent for TaN@sub x@ films deposited with N@sub 2@ only plasma at both high and low plasma power condition with improved C-V characteristics. Additionally, a comparative study with PVD TaN electrode will be presented focusing on the impurity effect of TaN metal gate.

9:40am **TF-MoM5 Nucleation and Electrical Characterization of Ruthenium formed by Selective Area Atomic Layer Deposition***, **K.J. Park**, J.M. Doub, G.N. Parsons,* North Carolina State University

Ruthenium is a promising candidate for advanced metal gate electrodes in complementary metal-oxide-semiconductor (CMOS) transistors because of its thermal stability and low resistivity. Ru metal films were deposited by Atomic Layer Deposition (ALD) in a flow tube reactor system using Ruthenocene with oxygen as a reducing reactant on hydrogen terminated silicon, silicon oxide, HfO@sub 2@, as well as patterned organic monolayer surfaces at temperatures ranging from 300 to 375°C. Films were characterized by Auger electron spectroscopy, atomic force microscopy, and capacitance voltage analysis. Self limiting ALD behavior with ~1Å/deposition cycle was observed between ~315 and 350°C at 1.2 Torr operating pressure. At higher temperatures, growth rate per cycle increased indicating the onset of CVD growth conditions. No growth was observed at 300°C on any surface indicating no precursor adsorption, consistent with previous studies of the ruthenocene/oxygen ALD process. The incubation time for deposition was strongly dependent on the substrate. Growth initiated quickly on chemical oxide whereas >100 cycles were required for growth on Si-H surfaces and methyl terminated organic monolayers. The difference in nucleation allowed for selective area deposition of Ru on micron-scale pre-patterned surfaces, where >300Å of growth proceeded on oxide, with no visible deposition on the organic monolayer. Capacitor structures were formed by selective Ru deposition and characterized electrically using various thicknesses of dielectric films. Fitting the flatband voltage vs thickness results in an effective workfunction of 4.8eV on SiO@sub 2@, indicating that selective area deposition may be useful for integration of multiple metals into dual-metal gate CMOS structures. Possible mechanisms associated with nucleation and substrate dependence will be discussed.

10:00am **TF-MoM6 Atomic Layer Deposition for Metal Gate and Capacitor Electrodes***, **D.-G. Park**,* IBM Microelectronics **INVITED**

An employment of atomic layer deposition (ALD) method into the semiconductor devices is becoming pivotal because of the excellent attributes offered by ALD process such as good coverage and low impurity level. The ALD technique provides thin film depositions of nanoscale high-permittivity (k) gate dielectrics, metal electrodes, deep metal contact fill, and liners and/or barrier layers of Cu. This paper will review and discuss about the properties of thin ALD films for direct metal gate and capacitor electrodes. As a direct metal gate electrode application, various ALD metal electrodes such as TiN, TaN, and WN films were evaluated on thin SiO2 and high-k gate dielectric films for metal-oxide-semiconductor (MOS) capacitors and transistors. The effects of impurities and process conditions on the MOS devices will be discussed. MOS devices gated with ALD thin films demonstrated much lower defect densities than those with sputtered films by means of lower interface trap density and orders of magnitude lower leakage current. This is most likely a result of the relatively damage-free ALD deposition process. Equivalent oxide thickness of sub-nanometer (< 1nm) was attained with ALD-metal/high-k stack against the thermal budget of complementary MOS device fabrication. Additionally, an application of ALD-TiN film into a capacitor electrode for extremely high aspect ratio (~ 70:1) trench capacitors for sub-100nm trench DRAM devices will be presented. It is necessary to keep focusing on the development of various ALD materials systems to meet device requirements such as relevant work function and stability across the required thermal cycle.

10:40am **TF-MoM8 Infrared Analysis of HfO@sub2@ ALD from Hafnium Diethyl-Amide on SiO@sub2@ and Si-H surfaces***, **M.J. Kelly**, G.N. Parsons,* North Carolina State University*; J.G. Han, C.B. Musgrave,* Stanford University

An important advantage of atomic layer deposition is the potential to control bond structure at the initial growth interface. Deposition of high dielectric constant metal oxides on silicon typically leads to substrate oxidation and uncontrolled interface structure. To explore mechanisms in interface layer growth, we have used attenuated total internal reflection infrared spectroscopy to study of HfO@sub2@ formation on Si-OH and Si-H terminated surfaces from a tetrakis (diethylamido)hafnium metal organic precursor. Precursor exposure at 200°C on the Si-OH surface results show self-limiting chemisorption consistent with formation of Hf-O-Si bonds with substantial Hf-ethylamine ligands remaining. Exposing the surface to H@sub2@O results in removal of C-H modes, consistent with surface oxidation and formation of Hf-OH surface units. Precursor chemisorption is also observed on the Si-H starting surface, likely due to reaction with some surface OH. Distinct changes in the surface Si-H stretching modes are observed upon precursor adsorption, possibly due to interactions between the amine ligands and the surface hydrogen. Exposing this surface to H@sub2@O does not completely oxidize the surface products, consistent with alternate stable surface bonding configurations, likely involving formation of Si-C or Si-N bonds. Ab-initio results describing potential mechanisms of precursor dissociation and Si-H/ligand interactions will be discussed.

11:00am **TF-MoM9 Area-selective Atomic Layer Deposition for high-@kappa@ Dielectric Materials***, **R. Chen**, D.W. Porter, S.F. Bent, H.S. Kim, R. Sreenivasan, P.C. McIntyre, H. Jagannathan, Y. Nishi,* Stanford University

Atomic layer deposition (ALD) is a technique that can be used to deposit a variety of materials. While ALD inherently provides nano-scale control of materials in the vertical direction, we are investigating an area-selective ALD technique that enables micro- and nano-scale definition of the lateral structure. Our research emphasizes controlling the substrate surface chemistry in order to impart spatial selectivity to ALD. Using a variety of analytical techniques, we show that functionalizing the surface with self-assembled monolayers (SAMs) can block the ALD chemistry in the growth of HfO@sub 2@ and ZrO@sub 2@, which are both high-@kappa@ materials for potential gate dielectrics. Specifically, we have investigated the surface chemistry needed to block ALD under the more extreme conditions used to deposit these metal oxide dielectrics from metal chloride and water precursors at temperature as high as 300 °C. The efficiency of blocking depends strongly on the quality of the SAMs and the chain length of the attached layer. The potential of the area-selective process for defining lateral structure has been examined using different patterning methods, including selective functionalization of patterned SiO@sub 2@/Si and soft lithography. Using a combination of image analysis by SEM and elemental analysis by scanning Auger microscopy, we demonstrate that the HfO@sub 2@ can be deposited with spatial selectivity. Other types of SAMs have also been investigated as monolayer resists against the HfO@sub 2@ ALD process on Si and Ge substrates. These monolayer films also exhibit good deactivation and selectivity.

11:20am **TF-MoM10 SiO@sub 2@ Atomic Layer Deposition Using HSi[N(CH@sub 3@)@sub 2@]@sub 3@ and H@sub 2@O@sub 2@***, **B.B. Burton**,* University of Colorado*; S.W. Kang,* Pohang University of Science and Technology, Korea*; S.M. George,* University of Colorado

The atomic layer deposition (ALD) of SiO@sub 2@ has proven to be challenging. SiO@sub 2@ ALD can be accomplished using SiCl@sub 4@ and H@sub 2@O reactants at 600-800 K with large exposures of ~10@super 9@ L. Catalytic SiO@sub 2@ ALD is also achieved at room temperature with the same reactants but requires the presence of a Lewis base catalyst. Recently, we have observed efficient SiO@sub 2@ ALD with HSi[N(CH@sub 3@)@sub 2@]@sub 3@ and H@sub 2@O@sub 2@ reactant exposures. HSi[N(CH@sub 3@)@sub 2@]@sub 3@ is tris-dimethylaminosilane (Tris-DMAS). SiO@sub 2@ ALD was monitored on high surface area ZrO@sub 2@ particles that allowed the use of Fourier transform infrared (FTIR) spectroscopy to monitor the surface chemistry. Following the H@sub 2@O@sub 2@ exposures, the surface displayed vibrational modes consistent with SiOH* species. Tris-DMAS exposure at 825 K converted these species to Si-N(CH@sub 3@)@sub 2@* species and SiH* species. The subsequent H@sub 2@O@sub 2@ exposure converted these species back to SiOH* species. The exposures required for Tris-DMAS and H@sub 2@O@sub 2@ were ~10@super 6@L and ~10@super 7@L, respectively. These exposures are much more favorable than the ~10@super 9@ L exposures required to grow SiO@sub 2@ ALD films with SiCl@sub 4@ and H@sub 2@O at 600-800 K. Other advantages of using Tris-DMAS are the avoidance of HCl as a byproduct and the elimination of possible chlorine contamination in the SiO@sub 2@ film. The SiO@sub 2@ thin films were deposited at temperatures ranging from 525-825 K. The maximum growth rate of 1.9 Å/cycle at 825 K was determined by measuring the SiO@sub 2@ film thickness on ZrO@sub 2@ particles by transmission electron microscopy (TEM). When the temperature was decreased below 825 K, residual SiH* species were observed in the film and led to a decrease in the SiO@sub 2@ ALD growth rate. SiO@sub 2@ growth was also confirmed by the increase in absorbance from the Si-O-Si asymmetric stretch measured by FTIR spectroscopy.

11:40am **TF-MoM11 Radical-Enhanced Atomic Layer Deposition of Pure and Erbium-Doped Y@sub 2@O@sub 3@ Thin Films***, T.T. Van, **J.P. Chang**,* University of California, Los Angeles

The deposition of pure and Er-doped yttrium oxide thin films, using radical-enhanced ALD (RE-ALD), was investigated in this work. Yttrium oxide can be used as a high dielectric constant material, or as a waveguide material due to its high refractive index and compatibility with high concentration doping of optically active Er@super 3+@ ions. The Y@sub 2@O@sub 3@ films were deposited on Si using alternating pulses of Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium(III) precursor, or Y(TMHD)@sub 3@, and O radicals. Erbium dopants were incorporated by introducing Er(TMHD)@sub 3@ after every ten ALD cycles of Y@sub 2@O@sub 3@. To assess the feasibility of RE-ALD, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were used to determine the chemical composition and distribution, crystallinity, surface morphology, and step coverage of the deposited films. Well-controlled RE-ALD of pure Y@sub 2@O@sub 3@ and Er@sub 2@O@sub 3@ were achieved with both precursors and O radicals. With reactant pulse time ratio of 1:1, stoichiometric films were deposited with minimal carbon incorporation. The ALD window for both materials ranged from 200 to 300°C. Above 300°C, the precursors decomposed, causing significant carbon incorporation into the films. AFM analysis yields a root mean square roughness of less than 5Å for films below 110Å. Conformal deposition of Y@sub 2@O@sub 3@ was achieved over 0.5-µm features with an aspect ratio of 4, determined by cross-sectional SEM. The Er@super 3+@ doping concentration was effectively controlled by varying the ratio of Y@sub 2@O@sub 3@:Er@sub 2@O@sub 3@ cycles. For example, up to 8 at.% of Er@super 3+@ concentration was achieved at 300°C with alternating 10 cycles of Y@sub 2@O@sub 3@ and 5 cycles of Er@sub 2@O@sub 3@. These results indicate that RE-ALD is a viable technique for doping and depositing metal oxide thin films.

Thin Films
Room 303C - Session TF-MoA
Mechanical Properties of Thin Films

Moderator: B.L. French, College of William and Mary

2:00pm **TF-MoA1 Nano-Mechanical Properties of a "Solid Liquid"**, ***J.E. Houston**,* Sandia National Laboratories

Understanding the unique properties of nano-phase materials requires analysis of the mechanical properties at the nano-scale. Since many such materials involve the inclusion of small particulates in a polymer matrix, it is important to be able to analyze the viscoelastic behavior of the matrix in the region adjacent to the particulates, the so called â?ointerphaseâ?⍰ region. Scanning probes have the potential to be very important for this type of analysis. However, such applications are made difficult because of the critical role played by contact mechanics in the process, and at the nano-scale this quantity is not directly observable. In this presentation, an example of such an analysis is outlined involving a classic viscoelastic material, which is often referred to as a â?osolid liquidâ?⍰ or â?odilatantâ?⍰ material, but is more commonly known under the popular name â?oSilly PuttyTMâ?⍰ (trademark: Binney and Smith). This material is unusual because it exhibits elastic behavior over short experimental times (high Deborah numbers) and viscous properties over long times (low Deborah numbers). The results are presented in terms of transient relaxation measurements, using both lyophilic and lyophobic tips, followed by a Fourier analysis to obtain the broad-range frequency response. These results are directly compared with more classical bulk rheological measurements. While these initial results are not done at the true nano-scale, the discussion will include an assessment of the potential, and contact-mechanics difficulties, involved in proceeding to that regime. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

2:20pm **TF-MoA2 Structure and Properties of Exothermic Metal Multilayers**, ***D.P. Adams**, C. Tigges, M.A. Rodriguez, T. Buccheit,* Sandia National Laboratories

Multilayer thin films composed of reactive material pairs are currently of interest for brazing, joining and other applications. As shown extensively by Weihs et.al. several thin film material systems can be stimulated such that a rapid, self-propagating reaction occurs within a multilayer. These layers have great potential for joining, because they act as a localized, short-lived heat source. In this talk, we evaluate the properties and microstructure of two multilayer systems, Co/Al and Pt/Al, which have vastly different heats of formation. Each material system was deposited by magnetron sputtering to thicknesses in excess of 1 micron having different designs. Propagation velocities were measured by high-speed photography for both material systems, and speeds are shown to depend on bilayer thickness, premixed volume, heat of formation and substrate thermal properties. Critical thicknesses required for propagation (when attached to substrates) have been identified and are described through comparison with analytical models. Secondly, we discuss the microstructure and mechanical properties of reacted films. New (previously not reported) phases have been found after exhibiting a self-propagating exothermic reaction. For example, rhombohedral AlPt has been produced in reacted Al/Pt multilayers. We currently attribute this to the rapid quench rate following reaction to high combustion temperatures. The mechanical properties (hardness, toughness) of reacted films are also investigated, because these are critical to future applications. Attempts are made to relate these properties to reacted film microstructure.

2:40pm **TF-MoA3 A Nanometrics Feasibility Approach to Reliable Devices**, ***W.W. Gerberich**, W.M. Mook, J.M. Jungk, M.J. Cordill,* University of Minnesota **INVITED**

Rapid advances in LIGA structures and other approaches to MEMS devices could be achieved by fast turn-around screening. This could be achieved on appropriate length-scale test samples fabricated by MBE (molecular beam epitaxy), CVD (chemical vapor deposition), ALD (atomic layer deposition), and electrochemically-produced small volumes. Using nanoindenters as either indenters or compression testers, we have already demonstrated that films, nanospheres, and thin-walled nanoboxes of Au, Ti and Si can exhibit three or four levels of length scale.@footnote 1@ These and further developments regarding possible computational and combinational approaches will be discussed. @FootnoteText@ @footnote 1@W.M. Mook, "Geometry and Surface State Effects on the Mechanical Response of Au Nanostructures," Zeiss Metalkunde (2004) in press.

3:20pm **TF-MoA5 Properties and Applications of Boron Carbide Thin Films**, ***Y. Chen**, C.A. Freyman, Y.-W. Chung,* Northwestern University

Boron carbide thin films have been synthesized with pulsed dc magnetron sputtering using a boron carbide target in an ambient of pure argon. We examined the effect of substrate bias and pressure on the surface roughness and hardness of these films. Wear rates and coefficient of friction data were also obtained. As expected, an optimum substrate bias results in the atomic scale surface topography and highest nanoindentation hardness (about 40 GPa). Under normal ambient conditions, boron carbide films result in lower friction coefficient, most likely due to the formation of boric acid as a solid lubricant, reported earlier by Erdemir and coworkers. The high hardness, smooth topography and low friction even in moist environments suggest that boron carbide may be a better protective overcoat for disk drive systems.

3:40pm **TF-MoA6 Mechanical Stress in PVD Deposited Chromium Films**, ***G.C.A.M. Janssen**,* Delft University of Technology, The Netherlands, Netherlands*; J.-D. Kamminga, S.Y. Grachev,* Netherlands Institute for Metals Research, The Netherlands

Thin films on substrates are usually in a stressed state. Apart from the well understood thermal stress - stress occurring due to different thermal expansion coefficient of layer and substrate in combination with an elevated deposition temperature - intrinsic stress can occur resulting from the growth and/or microstructure of the film. In this presentation the mechanisms behind both tensile and compressive intrinsic stress are discussed. A set of chromium films was deposited at room temperature using PVD. These films have a microstructure in zone 2 of the Thornton model. The grain boundary density is high near the substrate-film interface and lower higher up in the film. In fact the grain boundary density as function of height in the film follows a power law. We have shown that tensile stress and grain boundary density co-develop with film thickness. This observation proves the generation of tensile stress at grain boundaries. We calculated the amount of grain boundary shrinkage responsible for the generation of tensile stress to be 0.013 nm. Films deposited at higher Ar pressure exhibit a different power law dependence on thickness. TEM revealed dense grain boundaries and small grains for the films deposited at low pressure and porous grain boundaries, separating larger feather like grains, for films deposited at higher pressures. Grains in those films have less interaction and generate less stress. Stresses in films deposited under a bias voltage were tensile for thin films and compressive for thick films. This is due to a combined effect of atomic peening, leading compressive stress and grain boundary shrinkage leading to tensile stress. It is shown that the dependence of the total stress on film thickness is described by a thickness dependent tensile term and a thickness independent compressive term.

4:00pm **TF-MoA7 Development of Zrb@sub 2@ and Hfb@sub 2@ Hard Coatings by CVD from Single Source Precursors**, ***S. Jayaraman**, E.J. Klein, Y. Yang, L. Nittala, J.R. Abelson, D.Y. Kim, G.S. Girolami,* University of Illinois at Urbana-Champaign

The transition metal diborides ZrB@sub 2@ and HfB@sub 2@ are "metallic ceramic" materials with excellent properties, including high melting temperature (> 3000 °C), low electrical resistivity (9 µm@ohm@cm for ZrB@sub 2@), high thermal conductivity (23 Wm@super -1@K@super -1@ for ZrB@sub 2@), high hardness (20 and 29 GPa for ZrB@sub 2@ and HfB@sub 2@, respectively), and great corrosion resistance. This makes them attractive candidates for monolithic or nanocomposite based hard coatings. However, there have been relatively few attempts to deposit transition metal diboride coatings by chemical vapor deposition (CVD). Here, we investigate ZrB@sub 2@ and HfB@sub 2@ growth by CVD using the single-source precursors Zr[BH@sub 4@]@sub 4@ and Hf[BH@sub 4@]@sub 4@ over the substrate temperature range 200-1000 °C. At temperatures < 500 °C, we direct a flux of atomic hydrogen, generated by a remote plasma source, onto the growth surface in order to promote the removal of excess boron and improve stoichiometry. For deposition temperatures < 500 °C the films appear to be amorphous in X-ray diffraction; for higher temperatures crystalline peaks are detected. The crystalline films are strongly textured with either (0001) or (10@super-@10) planes normal to the growth direction and display characteristic microstructures. Initial experiments on trench coverage at low temperatures show that film growth is conformal. We will report the hardness of ZrB@sub 2@ and HfB@sub 2@ films determined by nanoindentation and the relationship between the hardness, crystallinity, and microstructure. We will also outline the prospects for the growth of nanocomposite hard coatings in this materials system.

4:20pm **TF-MoA8 Effects of Sulfur Addition to Magnetron Sputtered a-C:H Thin Films***, **C.A. Freyman**, Y.-W. Chung,* Northwestern University

Amorphous hydrogenated carbon films (a-C:H) have shown ultra low friction coefficients ($\mu<0.01$) in dry nitrogen testing environments. The ultra low friction properties degrade with the addition of water vapor to the testing environment. In this work, we explore the effects of sulfur addition to magnetron sputtered a-C:H films on elastic modulus, hardness and tribological properties as a function of relative humidity in the testing environment. Film microstructure and chemical state of sulfur have been investigated with transmission electron microscopy and electron energy loss spectroscopy. Hydrophobicity of these films are obtained via contact angle measurements. These studies show that with appropriate control of the film-substrate interface, sulfur addition of a few atomic percent is sufficient to reduce the adverse effect of humidity on friction.

4:40pm **TF-MoA9 RF MEMS Beam Stiffness Measurement Using Nanoindentation***, **J. Vella**, S. Pacheco, P. Zurcher,* Freescale Semiconductor

With wireless communications being a major technology driver for semiconductors, on-chip integration of analog functions that are often based on passive components is crucial for reduced system form factor, higher performance, improved functionality, and reduced cost. MEMS-based resonators promise to deliver smaller and more easily integrated IF and RF filters and oscillators. The operating frequency of such filters and oscillators is defined by the mechanical resonant frequency and is given by @omega@@sub n@=@sr@(k/m), where @omega@@sub n@ is the natural resonant frequency, k is the beam stiffness and m is the beam mass. Thus, direct determination of the beam's stiffness is paramount for the design of MEMS-based resonators. The stiffness, k, can be determined for a fixed-fixed beam under a concentrated load at its center using the following equation: k=16Ew@sub r@(h/L@sub r@)@super 3@, where E is the Young's modulus of the beam material, w@sub r@, h, and L@sub r@ are the width, thickness, and length of the fixed-fixed beam, respectively. This study compares modeled beam stiffness predictions with nanonindentation measurements. A 20 µm radius diamond tip is used to deflect a resonator laminate beam composed of tantalum nitride and silicon oxynitride. Nanoindentation loads are used to induce elastic deflection of the resonator beam. The unloading portion of the nanoindentation load versus deflection curve directly yields the beam stiffness. This measurement technique was used to determine the stiffness of several resonator beam designs. Stiffnesses in the 900-5000 N/m range were measured and were within 10% of the calculated values using the above stiffness equation. In addition, derived stiffnesses from measured beam resonant frequencies (as per the resonant frequency equation above) further confirm the nanoindentation measurements.

5:00pm **TF-MoA10 Effect of Trimethylsilylation on the Film Stress of Nanoporous Silica Ultralow-k Film Stacks***, **F.M. Pan**,* National Chiao Tung University, Taiwan*; A.T. Cho,* National Nano Devices Laboratories, Taiwan*; J.Y. Chen, L. Chang,* National Chiao Tung University, Taiwan*; K.J. Chao,* National Tsing Hua Univerisity, Taiwan

In advanced dual damascene interconnect structures, ultralow-k dielectrics must be integrated with etch stop and barrier layers, and, therefore, interfacial properties of the film stacks are critical to process yield and reliability of interconnects. In this work, the film stress and effective dielectric property of self-assembled nanoporous silica overcoated by various dielectric thin layers were studied. The nanoporous silica was prepared by spin-coating the sol-gel precursor on the silicon wafer, followed by baking and calcination. Due to the film shrinkage during thermal treatments, the as-prepared nanoporous silica films have a tensile film stress. In order to improve the dielectric property, the nanoporous silica thin film was exposed to hexamethyldisilazane (HMDS) vapor for trimethylsilylation, and a dielectric constant lower than 1.95 could be obtained. The film stress became less tensile after the HMDS treatment. The decrease of the tensile stress can be ascribed to the spring-back effect resulting from the introduction of bulky trimethylsilyl groups in the nanoporous silica layer. Three different capping layer, Si@sub 3@N@sub 4@, SiO@sub 2@ and @alpha@-SiC:H films were separately deposited on the nanoporous film at 300@sup o@C. When directly deposited on the Si wafer, all the three capping materials show compressive stress. While the capping layers were deposited on the as-calcined nanoporous silica, the film stress of the SiO@sub 2@ and Si@sub 3@N@sub 4@ layers was so large that the capping layers cracked. On the other hand, when the capping layers were deposited on the HMDS treated nanoporous silica, the film stacks showed no mechanical failure and the effective dielectric constant could be lower than 2.2. This study suggests that trimethylsilylation of the nanoporous silica low-k dielectric can effectively improve the integrity of the three film stacks in terms of mechanical strength and dielectric property.

Thin Films
Room Exhibit Hall B - Session TF-MoP
Poster Session

TF-MoP1 Effect of the Deposition Parameters on the Microstructure and Optical Properties of Yttria-stabilized Zirconia Thin Films Deposited by r.f. Reactive Magnetron Sputtering*, M.H. Shiao,* National Science Council, Taiwan*; **C.W. Peng**,* Kun Shan University of Technology, Taiwan*; C.Y. Su,* National Science Council, Taiwan*; C.C. Jiang,* Ming Hsin University of Science & Technology, Taiwan*; S.C. Chang,* Kun Shan University of Technology, Taiwan

Yttria-stabilized zirconia (YSZ) thin films were prepared on (100) Si and quartz substrates by r.f. reactive magnetron sputtering system. Different oxygen to Argon (O@sub 2@/Ar) flow rate ratios (0% and 2.5%) and working pressures (0.33 Pa to 0.8 Pa) were investigated in the substrate temperatures ranging from room temperature to 500°C. Microstructure and surface roughness (R@sub a@) were examined by X-ray diffraction (XRD) and atomic force microscopy. Optical properties such as refractive index, extinction coefficient and transmission spectrum were measured by spectroscopic ellipsometer and spectrometer. It was found that without oxygen flow rate and the working pressure controlled at 0.33 Pa, the process have the highest deposition rate (2.5 nm/min), the highest transmittance (92.65%) and the lowest surface roughness (2.5 Å) at the deposition temperature of 300 °C. The YSZ crystalline orientation gradually changes from (111) to (200) when the deposition temperature above 300°C. When the oxygen to Argon flow rate ratio was 2.5% and the working pressure controlled at 0.33 Pa, the surface roughness decreases with increasing deposition temperature. But it still has the highest deposition rate (1.52 nm/min) and the highest transmittance (92.35%) at the deposition temperature of 300°C. The phase changes from amorphous to crystalline above the deposition temperature of 300°C. The deposition rate, surface roughness and transmittance decreased with increasing working pressure when the oxygen to Argon flow rate ratio and deposition temperature were controlled at 0% and 300°C, respectively.

TF-MoP2 (CdTe)@sub 1-x@Al@sub x@ Thin Films Grown by RF Co-sputtering for Photovoltaic Applications@footnote 1@*, L.A. Estrada - Domínguez,* ESFM-IPN, México*; **M. Meléndez-Lira**,* Cinvestav-IPN, México, Mexico*; M. Becerril-Silva,* Cinvestav-IPN, México*; M. Zapata-Torres,* CICATA-IPN, México*; S.J. Jiménez-Sandoval,* Cinvestav-IPN, México

Solar cells based on the heterostructure CdS/CdTe have been under a continuous development and there are commercial devices available. However, still there are problems limiting the efficiency predicted theoretically. Between the limiting factors, we found the difference in crystal structure between de CdTe (cubic) and CdS(hexagonal) and the inherent production of defects at the CdS/CdTe interface. Besides the interface problems, there are some difficulties to doping CdTe as p-type . We have produced (CdTe)@sub 1-x@Al@sub x@ films by RF co-sputtering employing CdTe and Al targets under an Ar atmosphere. Al content was controlled by the RF power of the Al magnetron. An increase in the bandgap depending on the Al content was found and values up to 1.61 eV for 6% of Al content were obtained . The samples presented hexagonal structure with lattice parameters values depending on the Al content, as determined by EDX. Raman spectroscopy clearly shows the incorporation of aluminium into the CdTe lattice. We will present in this work the results of an electrical transport characterization obtained by the Van deer Paw resistivity method and Hall effect measurements. We have found that for some growth conditions we can produce low resistivity samples with p-type conductivity. The results of the electrical characterization will be correlated with studies of the spectral photoresponse, optical and structural characterization carried out on the (CdTe)@sub 1-x@Al@sub x@ films. We propose a (CdTe)@sub 1-x@Al@sub x@ film as a solution for some of the problems presented in photovoltaics devices based on the CdS/CdTe heteroestructure using it to replace the CdTe film. @FootnoteText@ @footnote 1@: work partially supported by CONACyT-México.

TF-MoP3 Tailored Stoichiometries of Silicon Carbonitride Thin Films Prepared by Combined RF Magnetron Sputtering and Ion Beam Synthesis*, **M. Bruns**, U. Geckle, V. Trouillet,* Forschungszentrum Karlsruhe GmbH, Germany*; M. Rudolphi, H. Baumann,* Universitaet Frankfurt /Main, Germany

There is great interest in the ternary system Si-C-N due to the expected attainability of materials combining the properties of silicon carbide and silicon nitride. Various precursor based techniques have been employed to synthezise silicon carbonitrides. Most of these efforts result in compounds of deficient nitrogen content and considerable hydrogen and oxygen impurities. In contrast, combined RF magnetron sputtering and ion implantation are suitable to achieve high-purity ternary phases with tailored stoichiometries. Si-C films with defined Si/C ratios can be obtained using co-sputter targets of different Si/C area ratios. In a subsequent step surface modification of these Si-C films by high fluence implantation of N ions results in suitable nitrogen concentrations. Severalfold N implantation at different energies enables us to synthesize films with homogeneous element depth-distribution up to the surface. In this work we focus on the most interesting tie lines C@sub 3@N@sub 4@ - Si@sub 3@N@sub 4@ and SiC - Si@sub 3@N@sub 4@. Implanting N ions into sputtered Si-C films enables us to achieve every stoichiometry within the Si-C-N phase diagram. However, the region of attainable stoichiometries is narrowed by formation of Si-C-N phases and N@sub 2@, respectively. For Si/C ratios @<=@1 the N content of 57.4 at.% required for the formation of Si-C-N compounds on the tie line C@sub 3@N@sub 4@ - Si@sub 3@N@sub 4@ cannot be reached by N implantation near RT. @paragraph@The chemical composition of the Si-C-N films was characterized by means of X-ray photoelectron spectroscopy. In addition, Auger electron spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, and Ellipsometry were used to achieve a comprehensive characterization. For quantification XPS and AES data were calibrated with absolute concentration values from non-Rutherford backscattering spectrometry. Resonant nuclear reaction analysis provides non-destructive depth profiles of @super 15@N.

TF-MoP4 Combinatorial Synthesis of Rare Earth-doped Yttrium Aluminum Garnet Thin Film Materials by Using rf Reactive Magnetron Sputtering*, **Y. Deng**, J.D. Fowlkes, P.D. Rack,* University of Tennessee

Yttrium aluminum garnet (YAG) is known to be good host material for rare-earth doped luminescent materials. The rare earth ion typically substitutes for the yttrium sites which have a D2 symmetry in the YAG. The emission spectrum depends on the dopant type. Gadolinium radiates in the ultra-violet region at a dominant wavelength of ~ 312 and 275nm due to intra-band 4f transitions, while cerium peaks from 500 to 650nm due to interband 4f-5d transitions. To investigate the luminescence characteristic of dopants, thin films of gadolinium-doped and cerium-doped yttrium aluminum garnet (YAG:Gd and YAG:Ce) have been deposited by rf reactive magnetron sputtering. The dopant concentration effect on the cathodoluminescent (CL) properties of the films has been studied. Optimized conditions have been achieved by using a combinatorial thin film synthesis technique. The structure and composition of the films have been characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The crystallinity of the films has been investigated by X-ray diffraction (XRD). The luminescence properties of the films will be correlated to the chemical and microstructural properties of the films.

TF-MoP5 Electrical Properties of Ni-Cr Thin Films Deposited by Co-Sputtering Method*, **G.-B. Park**,* Yuhan College, Korea*; P.-K. Shin, B.-J. Lee,* Inha University, Korea

For thin resistor films with low TCR (temperature coefficient of resistance) and high resistivity, we have prepared the thin films by co-sputtering method with pure Ni and Cr targets and studied the effect of the process parameters on the electrical properties. In sputtering process, DC/RF power and pressure are varied as controllable parameters. We have investigated the microstructure and measured the electrical properties. When the Ni/Cr ratios of the deposited thin films were 0.8â^¼1.5, the resistivity was 100â^¼120 µ @OMEGA@Â·ãŽ. Below a Ni/Cr ratio of 1.5 (above 40[wt%] of Cr), the TCR became negative. The TCR of the thin films decreased from â?"30 ppm/°C to â?"75 ppm/°C with increasing Cr content. It is suggested that the composition ratio and electrical properties of thin films can be controlled by variation of sputter process parameters.

TF-MoP6 Target Surface Oxide Layer Formed by Reactive Sputtering of Ti Target in Ar+O@sub 2@ Mixed Gas*, **Y. Abe**, K. Takamura, M. Kawamura, K. Sasaki,* Kitami Institute of Technology, Japan

Reactive sputtering is a useful method for preparing compound thin films by sputtering metal targets in active gas atmosphere. The surface state of the metal target changes with sputtering conditions and makes important effects on deposition rate, chemical composition of the thin films, and plasma state, however, quantitative studies on the surface state of the target were scarce. In this study, TiO@sub 2@ films were deposited by reactively sputtering a 2-inch diam. Ti target in a mixed gas of Ar and O@sub 2@ using a planar RF magnetron sputtering system. Ti model target, a 1 µmm-thick Ti film sputter-deposited on the surface of a Si wafer, was used as a sputtering target for an experiment on target oxidation. The thickness of the oxide-layer formed at the surface of the model target was measured by ellipsometry. Effects of oxygen flow ratio and RF power on the surface oxide-layer-thickness were studied. The oxide layer formed at the surface of the Ti model target was confirmed to be TiO@sub 2@. The measured oxide-layer-thickness increased with increasing oxygen flow ratio, however, the maximum oxide-layer-thickness formed by sputtering in 100% O@sub 2@ gas was only several nano meters. No appreciable dependence on RF power and the position at the surface of the target was observed. However, methods of target cooling influenced the surface-oxide-thickness, which indicates that the oxide-layer-thickness increases with increasing target temperature.

TF-MoP7 Water Absorption and Dielectric Changes in Crystalline Poly(vinylidene fluoride-trifluoroethylene) Copolymer Films*, **L.G. Rosa**, P.A. Jacobson,* University of Nebraska-Lincoln*; C.M. Othon,* University of Nebraska-LIncoln*; K.L. Kraemer, A.V. Sorokin, S. Ducharme, P.A. Dowben,* University of Nebraska-Lincoln

Crystalline Langmuir Blodgett Copolymer films of vinylidene fluoride with trifluoroethylene (70%:30% and 80%:20%) absorbs water. Water absorption is accompanied by film swelling as indicated by an increase in lattice spacing, sometimes by as much as 5%. This water absorption, between 0°C and 40°C, is a result of intercalation or occupation of interstitial sites between the layers of the film, not just water molecules filling voids and deffects site alone. An increase in the film capacitance is observed, although the polymer chains retain all trans configuration of the ferroelectric phase.

TF-MoP8 Water-incorporation in Reactively Sputtered Carbon Nitride Coatings*, **B.L. French**, Z. Yang, B.C. Holloway,* College of William and Mary

Carbon nitride is a candidate material for tribological/passivating overcoat layers on magnetic recording media due to its low friction coefficient, thermal stability, and high hardness. However, carbon nitride coatings are susceptible to damage from water in humid environments, resulting in an increase in friction coefficients, permeation of water to the underlying coating or delamination if sufficient stress is induced. In the present study carbon nitride coatings were prepared by DC planar magnetron sputtering. The working gas composition and pressure were systematically varied to manipulate coating morphology and composition. After growth, the deposition chamber was back-filled with air at a relative-humidity of 35% while stress in the coating was monitored in real-time with a laser-based wafer-curvature measurement system. The stress evolution during these experiments will be used to understand mechanisms of water-interaction with the coating and discussed in the context of existing models of water incorporation in thin films.

TF-MoP9 Deposition of Thin Films on Inclined Surfaces Using Ionized PVD*, **M. Lattemann**, J. Alami, J. Böhlmark, U. Helmersson,* Linköping University, Sweden

Titanium thin films were deposited, using a highly ionized flux of deposition material, onto substrates mounted at different angles (@gamma@ = 0, 45, 70, 90, 135, and 180°) with respect to the sputtering source. The results show that dense films were obtained independent of film orientation. In comparison films grown with conventional d.c. magnetron sputtering showed films of low density for @gamma@= 90° and higher angles. The deposition rate decreased in both cases with increasing angle @gamma@, but less so for the ionized deposition flux. The deposition rate, 5 mm from the edge of the sample, was reduced to 66 and 25% at @gamma@ = 90° and @gamma@ = 180°, respectively, in the case of ionized flux. This can be compared with less than 30% for @gamma@ = 90° in case of the non-ionized flux. The ionized-PVD technique used was high power pulsed magnetron sputtering (HPPMS) that is estimated to give an ionization degree of up to 70%. By applying a negative substrate bias the metal ions were attracted to the substrate surface independently of the inclination angle. The energetic ionized deposition flux leads to an effective transfer of kinetic energy to the surface which is the reason for the densification of the films grown using HPPMS. Due to its ease of use, the HPPMS technique is believed to have prospect of becoming an important technique for deposition of, e.g., hard coatings and corrosion resisting coatings onto substrates of complex shapes.

TF-MoP10 TCO Thin Film Characteristics with Respect to Multi Layer Coatings between Plastic Substrate and ITO Layer*, **M.G. Kim**, H.S. Jeong, Y.W. Seo,* ITM Inc., Korea*; S.J. Kwon,* Kyungwon Univ., Korea

Recently organic electro luminescence displays(OELD) using a plastic substrate such as PET and PES are emerging as a strong new candidate for flat panel displays. In this study we made the buffer layer which is multi-layer coatings such as (DLC/SiO@sub 2@)@sub n@ between plastic substrate and transparent conducting oxide(TCO). To minimize the oxygen transmission and the water vapor transmission of the TCO coated substrate, we also designed the thicknesses of multi-layer for high visible transmittance using optical thin film software. The DLC is characterized by strong hardness, flatness and low gas permeability to moisture and oxygen. The unipolar pulse mode of the power supply(IBP1030, ITM, Inc.) was used on a graphite target, and the mixed gas were argon and methane. ITO was deposited on the buffer layer of the plastic substrate in a horizontal single ended in-line sputter system equipped with a pulsed dual magnetron sputter. To understand the properties of the ITO films deposited on the multi-layered buffer layer, we investigated the electrical resistivity, film structure, optical transmission, surface roughness, and gas permeability.

TF-MoP11 Photoluminescence Behaviors of Eu-doped Sr@sub 2@SiO@sub 4@ Thin Film Phosphors Deposited by Pulsed Laser Deposition*, **S.S. Yi**,* Silla University, Korea*; J.S. Bae, J.H. Jeong,* Pukyong National University, Korea*; J.H. Kim,* Dongeui University, Korea*; H. Park,* Yonsei University, Korea

Sr@sub 2@SiO@sub 4@:Eu thin film phosphors were deposited on Al@sub 2@O@sub 3@ (0001) substrates by pulsed laser deposition. The Sr@sub 2@SiO@sub 4@:Eu thin films were grown at the various substrate temperatures and the different oxygen pressures. The crystallinity and surface morphology of the films were investigated using X-ray diffraction and atomic force microscope, respectively. And the photoluminescence spectra were measured at room temperature using a luminescence spectrometer and excitation by a broadband incoherent ultraviolet light source with a dominant excitation wavelength of 254 nm. The crystallinity and surface morphology of the films were influenced by the deposition conditions. It was found that the luminescence of the Sr@sub 2@SiO@sub 4@:Eu films is highly dependent on the crystallinity and surface roughness of the films. The Eu-doped Sr@sub 2@SiO@sub 4@ film shows two emission bands of 577 and 625 nm.

TF-MoP12 Luminescence Characteristics of Eu-doped GdVO@sub 4@ Thin Films Grown by Pulsed Laser Deposition, *J.H. Jeong, **J.S. Bae**, B.K. Moon, H.J. Seo,* Pukyong National University, Korea*; S.S. Yi,* Silla University, Korea

GdVO@sub 4@:Eu@super 3+@ thin film phosphors were deposited on Al@sub 2@O@sub 3@ (0001) substrates by pulsed laser deposition. The films were grown at the various substrate temperatures and the different oxygen pressures. The crystallinity and surface morphology of the films were investigated using X-ray diffraction and atomic force microscope, respectively. And the photoluminescence spectra were measured at room temperature using a luminescence spectrometer and excitation by a broadband incoherent ultraviolet light source with a dominant excitation wavelength of 254 nm. The photoluminescence brightness data obtained from GdVO@sub 4@:Eu@super 3+@ films grown under optimized conditions have indicated that sapphire is a good substrate for the growth of high quality GdVO@sub 4@:Eu@super 3+@ thin film red phosphor. Due to a @super 5@D@sub 0@-@super 7@F@sub 2@ transition within europium, GdVO@sub 4@:Eu@super 3+@ shows red luminescence at 612 nm. The crystallinity and surface morphology of the films were influenced by the deposition conditions. It was found that the luminescence of the GdVO@sub 4@:Eu@super 3+@ films is highly dependent on the crystallinity and surface roughness of the films.

TF-MoP13 Preparation of Transparent and Conductive Multicomponent Zn-In-Sn Oxide Thin Films by Vacuum Arc Plasma Evaporation*, T. Minami, **S. Tsukada**, Y. Minamino, T. Miyata,* Kanazawa Institute of Technology, Japan

A newly developed vacuum arc plasma evaporation (VAPE) method has recently attracted much attention for its high rate deposition of low-resistivity transparent conducting oxide (TCO) thin films on large area substrates. TCO thin films such as Ga- or F-doped ZnO and ITO were prepared by the VAPE method with resistivities on the order of 10@super -4@@ohm@cm. In this paper, we describe the preparation of transparent and conductive multicomponent Zn-In-Sn oxide thin films. Multicomponent Zn-In-Sn oxide fragments prepared by sintering a mixture of ZnO, In@sub 2@O@sub 3@ and SnO@sub 2@ powders were used as the target. The film depositions were carried out under the following conditions: substrate, large area glass; substrate temperature, RT to 350°C; pressure, 0.08 to 1 Pa; Ar and O@sub 2@ gas flow rates, 20 and 0 to 20 sccm; and cathode plasma power, 3.5 to 10 kW. Highly transparent and conductive multicomponent TCO thin films could be prepared by varying the composition of ZnO-In@sub 2@O@sub 3@, In@sub 2@O@sub 3@-SnO@sub 2@ and ZnO-SnO@sub 2@ fragment targets. It was also found that the metal content in the deposited films was approximately equal to that of the target used. In addition, a deposition rate above 100 nm/min as well as uniform distributions of resistivity and thickness on the substrate surface were obtained. Resistivities of 10@super -4@ to 10@super -3@@ohm@cm and average transmittances above 85% in the visible range were obtained in the ZnO-In@sub 2@O@sub 3@, In@sub 2@O@sub 3@-SnO@sub 2@ and ZnO-SnO@sub 2@ thin films deposited by varying the composition (metal content). In conclusion, approximately the same electrical and optical properties that had been previously reported in multicomponent Zn-In-Sn oxide thin films prepared by magnetron sputtering have now also been obtained using the VAPE method.

TF-MoP14 Cathodic Vacuum Arc Deposition of MgO Thin Films on the Large Area Glass Substrate*, **L. Sunghun**, B. Sung-Kyu, K. Jong-Kuk, L. Gun-Hwan,* Korea Institute of Machinery and Materials, Korea

It is well known that MgO film is used as the protective layer in AC-plasma display panels(AC-PDPs). Until now, e-beam evaporation and reactive magnetron sputtering method has been mainly adopted to produce MgO protective layer over the electrodes on the front glass panel of the PDP. However, there are still some problems such as the higher sputtering rate at e-beam method and the lower growth rate at magnetron sputtering method. In this work, cathodic vacuum arc deposition was introduced to produce MgO films on large area glass substrate, which shows higher deposition rates and the large number of ionized particles and high ion energy. Magnesium was used as a source material and oxygen was introduced as a reactive gas. We have investigated (1) appropriate shape of target for large area coating with one rectangular Mg target with size of 300 x 90 mm and two circular Mg target with diameter of 75 mm and (2) stable arc operating condition such as arrangement of magnet, magnet field strength, arc current and introduction method of oxygen gas. It was concluded that the rectangular type is not suitable for large area coating because of it's low mass utilization efficiency and the stable arc operating condition for circular Mg target . A properly designed arc source module with multiple circular Mg target for MgO protective layer with good quality will be presented.

TF-MoP15 Chemical Mechanical Polishing Characteristics of SnO2 Thin Film for Gas Sensor Application*, Y.J. Seo,* DAEBUL University, South Korea*; **K.W. Choi**, W.S. Lee,* Chosun University, South Korea

The metal oxide has been increasing interest for application of advanced technology. Of these oxides, tin dioxide (SnO2) is of interest as an oxidation catalyst, gas sensor material, thin film micro-battery, and transparent conductor. For the application of tin oxide films, the controls of microstructure and surface morphology are required because the electrical and optical properties are dependent on them. Although there have been many reports on the formation or smoothing of hillocks of the thin films, those works still report lack consistency. Hillocks on thin film surfaces deteriorate light reflection, ultra large-scale integration (ULSI) pattern resolution, and device performance because they are dependent on surface morphology or roughness. A chemical mechanical polishing (CMP) process is a useful method for removing sub-microscale hillocks. Therefore, an understanding and control of microstructure and surface morphology are required for the advanced application of tin oxide films. In this paper, we report the CMP effects on the variation of morphology for tin oxide films prepared by RF sputtering system. In order to compare the polishing characteristics of SnO2 thin film, we investigated the CMP removal rate (RR) and within-wafer non-uniformity (WIWNU%), particle size distribution, and the microstructures of surface and cross-sectional layer by atomic force microscopy (AFM) analysis. This work was supported by a Korea Research Foundation grant (KRF-2002-005-D00011).

TF-MoP16 Defect Study Post the Tungsten Etch Back Process Step*, A. Sidhwa, **J. Zhang**, V. Varadarjan, C. Li, B. Le, G. Magsamen,* STMicroelectronics, Inc.

The tungsten etch back defects generated during the process with their relations to the wafer yield is studied in this paper. By understanding these defects the wafer yields can be improved and one can achieve maximum tool up time. For the tungsten etch-back (WEB) process, two kinds of processes are widely used in the manufacturing world: One is the pattern tungsten etch and the other is the blanket tungsten etch back. The tungsten etch back can either stop on titanium nitride (SOT) or stop on the oxide (SOX). This paper mainly focuses on the SOT process for the tungsten etch-back defects. During the Fluorine (F-) etch process; the F- ions from SF6 gas will etch the Tungsten (W) film at a faster rate as compared to the Titanium Nitride (TiN) film. Some of the TiN film will still be etched during the Tungsten Etch Back step. The by-products generated during the etch back step is in the form of titanium fluoride (TiFx). Sometimes the residual etch by-products are not completely pumped out of the chamber. The residual etch by-products may re-deposit on the chamber hardware which consists of the Aluminum and Aluminum Oxide parts. The residuals may react with chamber hardware generating TixAlx defects. In addition other defects are generated in the etch-back chamber. This paper describes a new kind of C, O, F, and Ti based particles observed after the tungsten etch back step at via levels. These defects were generated due to poor via cleaning process step which leaves the EKC residuals on the wafer. The residual defects on the wafers were hard to catch after via cleaning and after the Via Liner deposition process step. These residual defects would re-appear after the WEB process step. The mechanism of the formation of these defects is discussed in this paper along with method and implementation processes to reduce these defects.

TF-MoP17 Fabrication of Well-defined Cu Nanodots Based on an Electroless Plating using Diblock Copolymer Nanotemplate*, **S. Asakura**,* Waseda University, Japan*; A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan*; K. Oda, A. Fuwa,* Waseda University, Japan

Increasing attention has recently been paid to the fabrication of copper (Cu) arrays of nm-scale in order to fabricate electronic devices. Among the several methods, the use of a diblock copolymer (DBC) thin film is promising, since an ordered nanostructure can be easily obtained by chemical or physical treatment. Here we report the fabrication of cylindrical Cu nanostructures onto a SiO@sub 2@/Si substrate through an electroless plating using a DBC thin film as a template. First, a polystyrene (PS, 70 wt.%)/Poly(methylmethacrylate) (PMMA, 30 wt.%) DBC was spin-coated on the SiO@sub 2@/Si surface from a 3 wt.% in toluene. After dried in air for 24 h, it was annealed in a vacuum oven for 24 h at a temperature of 170 °C. Due to this treatment, the PMMA component formed cylindrical domains in a PS matrix. Subsequently, the sample was photoirradiated with vacuum ultraviolet (VUV) light of 172 nm in wavelength for 15 min at 10@super 3@ Pa to decompose PMMA predominantly utilizing the difference in etching rate between PS and PMMA domains. Amino-terminated self-assembled monolayer (SAM) was absorbed onto the whole area of the substrate by chemical vapor deposition method using n-(6-aminohexyl)aminopropyltrimethoxysilane (AHAPS) as a precursor. After that, the substrate was sonicated in toluene and then rinsed with Milli-Q water. Finally, the substrate covered with the AHAPS-SAM was immersed into a PdCl@sub 2@ solution followed by treated in an electroless plating bath to deposit Cu selectively. Using an atomic force microscopy, we confirmed that the Cu deposition selectively occurred inside the cylindrical nanopores in which the PMMA domains were photochemically eliminated. This clearly indicates that Pd catalysts were tightly immobilized selectively on the nanopores even after sonication in toluene due to the existence of AHAPS-SAM. Cu nanodods with a diameter and a periodicity of about 20 and 30 nm were successfully fabricated on the 10 x 10 mm@super 2@ region.

TF-MoP19 Observation of Plastic Deformation in TIALCN/A-C Ceramic Nanocomposite Coating*, **J. Shieh**,* National Nano Device Laboratory, Taiwan*; M.-H. Hon,* National Cheng Kung University, Taiwan

Titanium aluminum nitride, a metastable refractory ceramic coating, is widely used for improving tribological properties of cutting tools due to the excellent hardness and oxidation resistance.@footnote 1@ However, brittleness is a great handicap for ceramics in their technological applications since dislocations cannot move rapidly to allow for plastic deformation. Thus we added amorphous carbon into the grain boundary of nanograins to improve the coating plasticity. Extensive plastic deformation of titanium aluminum carbonitride/amorphous nanocomposite coating at room temperature was observed in this study. Nanoindentation measurement showed that the coating hardness was 24.4 GPa with the plasticity of 57.6 percent. The critical load of 1.3 µm coating in scratch test was beyond 100 N. The depth of the 100 N scratch track identified by microstylus profilometer was 6.7 µm, while the thickness of the coating in the center of the scratch track observed by scanning electron microscopy was 0.4 µm, which is only about one third of that for the as-deposited coating. The amorphous carbon with sp@super 2@ hybrid and @pi@-bonding is proposed to account for this unique plasticity. @FootnoteText@ @footnote 1@ S. PalDey and S.C. Deevi, Mat. Sci. Eng. A 342, 58 (2003).

TF-MoP20 Strained Si n-channel Metal-oxide-semiconductor Transistor on Relaxed SiGe Film with an Intermediate Si:C Layer, ***S.-W. Lee,*** National Tsing Hua University, Taiwan; *P.S. Chen,* Industrial Technology Research Institute, Taiwan, Republic of China; *Y.L. Chieh,* National Tsing Hua University, Taiwan; *M.-J. Tsai, C.W. Liu,* Industrial Technology Research Institute, Taiwan; *L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China

An intermediate Si:C layer in the SiGe film, replacing the conventionally graded buffer layer, was used to form the high-quality relaxed SiGe substrate. With the 700-nm-thick SiGe overlayer, such a SiGe/Si:C/SiGe heterostructure has a threading dislocation density of 5.5x10@super5@ cm@super-2@ and a degree of strain relaxation of 98%. From the TEM observation, the numerous misfit dislocations were formed and confined at the top interface of SiGe/Si:C, maintaining a defect-free SiGe overlayer. Strained-Si n-channel metal-oxide-semiconductor transistors using this relaxed SiGe substrate were fabricated and their characteristics were examined. The effective mobility of the strained-Si device exhibits an enhancement of roughly 90% over that of Si control device at a given effective field. This work provides a simple method for the formation of strained Si layers.

TF-MoP21 Gas Barrier Properties of the Composite Films Consisting of SiO2 and SnO2, ***W.H. Koo,*** *S.M. Jeong, S.H. Choi, H.K. Baik,* Yonsei University, Korea; *S.M. Lee,* Kangwon National University, Korea; *S.J. Lee,* Kyungsung University, Korea

Composite thin films consisting of silicon oxide and tin oxide have been deposited on polycarbonate substrates as gas barrier films, using a thermal evaporation process in oxygen gas environment. Water vapor permeation through gas barrier films are significantly affected by the chemical interaction of water vapor with oxide films and the microstructure of the oxide films. The chemical interaction of water vapor with oxide films has been investigated by the refractive index from ellipsometry and OH group peak from x-ray photoelectron spectroscopy, and the microstructure of the composite oxide films characterized using x-ray diffraction, atomic force microscopy and transmission electron microscopy. As the tin oxide is added to the silicon oxide, the refractive index and OH group peak intensity of the composite films increase, and water vapor transmission rate through the composite oxide films shows the lower value than that through the sigle element oxide films such as tin oxide and silicon oxide. The results are discussed in terms of the chemical interaction with water vapor and microstructure of the oxide films.

TF-MoP22 Ultra High Resolution Tomographic Reconstruction Using Scanning Electron Microscope and Focused Ion Beam, ***R.K. Bansal,*** *R.V. Hull, J.M. Fitz-Gerald,* University of Virginia

The ever shrinking device dimensions in the semiconductor industry and the advent of nanotechnology has necessitated the developments of new characterization techniques which can work at smaller length scales with high precision. The present study aims at demonstrating a tomographic reconstruction technique capable of reproducing the morphology and chemical structure of a material with a sub-10nm resolution. This has been achieved by serial sectioning of the material using focused ion beam (FIB) and subsequent imaging using a high resolution field emission scanning electron microscope (FE SEM). This process was repeated to obtain a series of two dimensional cross sectional images. These images are then concatenated in the computer and interpolated into three dimensional space to asses and visualize the structure of the material. Multilayered structure of alternating 14nm thick Si-Ge/Si layers was reconstructed using linear interpolation of slices while a slightly more complex shape based interpolation routine was utilized to reconstruct @theta@' Al2Cu precipitates in Al matrix. As expected, the precipitates were found to be 10-20nm thick plates oriented along the orthogonal (100) directions even though this was not apparent from individual slices. High resolution alignment procedures were applied using FIB milled trenches and their profile was verified using cross sectional TEM. These trenches were also used to accurately predict the distance between individual slices. This is especially important as drift during milling in FIB often results in unequally spaced slices. Interpolation and visualization was performed using routines developed in MATLAB environment.

TF-MoP23 Deposition of Ti(C,N) AND Zr(C,N) Thin Films by Plasma Assisted MOCVD and In-Situ Plasma Diagnostics with Optical Emission Spectroscopy, ***J.-H. Boo,*** *S.W. Lee, Y.K. Cho, J.G. Han,* Sungkyunkwan University, South Korea

Ti(C,N), Zr(C,N) films are synthesized by pulsed D.C. plasma assisted metalorganic chemical vapor deposition (PA-MOCVD) using metal-organic compounds of tetrakis diethylamido titanium and tetrakis diethylamido zirconium at 200 °C to 300 °C. H@sub 2@ and He+H@sub 2@ gases are used as carrier gases to compare plasma parameter. The effect of N@sub 2@ and NH@sub 3@ gases as reactive gas is also evaluated in reduction of C content of the films. Radical formation and ionization behaviors in plasma are analyzed by optical emission spectroscopy (OES) at various pulsed bias and gases conditions. He and H@sub 2@ mixture as carrier gas is very effective in enhancing ionization of radicals, especially N@sub 2@ resulting is high hardness. However, NH@sub 2@ as reactive gas highly reduces formation of CN radical, there by decreasing C content of Ti(C,N) and Zr(C,N) films in a great deal. The hardness of film is obtained to be 1400 HK to 1700 HK depending on gas species used and bias voltage. Higher hardness can be obtained for H@sub 2@ and N@sub 2@ gas atmosphere and bias voltage of 600 V. Plasma surface cleaning using N@sub 2@ gas prior to deposition appear to increases adhesion of films on cold forming steel. The changes of plasma including radicals and film properties are illustrated in terms of carrier and reactive gases as well as pulsed power variation.

TF-MoP24 In-situ Characterization of HfO@sub 2@ and AlN Films on SiC, ***C.M. Tanner,*** *J. Choi, J.P. Chang,* University of California, Los Angeles

High dielectric constant materials are promising gate oxide materials for future generations of metal-oxide-semiconductor field effect transistor (MOSFETs). HfO@sub 2@ has a high dielectric constant and excellent thermal stability, indicating its suitability for high-power and high-temperature applications, especially when wide band gap semiconductors such as SiC are used as the substrate. Due to its close lattice matching with SiC, AlN is generally grown as a single crystalline layer on SiC and may provide an effective buffer layer between SiC and HfO@sub 2@. In addition, the AlN/SiC band offsets are quite symmetric, providing the needed barrier heights for an effective device operation. In this work, HfO@sub 2@ and AlN films were synthesized using atomic layer deposition (ALD) under high-vacuum conditions. Stacked HfO@sub 2@/AlN films were also grown on SiC in addition to the individual dielectric layers on SiC. The substrate temperature was controlled by infrared heating with a quartz tungsten halogen lamp. Hafnium tetra-tert-butoxide and oxygen were used to deposit HfO@sub 2@, while trimethylaluminum and ammonia were used to deposit AlN. Alternating pulses of chemicals were sequentially introduced into the reactor while film growth was monitored by in-situ reflection high-energy electron diffraction (RHEED) to study the surface structure. In-situ X-ray photoelectron spectroscopy (XPS) was used to study film composition and chemical bonding at the interface. The deposition kinetics of HfO@sub 2@ and AlN films were studied at various substrate temperatures and precursor doses. Film thickness and uniformity were determined by spectroscopic ellipsometry and confirmed with XPS. The microstructure of the interfaces of HfO@sub 2@/AlN/SiC stacked films was characterized using transmission electron microscopy (TEM).

TF-MoP25 Conduction Anisotropy in Nanostructured Titanium Films, ***D.W. Vick,*** *M.J. Brett,* University of Alberta, Canada

Considerable control over the microstructure of evaporated thin films has been demonstrated using dynamic control of the vapour incident angle (@alpha@) and the azimuthal orientation of the substrate during the deposition process.@footnote 1@ In the present study, advanced substrate motion is used to engineer the electrical properties of metallic films, and an attempt is made to relate measured electrical conductivity with observed film microstructure. Films with and without structural anisotropy will be included in the study. The regime of glancing angle deposition (GLAD) conditions (@alpha@ @>=@ 80°) is of particular interest to us. Under such conditions, significant voiding in the films results in a microstructure of isolated metallic islands whose mean size, shape, and separation are to some extent controllable. The experimental films consist of layers of Ti (nominal thickness 200 nm) deposited over barrier layers of SiO@sub 2@. Standard lithographic techniques are used to create arc-shaped tracks of 1 mm width, in a manner similar to that reported by

Kuwahara and Hirota.@footnote 2@ Metalization contacts and bonded wires are then added to the wafers, permitting measurement of electrical conductivity of the films and determination of the conduction anisotropy in the plane of the films. Preliminary results show that the ratio of conductivities along the two principal directions in the films can easily exceed a value of 7. Scanning electron microscope images that reveal the microstructure of the films will be presented together with conductivity measurements. Experimental results will be compared with the predictions of standard models of electrical conduction in discontinuous media. @FootnoteText@ @footnote 1@ K. Robbie, J. C. Sit, and M. J. Brett, J. Vac. Sci. Technol. B 16, 1115 (1998). @Footnote 2@ K. Kuwahara and H. Hirota, Jap. J. Appl. Phys. 13, 1093 (1974).

TF-MoP26 Monolayer Template Patterning of Ceramic Film on Flexible Plastic Substrate*, N. Shirahata, Y. Sakka,* National Institute of Materials Science, Japan*; A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan

Microfabrication technique for metal oxide film on polymeric sheet has been demonstrated to develop flexible device technology. A polyimide (PI) sheet was employed as a polymeric substrate. Oxide nanoskin (ONS) interlayer (~ 2.1 nm) was formed onto the photooxidized PI (PIox) substrate by photochemical modification of the triethoxysilane layer, which was previously covered over the substrate through chemical vapor deposition process. 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (FAS) molecule was used to prepare a microstructured chemical template for area-selective deposition of metal oxide films onto the predefined sites of the PIox surface. The film deposition was performed in aqueous solution of tin chloride based on under ambient air an environmental-friendly system. The ONS interlayer has played a key role through the microfabrication process. First, the ONS was indispensable to prepare a superior hydrophobic PI surface where highly ordered FAS molecules were densely formed. Second, the ONS enabled us to prepare an ideal FAS chemical template for the area-selective deposition of metal oxide film. Without the ONS interlayer, the reproducible results could not be obtained for the microfabrication. Additionally, on the ideal chemical template, thickness of the microfabricated films was well controllable in the ranging from nanoscale to microscale with keeping a perfect area-selectively. In this paper, the essential roles of ONS interlayer on both the preparation of high-quality chemical template and the reproducible microfabrication of metal oxide film, i.e., SnOx film, have been discussed in details.

TF-MoP27 Comparison of the Agglomeration Behavior of Thin Metallic Films on SiO@sub 2@*, P.R. Gadkari,* *A.P. Warren, R.M. Todi, T. Cubano-Cruz, K.R. Coffey,* University of Central Florida

The preparation of continuous thin films of metals on insulating oxide surfaces is of interest to applications, such as semiconductor interconnections, as well as fundamental studies of transport in thin films. Noble and near-noble metals tend not to wet amorphous oxide surfaces and thus the equilibrium shape for the deposited metal is an isolated island on the substrate surface. For sufficiently thick films and/or reduced surface mobility, continuous metallic films can be formed by non-equilibrium processing. However, the geometry of such films is unstable, and upon annealing they can agglomerate and again form isolated islands on substrate surface. In this work we report the study of the formation of voids and agglomeration of initially continuous Ru, Pt, Cu and Au thin films deposited on amorphous thermally grown SiO@sub 2@ surfaces. Polycrystalline thin films having thicknesses in the range of 5nm to 100nm were UHV sputter deposited on thermally grown SiO@sub 2@ surfaces. The films were annealed at temperatures in the range of 150°C to 800°C in argon and argon+3% hydrogen gases. Scanning electron microscopy was used to investigate the agglomeration behavior and transmission electron microscopy was used to characterize the microstructure of the as-deposited and annealed films. The agglomeration of Ru and Cu films was observed to follow a grain boundary grooving process, whereas fractal growth of voids was observed in Pt and Au films. It is also observed that the tendency for agglomeration can be reduced by encapsulating the metal film with an oxide overlayer. Lastly, the variation of agglomeration with annealing temperature, gas ambient and film thickness is described.

TF-MoP28 Effect of a Buffer Layer on the Photovoltaic Properties of AZO/Cu@sub 2@O Solar Cells*, T. Minami,* Kanazawa Institute of Technology, Japan*; H. Tanaka,* Gunze Limited, Japan*; T. Shimakawa, T. Miyata,* Kanazawa Institute of Technology, Japan*; H. Sato,* Gunze Limited, Japan

We have reported recently that high energy conversion efficiencies above 1% were obtained in Al-doped ZnO (AZO)/Cu@sub 2@O heterojunction solar cells fabricated by depositing transparent conducting AZO thin films on Cu@sub 2@O sheets. However, it is well known that a Cu metal thin film can easily be created at the interface by reducing the Cu@sub 2@O; therefore, the thin film deposition method and conditions are important considerations. In this paper, we describe the effect of a buffer layer and/or interface region on the photovoltaic properties of transparent conducting oxide (TCO)/Cu@sub 2@O solar cells fabricated with TCO thin films prepared by various deposition methods; we fabricated devices by depositing TCO films on Cu@sub 2@O sheets that had been exposed to various surface treatments or that had various thin films such as ZnO deposited as a buffer layer. The polycrystalline Cu@sub 2@O sheets (thickness of approximately 0.2 mm), prepared by heat treatment of Cu sheets (purity of 99.9%), functioned as the active layer as well as the substrate in the photovoltaic devices. Hall mobility in the resulting p-type semiconducting Cu@sub 2@O sheets was typically above 90 cm@super 2@/Vs. The TCO and buffer layer thin films were deposited by pulsed laser deposition, d.c. or r.f. magnetron sputtering. The obtained dark current-voltage and photovoltaic properties in the devices were considerably affected by both the Cu@sub 2@O surface treatments and the introduced buffer layers. In addition, these properties were dependent on not only the method used in the TCO and buffer layer thin film depositions but also the deposition conditions. For example, the rectifying characteristics and the photovoltaic properties such as conversion efficiency and fill factor were found to improve in devices incorporating an undoped ZnO thin-film buffer layer. These obtained properties are mainly related to the work function and crystallinity of the deposited thin films as well as the crystallinity of the Cu@sub 2@O sheets.}

TF-MoP29 Microstructural Evolution and Properties of the AlN Thin Films prepared under Different Processing Parameters*, C.-C. Wang,* National Chung Hsing University, Taiwan*; M.H. Shiao,* National Science Council, Taiwan*; C.-J. Lu, F.S. Shieu,* National Chung Hsing University, Taiwan

Polycrystalline aluminum nitride (AlN) thin films with wurtzite structure were deposited on silicon and glass substrates by an unbalanced magnetron (UBM) sputtering system equipped with a pulse dc power supply. Microstructure and chemistry of the AlN-coated substrates under different pulse power and deposition time were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy dispersive spectrometer (EDS) and atomic force microscopy (AFM). Optical transmission property of the AlN-coated glass was investigated by an UV/VIS spectrophotometer. XRD results show that the thin films exhibit enhanced (002) preferred orientation at higher pulse power and longer deposition time. It is also obtained that the AlN films have a columnar structure and that the size of the columns increases with the distance from the substrate and the deposition time, as revealed by FE-SEM and TEM. AFM analysis indicates that the surface roughness of the coatings increases with the pulse power and the deposition time. Furthermore, EDS analysis gives the chemical composition of the coatings as well as the percentage content of the elements. In addition, the energy band gap of the AlN films was evaluated to be 3.8-4.2 eV from the optical transmission spectra.

TF-MoP30 AFM and SNOM Characterization of Carboxylic Acid Terminated Silicon and Silicon Nitride Surfaces*, A. Cricenti,* National Research Council, Italy*;* ***R. Generosi****, M. Girasole,* CNR, Italy*; G. Margaritondo,* EPFL, Switzerland*; P. Thielen,* Naval Research Laboratory*; D. Vobornik,* EPFL, Switzerland*; J.S. Sanghera, I.D. Aggarwal,* Naval Research Laboratory*; N.H. Tolk, D.W. Piston,* Vanderbilt University*; A. Flamini, T. Prosperi, F. Cattaruzza, A. Mezzi, P. Perfetti, G. Ustione, A. Ustione,* CNR, Italy

Silicon and Silicon Nitride Surfaces have been successfully terminated with Carboxylic Acid monolayers and investigated by Atomic Force Microscopy (AFM) and Scanning Near-field Optical Microscopy (SNOM). On clean Si surface, AFM showed topographical variations of 0.3-0.4 nm while for the clean Si3N4 surface the corrugation was around 3-4 nm. After material deposition, the corrugation increased in both samples with a value in topography of 1-2 nm for Si and 5-6 nm for Si3N4. The space distribution of specific chemical species was obtained by taking SNOM reflectivity at several infrared wavelengths corresponding to stretch absorption bands of the material. The SNOM images showed a constant contribution in the local reflectance, suggesting that the two surfaces were uniformly covered.

TF-MoP31 Relationship of Microstructure and Discharge Characteristics of MgO Protecting Layer of AC-PDPs*, S.Y. Park*, *M.J. Lee, S.H. Moon, S.G. Kim, H.J. Kim,* Seoul National University, South Korea

MgO thin film is widely used as a protecting layer of the dielectric layer for alternating current plasma display panels(AC-PDPs) due to improvement of the panelâ?Ts discharge characteristics and lifetime. The discharge characteristics of AC-PDPs are critically dependent on the microstructure of MgO films; crystalline, surface morphology, and so on. We had focused on the relationship between microstructure of MgO protecting layer and discharge characteristics of AC-PDPs. MgO thin film was deposited with different E-beam evaporation source type; single crystal, melting, sintering, and powder. MgO thin film deposited with melting source had the highest density and peak intensity of (100) preferred orientation, but the film deposited with powder source had the lowest density, bimodal grain size distribution and oriented to (111) plane direction. It was due to the mobility of the adatom on the surface of growing MgO film. The variation of MgO source type led to change the various microstructures of MgO thin films in the same deposition condition, finally, it affected the discharge characteristics.

TF-MoP32 Thin Film Deposition of SiO@sub 2@ Using Electron-Beam Generated Plasmas*, D. Leonhardt*, *S.G. Walton,* Naval Research Laboratory*; C. Muratore,* ASEE/NRL Research Fellow*; R.A. Meger,* Naval Research Laboratory

The deposition of thin films of SiO@sub 2@ is an integral part of silicon and organic based electronics for flexible, large area applications such as flat panel displays, phased radar arrays and architectural lighting. The SiO@sub 2@ layer is the primary (high-k) dielectric of the device and must be uniform and defect free over large areas. Typical plasma-based deposition technologies that are presently used have limitations in both the quality of material being deposited and the uniformity over large (square meter) areas. NRL has been using electron beam-generated plasmas for a wide variety of applications [1], including the etching of silicon and polymeric material. These plasmas offer tremendous scaling and uniformity capabilities and possess extremely low electron temperatures. The inherent low electron temperature results in low plasma fields and potentials, which in turn provides low energy (< 3 eV) ions to the substrate. Mixtures of TEOS and O@sub 2@ were used to grow SiO@sub 2@ films in modulated electron beam generated plasmas. The film electrical and optical properties with respect to gas mixtures, substrate type, temperature and ion energy will be presented. Fluxes to the substrate determined by mass spectrometry measurements will be correlated to these process variables and final film quality. Together with the previous etching work, electron beam generated plasmas may provide the critical dry processing necessary for flexible, large area electronics. Work supported by the Office of Naval Research. @FootnoteText@ @footnote 1@ See presentations by these authors at this and previous AVS symposia.

Thin Films
Room 303C - Session TF1-TuM
Thin Films on Flexible and Polymer Substrates

Moderator: H. Kim, IBM Research

8:20am **TF1-TuM1 Mechanisms of Vapor Permeation Through Multilayer Thin-Films***, **G.L. Graff**, P.E. Burrows, R.E. Williford,* Pacific Northwest National Laboratory **INVITED**

Multi-layer, thin-film organic/inorganic composite barrier layers can achieve water vapor permeation rates (WVTR) of <10@super-5@ g/m@super2@/day at 25°C/40%RH on polyethylene terephthalate. Using both transient and steady-state vapor permeation measurements combined with classical Fickian diffusion models, we determine the mechanism of vapor permeation through such barrier structures and show the importance of an extremely long effective path length for the diffusing gas. We show that the barrier performance obtained is dominated by lag-time (transient) effects, rather than equilibrium diffusion. The implications for further improvement of flexible thin film vapor barriers are discussed.

9:00am **TF1-TuM3 Multi-layered ITO and SiO@sub 2@ Thin Films Deposited on Plastic Substrates by Vacuum Arc Plasma Evaporation***, **T. Miyata**, Y. Minamino, T. Minami,* Kanazawa Institute of Technology, Japan

Recently, a vacuum arc plasma evaporation (VAPE) method that provides a high rate deposition on large area substrates has been newly developed. This paper describes the preparation of multi-layered structures composed of ITO and SiO@sub 2@ thin films deposited on plastic substrates by the VAPE method. Structures such as ITO/SiO@sub 2@ and ITO/SiO@sub 2@/ITO were prepared for the purpose of improving the optical transmittance of flexible transparent conducting films that exhibit a desirable sheet resistance, e.g., ITO thin films deposited on thick PET films. The ITO and SiO@sub 2@ thin films were prepared on PET substrates by the VAPE method using sintered ITO and fused quartz fragments, respectively, as targets. The film depositions were carried out under the following conditions: substrate, PET (glass used as a monitor); substrate temperature, 100°C; pressure, 0.08 to 1 Pa; Ar and O@sub 2@ gas flow rates, 20 and 0 to 20 sccm; and cathode plasma power, 4.5 to 10 kW. The optical and electrical properties of the ITO thin films were strongly dependent on the deposition conditions. In addition, the optical transmission spectra of the SiO@sub 2@ thin films also were affected by the deposition conditions. By optimizing the deposition conditions, highly transparent and conductive ITO thin films were prepared at 100°C on both PET and glass substrates. The resistivity of ITO thin films increased from 2.9 to 7.8X10@super –4@@ohm@cm as the O@sub 2@ flow rate was increased from 5 to 20 sccm. In addition, SiO@sub 2@ thin films that were prepared on PET substrates under optimized conditions exhibited a high transmittance in the visible region. Using optimized deposition conditions, ITO/SiO@sub 2@ and ITO/SiO@sub 2@/ITO multi-layered structures with a desirable sheet resistance were prepared on PET substrates based on the theoretical calculation. However, the film thickness of the ITO top layer was determined by the desired sheet resistance. In conclusion, transmittance could be successfully improved in transparent and conductive ITO/SiO@sub 2@ and ITO/SiO@sub 2@/ITO multi-layered structures prepared on flexible plastic substrates by the VAPE method.

9:20am **TF1-TuM4 Mechanical Performance of Thin Films in Flexible Displays***, **J.S. Lewis**, S. Grego, E. Vick, B. Chalamala, D. Temple,* MCNC Research and Development Institute

In flexible organic light emitting diode (OLED) based displays, brittle thin films are typically used as transparent conductors, permeation barriers, and transistor backplanes. The use of brittle materials in flexible displays requires the understanding of the mechanical limitations of the materials and the various display architectures. We discuss the mechanical limitations of indium tin oxide (ITO) as a transparent conductor, and present results for a more mechanically robust multilayer transparent conductor made of a dielectric-metal-dielectric (DMD) stack. The DMD structures show dramatically improved mechanical properties when subjected to bending both as a function of radius of curvature as well as number of cycles to a fixed radius. Organic light emitting devices fabricated on DMD anodes showed improved performance compared with those made on ITO anodes. The mechanical properties of thin film conductors were investigated by monitoring electrical resistance during flexing, but this approach cannot be used in the analysis of the mechanical failure of transparent thin film permeation barriers. We present a novel approach for etching barrier-coated polymer substrates such that film cracking is readily visible under an optical microscope. We report on the bend test results for sputter-deposited SiO@sub x@N@sub y@ barrier films. This work was supported by the Army Research Laboratory (Contract No. DAAD17-01-C-0085).

9:40am **TF1-TuM5 Structural and Mechanical Properties of Dendrimer-mediated Thin Films***, **F.T. Xu**, S.M. Thaler, J.A. Barnard,* University of Pittsburgh

Dendrimers are three-dimensional, globular, highly-branched macromolecules made up of a central core surrounded by repetitive units all enclosed by a terminal group shell. They can be synthesized with highly controllable sizes (they are monodisperse) determined by the core type, extent of branching, and nature of the end groups, in the range from a few to several tens of nm in diameter. Dendrimers also assemble into monolayers on technologically interesting substrates using simple cleaning, dipping, and rinsing procedures. In this condensed monolayer phase dendrimers can act as surfactants mediating the growth of ultra-flat films, and create novel nanomechanical, adhesive, frictional, and tribological behavior. We have recently reported on the dramatically enhanced quality (superior flatness and adhesion) of metal films deposited on dendrimer monolayers@footnote 1@. Different tribological responses are also observed in dendrimer-mediated metal thin films@footnote 2@. To better understand substrate/dendrimer monolayer/adlayer interactions and how they determine the distinct physical, mechanical, and chemical properties of the resulting dendrimer-based nanocomposites, we are examining the structure and nanomechanical response of metal films formed with and without dendrimer mediation by atomic force and force modulation microscopy. @FootnoteText@ @footnote 1@ S.C. Street, A. Rar, J.N. Zhou, W.J. Liu, and J.A. Barnard, Chem. Mater. 13, (2001)3669.@footnote 2@ F.T. Xu, P.P. Ye, M. Curry, J. A. Barnard and S. C. Street, Trib. Lett. 12 (2002)189 .

10:00am **TF1-TuM6 Gas Diffusion Barriers on Polymer Films Using Al@sub 2@O@sub 3@ Atomic Layer Deposition***, **M.D. Groner**, C.A. Wilson, J.D. Ferguson, S.M. George,* University of Colorado*; R.S. McLean, P.F. Carcia,* DuPont CR&D

Polymer substrates are desirable for flexible organic light-emitting diodes (OLEDs). Unfortunately, gas permeability in polymers is high and gas diffusion barriers are needed to reduce H@sub 2@O and O@sub 2@ permeability. For OLEDs, the desired permeability rate for O@sub 2@ is 1 x 10@super -5@ cc/m@super 2@/day. Inorganic films, such as SiO@sub 2@ and Al@sub 2@O@sub 3@, can have extremely low gas diffusion rates and may be excellent gas diffusion barrier candidates if they are continuous and pinhole-free. Low temperature Al@sub 2@O@sub 3@ ALD has been investigated on a variety of polymer films including PET, PMMA, LDPE, PEN, and Kapton(R). Al@sub 2@O@sub 3@ ALD films were deposited at temperatures between 100-175°C and yielded thicknesses between 1-25 nm on the various polymer substrates. Al@sub 2@O@sub 3@ ALD film growth and film properties were characterized using several techniques including quartz crystal microbalance, FTIR spectroscopy and surface profilometry. O@sub 2@ permeability through the polymer films was also quantified using MOCON permeation measurements. O@sub 2@ permeation rates below the MOCON test limit of 1 x 10@super -3@ cc/m@super 2@/day were measured for Al@sub 2@O@sub 3@ ALD films @>=@ 5 nm thick on PEN and Kapton substrates. New testing methods are currently being developed to measure the extremely low O@sub 2@ and H@sub 2@O permeation rates required for OLED packaging. Studies are also characterizing the dependence of gas permeation rates on the Al@sub 2@O@sub 3@ ALD film thickness and growth temperature.

Thin Films
Room 303C - Session TF2-TuM
ALD and Applications

Moderator: H. Kim, IBM Research

10:20am **TF2-TuM7 Atomic Layer Deposition of Tungsten Disulphide Solid Lubricant Coatings***, **T.M. Mayer**, T.W. Scharf, S.V. Prasad, R.S. Goeke, M.T. Dugger,* Sandia National Laboratories

We have developed a new process for the deposition of polycrystalline tungsten disulphide (WS@sub 2@) solid lubricant coatings with monolayer precision by atomic layer deposition. Sequential reactions of WF@sub 6@ and H@sub 2@S in a viscous flow reactor at 1 to 2 torr and 300 to 400°C lead to growth rates of 0.1 to 0.2 nm/cycle. Nucleation of WS@sub 2@ is impeded on SiO@sub 2@ substrates such that no growth is observed even after 200 cycles. However nucleation occurs readily on ZnO and ZnS substrates and growth catalyzed by the presence of small quantities of Zn, which segregates to the surface of the growing film. SEM with EDS, and Raman spectroscopy determined the coating morphology, composition, and crystallinity, respectively. The friction coefficient was determined to be approx. 0.12 as deposited and decreased to approx. 0.04 when the coating was annealed, well within the acceptable range of other solid lubricant coatings like sputtered MoS@sub 2@ and pulsed laser deposited WS@sub 2@, making this material and process attractive for applications in micromachine technology.

10:40am **TF2-TuM8 Molybdenum Atomic Layer Deposition Using MoF@sub 6@ and Si@sub 2@H@sub 6@**, ***G.B. Rayner, Jr.,*** *S.M. George,* University of Colorado

Although many binary materials have been grown using atomic layer deposition (ALD) techniques, the growth of most single-element metals has been difficult. Tungsten (W) ALD has been demonstrated earlier using WF@sub 6@ and Si@sub 2@H@sub 6@ as reactants. In this study, we extend a similar surface chemistry strategy for Mo ALD. Auger electron spectroscopy (AES) was used to monitor the nucleation and growth during Mo ALD on thin SiO@sub 2@ films thermally grown on Si(100) substrates. Using MoF@sub 6@ exposures of 8 x 10@super 5@ L and Si@sub 2@H@sub 6@ exposures of 4 x 10@super 6@ L at 200°C, the Mo ALD was observed by the attenuation of the O(KLL) AES signal and growth of the Mo(MNN) AES signal. Mo ALD nucleation on SiO@sub 2@ required 10-15 MoF@sub 6@/Si@sub 2@H@sub 6@ reactant cycles. The Si(LMM) AES signal oscillated dramatically during the sequential MoF@sub 6@ and Si@sub 2@H@sub 6@ exposures. No Si(LMM) AES signal was observed following the MoF@sub 6@ exposures that deposit MoF@sub x@ surface species. Large Si(LMM) AES signals were monitored after the Si@sub 2@H@sub 6@ exposures that strip off the fluorine and deposit SiH@sub y@F@sub z@ surface species on the growing Mo surface. Mo ALD may be important for the fabrication of Mo/Si Bragg mirrors for extended ultraviolet (EUV) lithography.

11:00am **TF2-TuM9 Atomic Layer Deposition for the Conformal Coating of Nanoporous Materials***,* ***J.W. Elam,*** *G. Xiong, C.Y. Han,* Argonne National Laboratory*; J.P. Birrell,* Argonne National Laboratory, U.S.*; G.A. Willing, H.H. Wang, J.N. Hryn, M.J. Pellin,* Argonne National Laboratory

Atomic layer deposition (ALD) utilizes a binary reaction sequence of self-saturating chemical reactions between gaseous precursor molecules and a solid surface to deposit films in a layer-by-layer fashion. These attributes make ALD an ideal method for applying very precise, conformal coatings over porous materials. In this presentation, we describe recent work exploring the ALD coating of two porous solids: anodic aluminum oxide (AAO) and silica aerogels. The AAO and silica aerogels have been successfully coated by ALD with a variety of oxide films including Al@sub2@O@sub3@, ZnO, TiO@sub2@, Y@sub2@O@sub3@ and V@sub2@O@sub5@ as well as several metals. These materials were characterized with a host of analytical techniques including SEM, TEM, EDX, AFM, XRD and BET surface area measurements. The ALD coated AAO materials are being employed as mesoporous catalytic membranes as well as size-specific separations membranes. To fabricate the catalytic membranes from the AAO templates, the pore diameter of the AAO membranes is first reduced to the 5-10 nm regime using Al@sub2@O@sub3@ ALD. Next, TiO@sub2@ ALD is used to deposit several monolayers of catalytic support material. Finally, the active V@sub2@O@sub5@ catalyst is deposited by ALD. The resulting nanostructured catalytic membranes show remarkable selectivity in the oxidative dehydrogenation of cyclohexane when compared to conventional powder catalysts. Silica aerogels have the lowest density and highest surface area of any solid material. Consequently, these materials serve as an excellent substrate for fabricating catalytic materials by ALD. In addition to their use as catalysts, the ALD modified aerogel materials have applications in hydrogen storage and production, chemical sensing, and optics. In this study, both thin film and monolithic aerogels were coated by ALD and the coating process was investigated as a function of the reactant exposures.

11:20am **TF2-TuM10 High Reflectivity X-Ray Mirrors from W/Al@sub 2@O@sub 3@ Nanolaminates Fabricated by Atomic Layer Deposition***,* ***F.H. Fabreguette,*** *Z.A. Sechrist, R.A. Wind, S.M. George,* University of Colorado

Nanolaminates can display novel optical, thermal, electrical or mechanical properties. In this study, atomic layer deposition (ALD) was used to fabricate W/Al@sub 2@O@sub 3@ nanolaminates for x-ray mirrors. High x-ray reflectivity depends on precise thickness control, minimal interfacial roughness and high density contrast between the absorber (W) and spacer (Al@sub 2@O@sub 3@) layers in the superlattice that defines the Bragg mirror. The sequential, self-limiting ALD surface reactions allow for atomic control of each layer thickness. Al@sub 2@O@sub 3@ ALD films are amorphous, whereas W ALD films are polycrystalline. To minimize the surface roughness, the W ALD growth temperature was decreased from 177°C to 125°C. This temperature reduction lowered the surface roughness and also changed the tungsten crystalline phase from the @alpha@-phase with some @beta@-phase to the pure @alpha@-phase. This transformation is desirable because the @alpha@-phase has a higher density than the @beta@-phase. Quartz crystal microbalance (QCM) was used as an in-situ probe to optimize the nucleation of Al@sub 2@O@sub 3@ ALD on W and W ALD on Al@sub 2@O@sub 3@ at 125°C. Atomic force microscopy (AFM) studies revealed that smoother films resulted from nanolaminates that had shorter nucleation periods. The optimized W/Al@sub 2@O@sub 3@ nanolaminate growth parameters were used to grow W/Al@sub 2@O@sub 3@ x-ray mirrors. These Bragg mirrors were fabricated with variable bilayer thickness, D, spacer-to-absorber ratio, @gamma@, and number of bilayers, N. The measured x-ray reflectivities were compared with the predicted x-ray reflectivities from the Fresnel equations. Reflectivities as high as 70-80% were obtained using the best set of D, @gamma@ and N parameters. These results demonstrate that the W/Al@sub 2@O@sub 3@ nanolaminates fabricated by ALD are competitive with commercial x-ray mirrors prepared using sputtering techniques.

11:40am **TF2-TuM11 Atomic Layer Deposition of Nickel Oxide Films Using Ni(dmamp)@sub 2@ and Water***, T.S. Yang, W. Cho, M. Kim, K.-S. An, T.-M. Chung, C.G. Kim,* Korea Research Institute of Chemical Technology*;* ***Y. Kim,*** Korea Research Institute of Chemical Technology, South Korea

A novel precursor synthesized for the chemical vapor deposition of metallic nickel, Ni(dmamp)@sub 2@ (dmamp = 1-dimethylamino-2-methyl-2-propanolate), has been tested for its use as a nickel source for the atomic layer deposition of nickel oxide (NiO) using water (H@sub 2@O) as the oxygen source. The precursor is a solid at room temperature, but readily sublimes at 90 °C. The ALD temperature window for this precursor is between 90 °C and 150 °C. The NiO films deposited on Si(001) at 120 °C were characterized by x-ray diffraction, x-ray photoelectron spectroscopy, scanning electron microscopy, and atomic force microscopy. The growth rate of the films was found to be ~0.8 Å/cycle by ellipsometry. The XRD pattern showed no distinct peaks for NiO, indicating that the films deposited at this temperature were amorphous. XPS analysis showed the films to be stoichiometric with some carbon impurities. For a film with the thickness of 820 Å (with 1000 cycles) the rms surface roughness was only ~4 Å as measured by AFM. To elucidate the ALD mechanism of the Ni precursor with water, a quadrupole mass analyzer was employed using D@sub 2@O in lieu of H@sub 2@O. It was found that after a Ni precursor pulse no reaction seemed to take place, however, after a D@sub 2@O pulse, decomposition of the precursor was detected. It is speculated that when the precursor is sent to the substrate (or growing film) it is coordinated to the surface OH groups and when water is introduced, it undergoes a decomposition process to produce a hydroxylated nickel oxide surface. At present, an effort is being made to reduce the amount of carbon impurities. We are also trying to devise a method to deposit metallic nickel using this precursor.

Thin Films
Room 303C - Session TF+NS-TuA

Focused Beam Processing & Fabrication

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

2:20pm **TF+NS-TuA4 Localized Heating Effects During Electron Beam-Induced Deposition of Nanostructures***, **S. Randolph**, J.D. Fowlkes, P.D. Rack,* University of Tennessee, Knoxville

In recent years, electron beam-induced deposition (EBID) has shown promise for use in next-generation lithography applications and nanostructure fabrication. While many materials have been successfully deposited on various substrates by EBID, control of feature size and geometry has been lacking. One possible mechanism that makes process control problematic is the localized heating that occurs in the nanostructure while undergoing constant electron bombardment. While the electron beam-induced heating of a bulk sample in the typical SEM is negligible, a focused beam projected onto a raised high aspect ratio feature can cause significant temperature rises in the feature. As the sticking coefficient and residence time of the impinging precursor gas are strong functions of the substrate temperature, it is expected that the deposition rate will vary with the surface temperature of the nanostructure if the process is mass transport limited. Assuming that there are no radiative and convective heat losses through the surface of the sample, the nanostructure growth creates a quasi one dimensional structure that does not dissipate heat as well as a bulk film. Consequently, as the nanostructure grows the surface temperature increases thereby reducing the sticking coefficient and residence time of the impinging gas. In this presentation, a Monte-Carlo electron-solid model will be illustrated which calculates the energy deposition profiles in the bulk and nanostructured features. Using these profiles, a finite element model is used to calculate the temperature profiles. Bulk and nanostructured features will be compared and discussed in context with experimentally observed growth rates.

2:40pm **TF+NS-TuA5 Electron Beam Micromachining***, **P.E. Russell**, D.P. Griffis, A. Garetto,* NC State University **INVITED**

While chemically enhanced focused ion beam micromachining (CE-FIBM) or other ion based micromachining techniques have many practical applications, any ion beam based micromachining technique typically results in some degree of sample damage as well as residual implanted ions. In many cases, these implanted ions cause deleterious effects such as staining in the case of mask repair, alteration of the electrical characteristics of semiconductor and optoelectronic samples and/or surface damage in samples prepared for high resolution electron microscopy or microanalysis. In order to avoid ion staining and following up on our earlier efforts in electron beam induced deposition and material removal, our efforts are currently focused on gaining increased understanding of and development of chemically enhanced electron beam micromachining (CE-EBM) of technologically important materials. The interaction of incident and emitted (secondary and backscattered) electrons with surfaces in the presence of a suitable chemical precursor can induce useful chemical reactions. Electron beam energies from a few hundred eV to 30 keV are routinely available on scanning electron microscopes, and a few systems allow much lower beam energy. The magnitude of the emission of secondary electrons peaks in the range of a few eV to tens of eV's while backscattered electrons are emitted over a broad, albeit higher range of energies up to the full primary energy. This wide range of electron energies coupled with the richness of possible beam/sample/precursor interactions makes available a wide range of possibilities for both deposition and etching with, when compared to damage resulting from ion beam exposure, a dramatically reduced probability of damage and/or unintentional alteration of samples. This talk will review recent developments in both the application and understanding of CE-EBM.

3:20pm **TF+NS-TuA7 Nanoscale Structures and Devices Produced Using Energetic Atomic Beams***, **E.A. Akhadov**,* Los Alamos National Laboratory*; D. Read,* Florida State University*; A.S. Cavanagh, A.H. Mueller,* Los Alamos National Laboratory*; J.C. Gregory, G.P. Nordin,* University of Alabama in Huntsville*; M.A. Hoffbauer,* Los Alamos National Laboratory

Nanoscale patterning of polymeric materials and low temperature thin film growth become possible using atomic species with kinetic energies similar to chemical bond strengths. We have developed a technique exclusive to LANL, called Energetic Neutral Beam Lithography/Epitaxy (ENABLE), that utilizes energetic neutral atoms for materials processing at the nanoscale. In this presentation, we demonstrate the use of atomic oxygen for nanoscale polymer etching and atomic nitrogen for templated nitride thin film growth. High-precision nanoscale formations (<50nm) with aspect ratios exceeding 35:1 were fabricated in polymer films. Taking advantage of the low temperature thin film growth afforded by ENABLE, we have fabricated AlN-based structures using pre-etched polymeric templates for potential electronic, photonic, and nanofluidic applications.

3:40pm **TF+NS-TuA8 A Three - Dimensional Computer Simulation of Electron - Beam Induced Deposition (EBID)***, **J.D. Fowlkes**, P.D. Rack, S. Randolph,* University of Tennessee, Knoxville

A simulation will be presented of the electron - beam induced deposition (EBID) process that was coded using the Matlab(R) program. The simulation has a Monte Carlo component to predict electron trajectories as well as elastic and inelastic electron â?" substrate interactons. A discretization scheme projects each electron scattering event onto a three dimensional matrix to provide a reference point to test for a host of possible events per matrix node including secondary electron generation and/or EBID. Three phases coexist in the matrix including the precursor gas, the deposited phase and the substrate phase. A dynamic model tracks the gas - surface interaction including precursor adsorption, deposition and desorption under thecontext of a Langmuir type surface coverage. Primary, backscattered, and secondary electrons that escape the gas - pillar and gas - substrate interface may induce deposition based on their trajectory, energy and precursor surface coverage. The probability of EBID is based on a "shifted and scaled" ionization cross-section for the precursor gas molecule to be roughly applied as a dissociation cross - section. Primary (PE) and secondary electrons (SE) contribute most signficantly to the EBID growth of high-aspect ratio nanopillars while backscattered electrons (BSE) play more of a feature coarsening role. Two regimes of pillar growth are observed; a region characterized by linear a growth rate where the electron interaction volume interacts with both the growing pillar and the substrate and a second regime, again linear in growth rate, whereby the penetrating electrons interact solely with the high aspect pillar.

Thin Films
Room 303C - Session TF-WeM
Optical Thin Films

Moderator: G. Ockenfuss, OCLI - JDS Uniphase

8:20am **TF-WeM1 Optical Properties of Uranium and Thorium-Based Thin Films as Highly Reflective EUV Mirrors***, D.D. Allred, J.E. Johnson,* ***W.R. Evans****, N. Farnsworth, A.E. Baker, R.S. Turley,* Brigham Young University

We present measured reflectances (Beamline 6.3.2, ALS at LBNL) of air oxidized sputtered uranium and thorium, reactively sputtered (O_2) uranium oxide and thorium, and reactively sputtered (N_2) uranium nitride thin films. The thin films were also characterized using AFM, spectroscopic ellipsometry, LAXRD, TEM, XPS, and XANES. We compare these with our measurements of the reflectance of nickel, gold, and iridium thin films (commonly used soft x-ray reflectors for astronomy and synchrotrons) from 50 to 500 eV at 5Ës, 10Ës, and 15Ës grazing incidence. These show that these two uranium compounds, as UO_2 and UN, and thorium as air oxidized thorium can fulfill their promise as the highest-known, single-surface reflector for this portion of the soft x-ray region, being nearly twice as reflective as nickel in the 120 to 200 eV region. We additionally report complex indices of refraction for ThO_2, UO_2, and UN obtained from reflection and transmission measurements taken at the ALS. Shifts in energy of up to 20 eV between features in the Th spectra suggest the need for possible revision in the atomic scattering factor approach for obtaining optical constants for compounds. There are also important discrepancies between UO_2â?Ts and UNâ?Ts actual reflectance with those estimated using the atomic scattering factor approach.

8:40am **TF-WeM2 Determining Physical and Chemical Properties of Sputtered Uranium and Thorium Thin Films Useful as Extreme Ultraviolet Reflectors***,* ***R.W.L. Larsen****,* Provo High School*; D.D. Allred,* Brigham Young University

As applications for extreme ultraviolet radiation have been identified, the demand for better optics has also increased. Recently, sputtered thin films containing uranium and thorium have been shown to produce the highest low-angle reflectors for portions of the EUV/soft x rays. For more progress to be made in this area optical constants needed to be obtained. In addition, optical properties need to be assigned to specific compounds and structures. The purpose of this project was to determine the composition, density, lattice structure, and roughness of these sputtered uranium and thorium thin films and their oxides and nitrides via TEM, XPS, AFM and to relate these structural effects to the reflectance of the thin films. We have found that the thorium samples oxidize more slowly in air than uranium so we can talk about the reflection of these films being a mixture of thorium and thorium oxide. Sputtered uranium on the other hand quickly becomes uranium dioxide which is moderately stable for periods of months. Whereas the sputtered uranium nitride samples are uranium mononitride only in the bulk and their surfaces become oxidized.

9:00am **TF-WeM3 Mechanical Characteristics of Optical Films: Their Origin and Evaluation***,* ***L. Martinu****, J.E. Klemberg-Sapieha,* Ecole Polytechnique Montreal, Canada **INVITED**

Control of the mechanical properties is essential in order to achieve reliable performance of optical thin film systems such as filters, waveguides, optical MEMS, sensors, optical coatings on plastic substrates and others. Mechanical properties are closely related to the film microstructure and composition that, in turn, depend on the choice of materials and processes and on the energetic conditions during deposition. In order to assure successful performance and high stability of optical films, the mechanical properties have to be optimized together with the optical characteristics and other film functional properties (electrical conductivity, thermal and environmental stability, surface energy etc.). This presentation will give an overview of the methodology of mechanical testing and will describe the advantages and limitations of individual methods. We will concentrate on the effect of process parameters on the mechanical properties of the individual low, medium and high index optical films, especially those prepared by Physical Vapor Deposition (PVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD). After a detailed review of the basic mechanical properties of films and substrates used in optical applications, we will illustrate the advances in this filed by examples of complex optical systems in which the control of the mechanical behavior is particularly important. This includes a comparison between inhomogeneous and multilayer films, optical coatings on plastics, complex optical filters used in optics, optoelectronics, photonics, architecture, and in medical, security, aerospace, automobile and other applications.

9:40am **TF-WeM5 Improved Optical Heterodyne Detected Transient Grating Method by using a Thin Film Grating***,* ***K. Okamoto****, Z. Zhang,* California Institute of Technology*; D.T. Wei,* Wei & Assoc.*; A. Scherer,* California Institute of Technology

Transient grating (TG) spectroscopy based on the third order nonlinear optical effect has been applied to material, chemical, and biological research. Optical heterodyne detected (OHD) TG measurements have been reported by several groups, but experimental setups were mostly complicated. Here, we demonstrate a convenient new technique of OHDTG by transferring a pattern directly from a metal film grating into sample solution. This method has the same advantages of existing OHDTG techniques but the setting is much simpler. Thin film gratings having submicron periods are fabricated by: evaporating metal on a glass substrate, laser beam writing lithography, and chemical etching. The narrowest metal width of our grating is 333nm. The fabricated grating is then placed in the front side of a quartz cell containing the sample solution with 10mm optical pass length. An UV pump beam (a frequency-tripled Nd:YAG laser) casts a shadow from the grating to the sample solution such that a dark/bright pattern is formed in the solution liquid called transient grating. Such spatial modulation of the optical intensity induces changes of temperature, density and the molecular excitation. Through this transient grating, the modulated refractive index and absorbance of sample materials can be detected by the diffraction of a probe beam (a He-Ne laser). By analyzing the probe beam diffraction, we can obtain the intensity and dynamics of the modulated parameters named above. This technique has many advantages compared with existing OHDTG techniques; such as: (1) simple setting, easy alignment, (2) high signal stability, (3) easy control of phase shift, and (4) quick interchange of grating periods. We shall demonstrate this technique from several materials and discuss about the potential benefit of this new technique.

10:00am **TF-WeM6 Infrared Emission from Zinc Sulfide Doped with Rare Earth Fluorides***,* ***D. DeVito****, A. Kale, W. Glass, M. Davidson, P.H. Holloway,* University of Florida

Thin film electroluminescent devices are excellent sources for high efficiency infrared emission. Rare earth elements, such as Erbium, Thulium and Dysprosium, are good dopants for infrared emitting phosphors because of the many transitions they exhibit in the infrared region. Zinc sulfide is a stable, wide bandgap semiconductor in which electrons can be excited to appropriate energies to produce excitation of the luminescent centers. Achieving good brightness requires a combination of precise composition, deposition conditions and post-deposition annealing. Lanthanide doped zinc sulfide electroluminescent thin films were deposited from two planar magnetron sources using ZnS and lanthanide trifluoride targets. Infrared emission from devices shows a marked improvement for films annealed at temperatures above 350°C. Maximum brightness was achieved for samples annealed at 425°C and, based on SIMS data, is associated with a reduction in the fluorine concentration in the films. Mechanisms for the loss of fluorine include solid state diffusion, with replacement of F with S on the substitutional site. The mechanism for increased electroluminescence will be discussed based on oscillator transition strength relative to nearest neighbor bonding.

10:20am **TF-WeM7 Spectrally Stable Optical Coatings Using Closed Field Reactive Magnetron Sputtering***,* ***J.M. Walls****, D.G. Gibson,* Applied Multilayers Ltd, UK

Magnetron Sputtering has many advantages for the deposition of multilayer optical coatings. The sputtering process is "cold", making it suitable for use on the widest range of substrates including polymers. This paper will describe the "Closed Field" process that allows high quality, multilayer metal-oxide thin films to be deposited at high rates with exceptionally low absorption. In contrast to previous reactive dc sputtering strategies the Closed Field process does not require a separate ion or plasma source. The Closed Field creates a magnetic bottle that extends the electron mean free path leading to high ion current densities. The combination of high current densities with ion energies in the range 30eV to 50eV creates optimum thin film growth conditions. As a result the films are dense and spectrally stable. Also, they are exceptionally smooth as measured using FEGSEM and Coherence Correlation Interferometry Examples of the morphology and optical properties of single layer electrically insulating (SiO_2, Nb_2O_5 and TiO_2) and conducting meat oxides (ITO) will be presented. The structure and morphology of a series of multi-layer metal oxide coatings will also be presented These will include antreflective coatings, UV and infra-red blockers, lighting filters and conductive oxides for flat screen displays.

10:40am **TF-WeM8 Multilayered SiN@sub x@/SiO@sub 2@ AR Coatings with Cylindrical Cathode by Unbalanced Compressive Magnetron Sputtering*, C.-S. Wang*,** *K. Sasaki,* Kanazawa University, Japan*; S.-F. Chen,* National Taipei University of Technology, Taiwan*; T. Hata,* Center of Optical Coating Research, Japan

Excellent adhesion and high throughput production of anti-reflection (AR) coatings were examined by high and low refraction index SiN@sub x@/SiO@sub 2@ combined system. In general, the refraction of SiN@sub x@ was strongly dependent on the composition of nitrogen and it is difficult to obtain stoichiometric SiN@sub x@ in state-of-the-art techniques. In order to satisfy the requirements, we employed a cylindrical unbalanced compressive magnetron (UCM) sputtering technique. A pair of permanent magnets was adjacent to a cylindrical rotating target to increase and compress the ionization density in the region near the substrates. And the reactive gases were introduced between the cathode and UCM so as to produce discharge uniformly. We used a plasma-sprayed Si cylindrical target (6 cm in diameter and 50 cm in length) in which a 4.5 kGauss permanent magnet was built-in. Moreover, the same magnets were also sited to the both sides of the target to form convergence plasma stream forward to a glass substrate. The distance of target to substrate was 5 cm. SiN@sub x@ and SiO@sub 2@ films were deposited by alternatively changing N@sub 2@ and O@sub 2@ gases. The deposition rates of the films were as large as 2.01nm/s and 2.23nm/s respectively. The refraction index of SiN@sub x@ films was varied from 1.63 to 1.75 at 500 nm wavelength by varying Ar/N@sub 2@ flow ratio from 1 to 0, while that of SiO@sub 2@ films was 1.45 stably. According to AR simulation using above values, 4 layers system of SiN@sub x@/SiO@sub 2@ satisfies a reflection less than 1% in wide visible range (420~680 nm). Whole process without evacuation was completed within just 4 min. Additionally, according to spectroscopic ellipsometry measurement, the extinction coefficient was small resulted that high density and less defective films were obtained. This technique is useful for large scale and high performance AR coatings.

11:00am **TF-WeM9 Analysis of a Combined Sputtering and Plasma-Heating-Evaporation Process of Magnesium Fluoride by using Plasma Emission Spectroscopy and Energy Resolved Type Mass Spectrometry*, T. Deguchi,*** Kanazawa Institute of Technology, Japan, Ishikawa*; T. Sasaki, E. Kusano,* Kanazawa Institute of Technology, Japan*; S. Iura, K. Kawamata,* Olympus Co., Ltd., Japan*; A. Kinbara,* Kanazawa Institute of Technology, Japan

A sputtering deposition process combined with plasma-heating-evaporation is an attractive technique to deposit MaF@sub 2@ thin films onto unheated substrate. However, poor understandings of the mechanisms prevent stabilization of the process. In this study, we have analyzed the process by using plasma emission spectroscopy and energy resolved type mass spectrometry. A sputtering machine used for mass spectrometry was a UHV system equipped with a 55 mm diameter cathode and that for film deposition and plasma emission spectroscopy was a commercial batch type system equipped with a 75 mm diameter cathode. The plasma process monitor (PPM-421, Balzers AG) was used to analyze a mass/charge ratio and energy of ions arriving to the substrate. A spectrometer (TYPE HR-2000, Ocean Optics) was used for plasma emission spectroscopy. Ions typically detected were Mg@super +@, F@super +@, MgF@super +@ both in Ar and O@sub 2@ atmospheres. While in Ar atmosphere the number of MgF@super +@ decreased with increasing rf plasma power, in O@sub 2@ atmosphere it increased drastically after the plasma power exceeded 250W. At this point in O@sub 2@ atmosphere the plasma-heating-evaporation occurred. Results obtained by the plasma emission spectroscopy well agreed to these results; i.e., the emission intensity ratio MgF@super *@/O@super *@ increased significantly at an rf power of 200W. Furthermore, the high energy tail in ion energy spectra, resulting from momentum transfer in sputtering process, observed for Mg@super +@ or F@super +@ in Ar atmosphere disappeared for those in O@SUB 2@ atmosphere, showing that the evaporation process in O@sub 2@ atmosphere was not dominated by sputtering, but by thermal evaporation.

11:20am **TF-WeM10 Silicon-rich Nitride Characterization for Polysilicon Gate Patterning*, F. Celii*,** *K. Hewes, S. Zheng, E. Mickler,* Texas Instruments

For manufacturable patterning of sub-0.10 µm poly-Si gates, advanced etch techniques must complement current lithography capability. One approach uses photoresist line-narrowing combined with an etch hardmask that serves the dual purpose of forming a low-reflectivity patterning substrate. The hardmask suitability is determined by the poly-Si etch resistance, the optical properties (if used as an anti-reflection coating (ARC) layer) and integration issues (e.g., cleanup and cost). The requirements on the hardmask will change with subsequent generations, as the material stack layers and thicknesses change. We report the characterization of silicon-rich nitride (SRN) films used in poly-Si gate patterning. SRN films were deposited by PECVD in commercial reactors. Initial characterization used variable-angle spectroscopic ellipsometry (VASE), over the wavelength range 140 - 1100 nm. Modeling of the VASE data provides optical constants at lithography wavelengths (193, 248 nm) of the various film compositions. Based on previous work, the spectral dependence of the optical constants also provided a measure of the Si-loading of the film. The Si-content of the previously-studied sample set (37 to 41%),@super 3@ which gave k@sub 193@ values up to 1.0, was significantly extended with the current set, with k@sub 193@ values up to 2.0. Moreover, the (n,k) values of the current SRN films fall along a fairly narrow line. Additional characterization of these films will include composition measurement by RBS spectroscopy and FT-IR spectroscopy characterization over 400 - 4000 cm,@super -1@ which yield an independent measure of Si-dimer concentration. Simulations of gate patterning structures show (n,k) values which yield reasonable patterning process margin. CD swing curves of patterned films will also be presented.

11:40am **TF-WeM11 Film Stress and Discharge Properties of MgO protective layer of AC-PDP*, M.J. Lee*,** *S.Y. Park, S.H. Moon, S.G. Kim,* Seoul National University, Korea*; H.J. Kim,* Seoul National University, Korea, South Korea

To increase the lifetime of PDP (Plasma Display Panel), MgO thin films are applied on dielectric layer to protect the dielectric layer from ion bombardments of plasma. Because MgO film is unlikely sputtered by ion bombardments and reduces the discharge voltage of PDP due to high secondary electron emission coefficient (@gamma@@sub i@), in turn less energy consumption. In this work, discharge characters of PDPs related to the stress formed in MgO thin films are investigated. MgO thin films were deposited on glass substrate with dielectric by e-beam evaporation in vacuum chamber, 5 x 10 @super -7@ Torr. Substrate temperature was varied from room temperature to 300°C, then annealing process is carried out at 300°C in vacuum chamber for 1hr and 3 hr respectively. The stresses of each sample were measured by laser scanning method to detect the substrate curvature change. To examine the effect of the change of stresses in MgO layers in different formation process on discharge character of real panel, firing voltage (V@sub f@) and sustaining voltage (V@sub s@) were observed. Surface roughness, morphology, and crystallographic preferred orientation of MgO films were also evaluated by XRD, AFM, SEM. And the impurities and hydrates of MgO surface before and after annealing were analyzed by XPS. MgO films on glass substrate have compressive stresses, which were varied according to deposition condition. After the annealing, the compressive stresses were released relatively, and definitely changed at specific temperature condition. The relation between the discharge characters and MgO thin film stress change and the relevancy with other properties of films was also evaluated.

Thin Films
Room 303C - Session TF-WeA
Transparent Conducting Oxides

Moderator: S. McEldowney, OCLI - JDS Uniphase

2:00pm **TF-WeA1 Structural, Electrical and Optical Properties of Transparent Conductive In@sub 2@O@sub 3@-SnO@sub 2@ Films***, Y. Sato, R. Tokumaru,* Aoyama Gakuin University, Japan*; K. Utsumi, H. Iigusa,* Tosoh Corporation, Japan*; P.K. Song, Y. Shigesato,* Aoyama Gakuin University, Japan

Transparent conductive In@sub 2@O@sub 3@-SnO@sub 2@ films were deposited by dc magnetron sputtering using high density ceramic targets which contained various SnO@sub 2@ contents (0-100 wt.%) on unheated glass substrates. These films were post-annealed under various atmospheres (Air, Ar or Ar+3%H@sub 2@) at 200 @super o@C for 1 hr. The structural, electrical and optical properties of these films were investigated. XRD profiles of all the as-deposited films exhibited amorphous structure. After post-annealing under various atmospheres, XRD profiles of the films deposited using targets of up to 20% SnO@sub 2@ contents showed bixbyte crystal structures of In@sub 2@O@sub 3@, whereas all the films deposited using the targets of SnO@sub 2@ contents higher than 20 wt.% showed amorphous structure. Resistivity of the films deposited using the targets of up to 20% SnO@sub 2@ contents was reduced from about 400 to 200 @micro@@ohm@cm by post-annealing under each condition, because carrier density increased with increasing the number of the substitutional Sn@super 4+@ at In@super 3+@ site as the result of the crystallization. All the post-annealed films possessed high transmittance of over 80 % in the region of visible light. In the region of over 1000 nm, the transmittance decreased with increasing Sn concentration, where reflectance increased. Work functions of the all films were analyzed by electron spectroscopy in air (ESA, AC-2). The work function of the films showed clear negative relationship to the carrier density. This could be explained in terms of the shift of the Fermi level to the higher energy in conduction band with the increasing carrier density.

2:20pm **TF-WeA2 Optimization of RF Magnetron Sputter Deposited Indium Tin Oxide (ITO) Transparent Conductors using a Taguchi Statistical Method***, **S.I. Jun**, P.D. Rack,* The University of Tennessee

In order to optimize the electrical and optical properties of ITO (indium tin oxide) thin films a statistical analysis called the Taguchi design was employed. The sputtering parameters that were considered included RF magnetron sputtering power, oxygen partial pressure, total sputtering pressure, and substrate temperatures. The responses that were considered included sheet resistance, transmission, deposition rate, and etch rate (in 22%HCl+6%CH3COOH+72%H2O). From this design of experiments it was determined that the sheet resistance and transmittance are inversely proportional to each other as a function of the process parameters. The preferred orientation of crystalline ITO film is distinguishably changed with an increase of sputtering temperature and oxygen fraction (O2/O2+Ar) in the sputtering ambient. The change in crystallinity results from the content of incorporated oxygen, which significantly affects the electrical and optical properties of ITO films and causes a rearrangement of atoms to form a preferred closed-packed plane orientation. Finally the microstructure of the ITO films becomes denser with increasing oxygen fraction. As a result of this work, we have successfully achieved low sheet resistance (7.0 ohm/sq.) and high transmittance (~90%) for our targeted 300nm thick films. In this presentation we will briefly review our design of experiments and illustrate our experimental procedure. Subsequently, we will discuss how each process parameter affects each measured response. Finally, will correlate the observed electrical and optical properties of the ITO films to the measured crystal structure and microstructure.

2:40pm **TF-WeA3 Optimization of Process Parameters to Achieve High Quality as-Deposited Indium-Tin Oxide Films for Display Applications***, **S. Gupta**,* The University of Alabama

High quality as-sputtered indium-tin oxide (ITO) films have been achieved by careful optimization of the process parameters@footnote 1@. Oxygen flow, deposition power, process pressure and deposition temperature were varied to achieve optimal resistivity and transmission characteristics of the ITO film. Resistivities below 300 µ@ohm@-cm and transmission of over 75% over most of the visible wavelength range of 400-800 nm, with a peak of 85% at about 550 nm, have been obtained for deposition temperatures below 180 @super o@C. For deposition temperatures of about 260 @super o@C, these numbers were improved to about 225 µ@ohm@-cm resistivity and over 90% transmission. The transmission numbers quoted are for the film plus the quartz substrate -- the film-only values exceed 95%. The thermal stability of the films was studied as a function of in-situ pre- and post-deposition annealing. It was seen that deposition of the ITO films at elevated temperatures improved thermal stability of the as-deposited films, and led to no further change in resistivity or transmission upon post-deposition annealing in atmosphere. ITO film properties vs. process parameters were also studied using two types of magnetron cathodes with maximum field strengths of a) 200 Oe, commonly used for non-magnetic materials, and b) 600 Oe, commonly used for magnetic materials. The purpose of changing cathode field strength was to determine whether lowering the plasma impedance by using a stronger field helped to lower the film resistivity, as reported by some researchers. We did not find any such correlation in our studies. @FootnoteText@ @footnote 1@ This study was performed at KDF, while the author was Director of Technology at KDF, 10 Volvo Drive, Rockleigh, NJ 07647.

3:00pm **TF-WeA4 Analysis on Thermal Properties of Tin-doped Indium Oxide Films by Picosecond Thermoreflectance Measurement***, **T. Yagi**, K. Tamano, Y. Sato,* Aoyama Gakuin University, Japan*; N. Taketoshi, T. Baba,* National Metrology Institute of Japan*; Y. Shigesato,* Aoyama Gakuin University, Japan

First time attempt of observation of thermal diffusion across tin doped indium oxide (ITO) thin films perpendicular to the film plane has been carried out using a picosecond thermoreflectance measurement@footnote 1@. ITO films sandwiched by molybdenum (Mo) films were prepared on fused silica substrate by rf magnetron sputtering using ITO and Mo multi-targets. Such Mo/ITO/Mo layered structure was fabricated without exposure to the atmosphere between each deposition. The Mo films with thickness of 70 nm are necessary because the wavelength of pulse laser used in this study is 780 nm at which wavelength ITO is transparent. The ITO films with different thickness of 30, 50 and 70 nm were prepared as the intermediate layer in order to estimate thermal resistance at the interface between Mo/ITO. The resistivity, carrier density and Hall mobility of the ITO film was 4.2e-4 ohm cm, 3.5e20 cm@super -3@ and 35 cm@super 2@/Vsec, respectively. The interface between the Mo films and the fused silica substrate was irradiated by picosecond laser pulse (2 ps). 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 reflectivity of another picosecond laser pulse. The thermal diffusion time increased with the increase in the thickness of the ITO layers. The thermal diffusion coefficient of the ITO films and thermal resistance at ITO/Mo were found to be 3e-6 m@super 2@/s and 1e-8 mK/W, respectively. This research was supported in part by the New Energy and Industrial Technology Development Organization (NEDO) in Japan. @FootnoteText@ 1: N. Taketoshi, T. Baba, E. Schaub, A. Ono: Rev. Sci. Instrum., 74, (2003), pp. 5226-5230.

3:20pm **TF-WeA5 Direct Observation of Hydrogen Generated Free Carriers in ZnO Thin Films***, **C.A. Wolden**,* Colorado School of Mines*; J.B. Baxter,* University of California Santa Barbara*; T.M. Barnes,* Colorado School of Mines*; E.S. Aydil,* University of California Santa Barbara

Zinc oxide is a versatile wide band-gap semiconductor that has generated tremendous interest due to its unique combination of optical, electronic and mechanical properties. Hydrogen is common to many ZnO processing environments, and recent first principle calculations have suggested that it behaves exclusively as an electron donor in ZnO. Although hydrogen in ZnO has been observed in bulk single crystals, its behavior has not been examined in commonly used polycrystalline thin films. We report on the use of in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy to probe the changes in free carrier absorption when thin ZnO films are exposed to H or O atoms generated by H@sub 2@ and O@sub 2@ plasmas, respectively. Polycrystalline ZnO films were deposited on ATR crystals using metalorganic chemical vapor deposition or a plasma-assisted CVD technique. For both types of films, room temperature exposure to hydrogen plasma resulted in a sharp increase in free carrier infrared absorption and free carrier density. Carrier concentrations and mobilities were extracted from the infrared spectra using a model for the complex dielectric function. Hydrogen uptake was rapid and the carrier concentration reached its saturation level (~10@super 18@ /cm@super 3@) in less than a minute of H@sub 2@ plasma exposure. Room temperature oxygen plasma exposure of the hydrogenated films decreased free carrier absorption, but this decrease was only a fraction of the free carrier density increase after H exposure. Extended exposure to oxygen plasma at elevated temperatures (~200°C) was required to return the carrier concentration to levels that are comparable to those in the as-deposited films. The results are contrasted with observations from single crystal experiments, and the ramifications for device processing are discussed.

4:20pm **TF-WeA8 A Note on the Measurement of Carrier Density by Hall Effect in p- Type Transparent Conducting Oxide (TCO) Thin Films**, ***A. Subrahmanyam,*** Indian Institute of Technology Madras, India

P- type transparent conducting oxide (TCO) thin films are the emerging new materials with a vast potential in transparent electronics. Many research groups are working on the preparation and characterization of these films but with a limited success. The Silver Indium oxide (AIO) and Copper Aluminum oxide (CAlO) belonging to the Delafossite crystal structure have shown p- type conductivity, however, the preparation conditions have a very narrow window for the growth parameters to realize p- type conduction. These materials being metal oxides, any small oxygen deficiency leads to metal rich films with sufficient free electrons. Thus, there exists a bipolar conduction in these p-type TCO films. The conventional Hall effect measurement with bipolar conduction (with comparable free carrier concentrations) and the electrons and holes having different mobilities leads to an incorrect sign of the Hall coefficient and erroneous estimation of the majority carrier concentration. In the present paper, Hall effect data from several groups (including the author's group) on several thin films (prepared with different growth conditions) of silver indium oxide (AIO) and copper aluminum oxide (CAlO) have been analyzed. The analyses clearly reveal that a lot of caution is to be exercised while measuring and interpreting the Hall effect data. The concept of Quantitative Mobility Spectrum Analysis (QMSA) for evaluating the mobility and carrier concentration in bipolar semiconductors is discussed in light of the TCO thin film samples. The contact potential difference (CPD) measurements by Kelvin probe technique to estimate the work function (and thus the Fermi level) in these p- type TCO thin films seems to be one of the potential techniques to estimate the p- type nature of conduction.

4:40pm **TF-WeA9 Electrical and Optical Properties of Reactive DC Magnetron Sputtered Silver Doped Indium Oxide Thin Films**, ***S. Srinivasan,*** *A. Subrahmanyam, B. Ullash Kumar,* Indian Institute of Technology, India; *C.L. Nagendra,* Indian Space Research Organization (ISRO), India

In the present study, the role of oxygen in the formation of semiconducting Silver doped Indium oxide thin films is reported. This material has potential application in opto-electronic devices. The Silver doped Indium oxide thin films have been prepared on quartz and soda lime glass substrates at room temperature (300 K) by reactive DC Magnetron sputtering technique. The target is a pure Silver: Indium metal of composition 5: 95 At %. The oxygen flow rates in the growth chambers have been varied in the range of 12.5-14.0 sccm. The sputtering power is kept constant at 50 watts. The X-ray diffraction pattern shows the amorphous nature of these thin films. The electrical resistivity measured at room temperature increases (2.158Ã-10-2 â?"1.545Ã-10-1 â"¦-cm) with increasing oxygen flow rates. The films show an n-type behavior as shown by the Hall effect measurements. The Hall mobility is observed to be decreasing (12.071- 1.984 cm2v-1s-1) with increasing the oxygen flow rates. The thickness and refractive index of these films have been measured by using a spectro-photometric technique and the associated computation algorithm. The thickness of the film as determined by the technique is in the range 165-220 nm. The refractive index and absorption index of these films varies in the range 1.9- 2.1 and 0.01-0.02 over the spectral range from 2500-400nm. The work function has been measured on these films by contact potential method using Kelvin Probe. These data are being analyzed for an understanding of transport mechanism of these films.

Thin Films
Room 303C - Session TF-ThM
Modeling & Fundamentals in Thin Film Deposition

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

8:20am **TF-ThM1 Evolution of Surface Morphology during Thin Film Growth by Hot-Wire CVD: Short-Range Smoothening and Long-Range Roughening**, ***B.A. Sperling***, *J.R. Abelson,* University of Illinois at Urbana-Champaign

During thin film growth by low-pressure chemical vapor deposition, the surface morphology evolves due to a kinetic competition between roughening, driven by self-shadowing or stochastic processes, and smoothening due to surface diffusion. When a very smooth substrate is used, the surface roughness increases only very slowly. A more powerful way to study the surface dynamics is to prepare a substrate with an intentional roughness of ~ 5 nm, then deposit film under "high quality" conditions that favor smoothness, and measure the rapid decrease in surface roughness with increasing film thickness. We use this procedure to study the growth of hydrogenated amorphous silicon by hot-wire chemical vapor deposition. Using in situ spectroscopic ellipsometry, we observe that the surface roughness of the film decreases as it grows. However, post-deposition atomic force microscopy reveals a linear increase in the roughness. We resolve this apparent discrepancy by analyzing the power spectrum densities of the atomic force images, which indicate that the growth surface is experiencing both short-range smoothening and long-range (global) roughening. The ellipsometry data agree semi-quantitatively with the short-range atomic force microscopy data, but due to light scattering they exclude information about the long-range components of roughness. The slope of the power spectrum density (short-range scaling) indicates that surface diffusion is the dominant smoothening mechanism, while the linear increase in roughness is consistent with columnar growth caused by self-shadowing. We also discuss possible means to interpret the rate of smoothening data in terms of the adspecies surface diffusivity during hot-wire chemical vapor deposition.

8:40am **TF-ThM2 Atomic-Scale Analysis of SiH@sub 3@ and H Surface Diffusion on Plasma-Deposited Amorphous Silicon Thin Films**, *M.S. Valipa,* University of California, Santa Barbara*; T. Bakos,* University of Massachusetts, Amherst, usa*; E.S. Aydil,* University of California Santa Barbara*; **D. Maroudas**,* University of Massachusetts, Amherst

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from silane-containing discharges are used widely in the fabrication of solar cells and flat panel displays. Film properties, such as surface roughness and film crystallinity, depend on the mobility of reactive species that impinge on the film surface during deposition. Surface transport of SiH@sub 3@ radicals and H atoms is particularly important in determining film smoothness and affecting film crystallinity, respectively. This presentation focuses on detailed atomic-scale analysis of diffusion of SiH@sub 3@ and H on the a-Si:H surface. Using molecular-dynamics (MD) simulations of repeated impingement of SiH@sub 3@ radicals on the growth surface, we modeled the deposition of a-Si:H films on crystalline Si (c-Si) substrates. MD-grown a-Si:H film surfaces were found to be remarkably smooth due to valley-filling mechanisms mediated by diffusion of SiH@sub 3@, the mobile precursor, and resulting in passivation of dangling bonds present in surface valleys or at valley edges. Surface migration of SiH@sub 3@ is driven by the Si-Si bond strain distribution on the surface, which is strongly coupled with the surface morphology and reactivity. In addition, exposure of MD-grown a-Si:H films to H atoms from an H@sub 2@ plasma leads to formation of nanocrystalline regions in the films. Analysis of MD trajectories revealed that H atoms diffuse on the a-Si:H surface and into the bulk film and insert into strained Si-Si bonds; this leads to local structural relaxation and triggers disorder-to-order transitions. We also report results of first-principles density functional theory (DFT) calculations performed using c-Si surfaces as representative models of atomic bonding at film growth surfaces. The DFT results are consistent with the mechanisms of SiH@sub 3@ and H transport identified by the MD simulations and provide quantitative predictions of the migration energetics.

9:00am **TF-ThM3 Substrate Temperature Dependence of the Roughness Evolution of Hot-wire Deposited a-Si:H Studied by Real-Time Spectroscopic Ellipsometry and Atomic Force Microscopy***, **W.M.M. Kessels**, J.P.M. Hoefnagels, E. Langereis, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The growth process of hydrogenated amorphous silicon (a-Si:H) by hot-wire CVD is studied by analyzing the surface roughness evolution during film growth for different substrate temperatures. This analysis gives information on aspects such as nucleation and initial film growth, surface roughening and smoothening, and surface diffusion mechanisms. Purely amorphous films have therefore been deposited at low deposition rates while monitoring the growth by real time spectroscopic ellipsometry for temperatures between 70 and 450 @degree@C. The thickness of the surface roughness is deduced from a two-layer optical model and analyzed as a function of the film thickness. Furthermore, the surface roughness of the as-deposited films has also been analyzed by atomic force microscopy (AFM) yielding information about the lateral scaling of the roughness. The initial film roughness is identical for all substrate temperatures indicating a similar nucleation behavior at the different temperatures. The position of the amorphous-to-amorphous roughening transition is observed within the film thickness range of 10-20 nm while an optimum is found for 250 @degree@C. The final surface roughness at a film thickness of 200 nm decreases up to substrate temperatures of 250 @degree@C after which the surface roughness remains fairly constant. The growth exponent @beta@ deduced from the roughness evolution as a function of deposition time, however, decreases for increasing temperature from ~0.20 at 70 @degree@C to ~0.05 at 450 @degree@C in agreement with the temperature dependence of the roughness exponent @alpha@ deduced from the AFM measurements. This suggests a thermally activated surface diffusion mechanism which will be discussed in detail and the relation between the surface roughness evolution and the a-Si:H film properties will be addressed.

9:20am **TF-ThM4 A Self-Consistent Prediction of a Deposition of Cu Sputtered in a rf Magnetron Plasma***, **T.Y. Yagisawa**, T.M. Mine, S.K. Kuroiwa, T.M. Makabe,* Keio University, Japan

Magnetron sputtering has been widely used for thin film deposition in material processing. Radio frequency magnetron is practically employed in the field of dielectric material sputtering in addition to metal targets. In the rf magnetron sputtering system, neutral transport sputtered from a target is of first importance to deposit uniform film. In this paper, we have performed a self-consistent prediction of an rf magnetron plasma structure, velocity of ions impinging a target surface and its erosion profile, ejection neutral atom from the target, and neutral transport to the substrate by using a hybrid model consisting of PIC/MC model of electrons, RCT model of ions and MCS of sputtered neutrals. Typical example is shown in an rf sputtering of Cu target at 13.56 MHz in Ar at 5 mTorr. It is found that rf magnetron at low power supply is maintained mainly by the electron multiplication at the region where ExB is maximum, and auxiliary by the secondary electrons from the target in the region with ExB=0. The latter mechanism which is completely different from the dc magnetron sputtering will become dominant with increasing the dissipated power. Ion velocity distribution at the target surface shows a strong anisotropy due to low pressure and radial dependence. Flux and velocity distribution of sputtered neutrals incident on the substrate surface will be shown and discussed.

9:40am **TF-ThM5 Effects of Steering and Shadowing in Epitaxial Growth***, **J.G. Amar**,* University of Toledo **INVITED**

While shadowing has been known to play a role in some thin-film deposition processes, until recently it has been assumed that in epitaxial growth the effects of steering and shadowing are negligible. Here we present theoretical and molecular dynamics results describing the effects of steering due to both the short-range and the long-range van der Waals attraction on metal (100) and (111) epitaxial growth. Our results lead to a general picture of the process of deposition near step-edges@footnote 1,@@footnote 2@ which is quite different from the standard downward funneling picture. In particular, we find that short-range attraction plays an important role both after as well as before collision with the step. As a result, it can significantly enhance the uphill current, selected mound angle, and surface roughness for typical energies used in epitaxial growth. For the case of deposition on metal (111) surfaces we also find a significant asymmetry between the interaction at A and B steps which may be explained by differences in the step geometry. We have also calculated the van der Waals constant describing the long-range interaction between a Cu atom and a Cu(100) surface. Our result is large enough to explain recent observations@footnote 3@ of a significant increase in mound angle in Cu/Cu(100) growth for large angles of incidence (@theta@ > 50 °) and also indicates that for smaller angles of incidence the dominant effects are due to the short-range rather than to the long-range interaction. Finally, we discuss the effects of shadowing in oblique incidence epitaxial growth and its implications for the formation and control of nanoscale patterning during growth. @FootnoteText@ @footnote 1@ J. Yu and J.G. Amar, Phys. Rev. Lett. 89, 286103 (2002).@footnote 2@ J. Yu and J.G. Amar, Phys. Rev. B 69, 045426 (2004)@footnote 3@ S. van Dijken et al, Phys. Rev. B 61, 14047 (2000).

10:20am **TF-ThM7 Inhomogeneous Transport of Energetic and Thermalized Neutrals in a Magnetron Sputter System***, **F.J. Jimenez,*** University of Alberta, Canada*; S. Leonard,* Matrikon, Canada*; P. Beatty, S. Dew,* University of Alberta, Canada

Thermalization of energetic neutrals in a typical magnetron sputter deposition system occurs as energetic particles collide with background gas atoms. Most of these energetic neutrals are created at the cathode as a result of positive ions striking the target and causing sputter ejection/reflection. After a few collisions these energetic neutrals are greatly slowed until they reach thermal energies and their transport is believed to be governed by diffusion phenomena. This effect is responsible for reducing the energy of incoming particles to the substrate which in turn affects the characteristics of the film being deposited. It is known that island formation and coalescence stages of film growth strongly depend on temperature, angle of incidence and energy of neutrals. A coupled model that approximates transport of the thermalized particles in a typical magnetron sputter chamber is presented. The thermalized model follows a fluid approach to predict steady state spatial distributions of thermalized particles as a function of space. Transport equations are solved in a three dimensional space with a nonuniform grid and anisotropic transport coefficients. Particle diffusion is coupled with a temperature solver to consider the impact of gas heating. Shadowing effects due to the rather complex geometry of a common magnetron chamber are also taken into consideration in the model. Transport of energetic reflected neutrals and sputtered atoms from the target is simulated with a MonteCarlo approach which includes the gas rarefaction and heating effects. A study of the effect that power has on the steady state temperature of the gas is included. The simulation is performed assuming a typical aluminum deposition in an argon environment at constant voltage and pressure. Steady state temperature profiles and particle distributions in the whole chamber are presented indicating a clear temperature dependence on power as previous works have reported.

10:40am **TF-ThM8 A Target Material Pathways Model for High Power Pulsed Magnetron Sputtering***, **D.J. Christie,*** Advanced Energy Industries, Inc.

The potential of high power pulsed magnetron sputtering (HPPMS) has created growing interest, because it can generate a dense plasma with high target material ion content. However, deposition rates are significantly lower than for DC sputtering at the same average power.@footnote 1@@super ,@@footnote 2@ The HPPMS rates are typically only 25% to 35% of the DC rates at the same average power when the process parameters are equal. The fraction of target material arriving at the workpiece which is ionized ranges from 5% to 70%@footnote 3@@super ,@@footnote 4@@super ,@@footnote 5@ as reported so far by workers in the field. Optical emission spectroscopy suggests a highly metallic plasma, but even so, the fraction of ionized target material arriving at the workpiece can be low. A simple pathways model has been developed to explain these experimental results. In addition, parametric evaluation of the model suggests target material characteristics which are desirable in order to achieve higher deposition rates and a greater ionized fraction of target material reaching the substrate. The model will be presented, with representative characteristic results and implications on HPPMS processes. In addition, insights from approximate model equations and their significance will be presented. @FootnoteText@ @footnote 1@J. A. Davis et al., to be published in Proc. 47th Annual SVC Tech. Conf., (2004).@footnote 2@W. D. Sproul et al., to be published in Proc. 47th Annual SVC Tech. Conf., (2004).@footnote 3@V. Kouznetsov et al., Surface and Coatings Technology 122, 290 (1999).@footnote 4@A. P. Ehiasarian et al., Surface and Coatings Technology 163-164, 267 (2003).@footnote 5@B. M. DeKoven et al., Soc. of Vac. Coaters 46th Annual Tech. Conf. Proc., 158 (2003).

11:00am **TF-ThM9 Complex Target Poisoning Effects in Reactive Sputtering***, **D. Rosen**, O. Kappertz, T. Nyberg, I. Katardjiev, S. Berg,* Uppsala University, Sweden

Target poisoning is the major factor limiting the deposition rate in reactive sputtering processes. Chemisorption of the reactive gas at the target surface is the main poisoning mechanism which has been studied in detail and is realatively well understood. However, there are both experimental and theoretical indications that there exists an additional target poisoning process taking place simultaneously with chemisorption. This is implantation of ionized reactive gas molecules into the subsurface of the target. These ions will penetrate some 40-80 Angstrom beneath the surface depending on target voltage. At this position these molecules will also undergo chemical reactions with the target metal atoms and form compound molecules. The target is continously etched by the mixture of energetic argon ions and ionized reactive gas molecules. Thus, the compound molecules formed by ion implantation will be brought to the surface as the target is etched. In this way additional compound molecules will be brought to the surface as compared to the case when only chemisorption at the surface would have taken place. We present a simple treatment for how these two target poisoning mechanisms will affect the processing behaviour of the reactive sputtering process. Our results indicate that the chemical reactivity between the target metal atoms and reactive gas molecules will determine if chemisorption or ion implantation is the dominating mechanism for taget poisoning. The most surprising result, however, is that we found that due to recoil implantation with the energetic argon ions the depth of the partly formed compound sub-layer will be almost identical irrespective whether chemisorption or ion implantation is the dominating target poisoning mechanism.

11:20am **TF-ThM10 Process Parameter - Film Structure/Optical Property Study of Reactive Sputter Deposited Hafnium Dioxide***, **E. Hoppe**, C.R. Aita,* University of Wisconsin-Milwaukee

HfO@sub 2@ is a refractory material that has gained importance in thin films for high k, high n, wide band gap applications. Here, we deposited HfO@sub 2@ films by sputtering a Hf target in rf-excited Ar/O@sub 2@ discharges. 150-nm thick films were grown at room temperature on Si and fused SiO@sub 2@ substrates. Nine combinations of cathode voltage (500 to 1000 V) and O@sub 2@ gas content (10 to 40%) were used. Our goal was to determine the relationship between deposition process parameters and the films atomic structure (long and short range order) and near ultraviolet-visible-infrared absorption and reflection behavior. X-ray diffraction showed the following results: (1) All films were nanocrystalline with monoclinic (m) HfO@sub 2@, the STP phase, predominant. (2) For a fixed cathode voltage, m-HfO@sub 2@ orientation with respect to the substrate was strongly dependent upon the gas O@sub 2@ content. Specifically at high gas O@sub 2@ content, a preferred m(11-1) orientation, the lowest energy growth orientation, was observed. Other orientations of m-HfO@sub 2@ became strong at low gas O@sub 2@ content and low cathode voltage, including a preferred m(111) orientation. (3) A trace amount of tetragonal (t) HfO@sub 2@, a high temperature phase, was observed in some films. This phase was possibly stabilized by a finite crystal size effect, analogous t-ZrO@sub 2@. However, the tetragonal phase occurs in significant amounts in ZrO@sub 2@ but in trace amounts in HfO@sub 2@ films grown under similar conditions, suggesting that the critical radius above which t transforms to m is smaller in HfO@sub 2@ than in ZrO@sub 2@ films, consistent with a lower t-to-m transformation temperature in bulk ZrO@sub 2@. All films are highly transparent. Transmission v. wavelength curves yielded an optical band gap of ~6.4 eV. Optical absorption edge characteristics were independent of film nanocrystal orientation, consistent with this property depending chiefly upon short-range order in wide band gap oxides.

11:40am **TF-ThM11 Integrated Modeling of Al@sub 2@O@sub 3@ Atomic Layer Deposition***, **H. Simka**, D. Thakurta, S. Shankar,* Intel Corp.

Atomic Layer Deposition (ALD) has become an increasingly attractive option for deposition of various crucial semiconductor material layers, including high-K dielectrics and barrier metal applications. ALD advantages, which include excellent film coverage, uniformity, composition and thickness targeting, can be realized by optimizing precursor reactivity and process conditions. Fundamental understanding of these factors is often limited, especially for surface reaction pathways involving new materials. One possible approach, based on first-principles quantum chemistry investigations of precursor reactions, is described in this work. The goal of this general approach is to reduce the amount of process characterizations needed, and to complement available surface science and growth data. As an example, Density-Functional Theory was used to determine molecular properties and reaction energy barriers for Al@sub 2@O@sub 3@ ALD with Trimethylaluminum (TMA) and H@sub 2@O precursors, building on results from a previous quantum chemical study (1). A reaction mechanism containing important surface reactions controlling ALD behavior was developed, and integrated with a reactor model. The approach was validated against Al@sub 2@O@sub 3@ ALD data in a well-characterized flow-tube reactor (2). Model predicted growth rates in excellent agreement with data, and explained effects of process conditions (temperature, pressure, precursor cycle-times) on ALD growth. Differences in species reactivity on both alumina (important for growth) and silica substrates (important for nucleation) will be discussed. Acknowledgements: Prof. Steven George (U. Colorado-Boulder), Prof. Charles Musgrave (Stanford U.). References: (1) Y. Widjaja and C.B. Musgrave, Applied Physics Letters, 80(18), 3304 (2002) (2) J.W. Elam, M.D. Groner, and S.M. George, Review of Scientific Instruments, 73(8), 2981 (2002).

Thin Films
Room 303C - Session TF-ThA
Photovoltaic Thin Films

Moderator: T. Klein, The University of Alabama

2:00pm **TF-ThA1 Study of Molybdenum Back Contact Layer to Achieve Adherent and Efficient CIGS2 Absorber Thin-Film Solar Cells***, N.G. Dhere,* Florida Solar Energy Center*; **A.A. Kadam,*** University of Central Florida

Molybdenum is used as back contact layer in CuIn@sub 1-x@Ga@sub x@S2 (CIGS2) absorber thin film solar cells. Mo is sputter deposited using DC magnetron sputtering. Mo being refractory material develops stresses. It is essential to deposit stress-free and relatively inert Mo in order to achieve well adherent and highly efficient CIGS2 absorber thin film solar cells on stainless steel and glass substrates. Earlier studies have shown that films deposited at 300 W and 0.3 mT pressure develops compressive stress, while the films deposited at 200 W and 5 mT pressure develops tensile stress. Four experiments were carried out to achieve optimum deposition cycle to deposit stress free Mo. In first experiment two cycles of 200 W/5 mT were sandwiched between three cycles of 300 W/0.3 mT. In second experiment two cycles of compressive stress were sandwiched between three cycles of tensile stress. In third experiment two cycles each of compressive stress and tensile stress were deposited alternatively starting with compressive cycle and ending with tensile cycle. The fourth experiment was conducted in reverse order, starting with tensile and ending with compressive. All the depositions were carried out on 15 x 10 cm@super 2@ stainless steel substrates. 5 x 10 cm@super 2@ strip was cut and remaining 10 x 10 cm@super 2@ was deposited with metallic precursors copper-gallium and indium. Metallic precursors were sulfurized at 475°C for 20 minutes in a gas mixture of 4% H@sub 2@S/N@sub 2@. The presentation describes the XRD and SEM analysis to study the quality of films as a consequence of deposition cycle of Mo back contact layer. TEM analyses are also presented to study Mo/CIGS2 interface behavior. Small region of Mo films on remaining 5 x 10 cm@super 2@ strips were tested for adhesion by simple scotch tape test and remaining part was sulfurized at 475°C for 20 minutes to study the reactivity of Mo with H@sub 2@S at the operating temperature.

2:20pm **TF-ThA2 Formation of Chalcogen Containing Plasmas and Their Use in Synthesis of Photovoltaic Absorber Layers***, **S. Kosaraju,*** Colorado School of Mines*; C.A. Wolden,* Colorado school of Mines*; R. Ingrid,* ITN Energy Systems, Inc.

The synthesis of copper chalcopyrite solar absorbers requires high temperature and excess chalcogen due to low chalcogen reactivity. This paper describes work aimed at addressing these issues through plasma processing. An inductively coupled plasma (ICP) source was used to activate both sulfur and selenium vapors into high-energy atomic and radical species. Stable ICP discharges were achieved with both sulfur and selenium vapors using argon as a carrier gas. ICP processing configurations are described for both a flowtube geometry used for metal selenization as well as for incorporation into a high vacuum co-evaporation environment. Actinometry was employed to measure the flux of chalcogen vapors from solid sources as a function of source temperature and the RF power. The potential of this approach was demonstrated by converting indium and copper/indium/gallium films to chalcopyrites using the ICP source. It is shown that indium is readily converted to In@sub 2@Se@sub 3@ using argon/selenium plasma at room temperature. Similarly, Cu/In/Ga precursor thin films on a stainless steel substrate were exposed to plasma-activated selenium at 300@super o@C. The foils were converted into ternary and quandary chalcopyrite compounds, and no crystalline binary phases (i.e. In@sub 2@Se@sub 3@, CuSe) were observed. Films were additionally characterized by scanning electron microscopy and energy dispersive spectroscopy.

2:40pm **TF-ThA3 Thin Film Photovoltaics***, **N.G. Dhere,*** Florida Solar Energy Center **INVITED**

The world production of photovoltaic (PV) cells/modules has increased at a rate of >35%/year from 88.6 MW in 1996 to 744.8 MW in 2003 with concomitant reduction in cost. During this period U.S. fraction of PV production has dropped from 44% to 14%. Last year, U.S. production of thin-film PV modules was as follows: CdTe First Solar 2.5 MW, CuIn@sub 1-x@Ga@sub x@Se@sub 2-y@S@sub y@ (CIGS) Shell Solar 2 MW, a-Si:H UniSolar 7 MW and CIGS Global Solar 0.5 MW. Because of considerable increase in the production capacity, it is expected that the cumulative U.S. production of thin-film PV modules will double to 25 MW this year and again to 50 MW next year, thus spearheading production growth. Present PV conversion efficiencies of champion thin-film solar cells are CIGS 19.3%, CdTe 16.5% and a-Si:H 12.4%. However, those of PV modules lag considerably behind. In addition to increasing efficiency and production volume of thin-film PV modules and reducing their cost, it is also important to assure their long-term reliability. Other principle research issues in thin-film photovoltaics are discussed below. Even though the bandgaps of CdTe and CuIn@sub 1-x@Ga@sub x@S@sub 2@ (CIGS2) are near optimum for terrestrial and space applications, their open circuit voltages are considerably below theoretical attainable values. Therefore, interdiffusion, phase formation, and accumulation of impurities in the active junction region must be studied. Moreover, as CIGS film transitions from Cu-rich to In-rich composition, its microstructure must be studied. Obtaining ohmic contacts is difficult especially for CdTe because of the inherently low p-type doping level. Therefore, increasing p-type doping level is important. FSEC PV Materials Lab is participating in this effort with research and development on large area CIGS thin-film solar cells as well as by leading in testing of U.S. thin-film PV modules in the hot and humid environment as well as under high-voltage bias conditions.

3:20pm **TF-ThA5 Reaction Kinetics of Cu with the CdTe(111)-B Surface***, **G. Teeter,** C.L. Perkins, T. Gessert,* National Renewable Energy Laboratory*; C. Corwine,* Colorado State University*; S. Asher,* National Renewable Energy Laboratory

Copper is frequently incorporated at the back contacts of CdTe-based thin film photovoltaic devices, where it is believed to dope the CdTe p-type and aid in the formation of a pseudo-ohmic contact. In the present study, the reaction kinetics of Cu thin films (0-30 Å) with the CdTe(111)-B surface have been measured via mass spectrometry in ultrahigh vacuum. Cu was deposited on the clean surface, and upon annealing it was observed that atomic Cd desorbs from the surface in proportion to the amount of deposited Cu. Temperature programmed desorption (TPD) measurements reveal zero order reaction kinetics for the Cu/CdTe(111)-B system. In addition, surface composition maps generated by scanning Auger Electron Spectroscopy (AES) show that a metastable copper telluride phase forms at the surface under certain conditions.

3:40pm **TF-ThA6 Transparent and Semi-Transparent Conducting Film Deposition by Reactive-Environment, Hollow Cathode Sputtering***, A.E. Delahoy, **S.Y. Guo,*** Energy Photovoltaics, Inc.

Highly transparent and conductive In@sub 2@O@sub 3@ and ZnO films containing different doping elements such as Mo, Zr, Nb, Ta, W (for In@sub 2@O@sub 3@) and Al, B (for ZnO) have been prepared by the reactive-environment, hollow cathode sputtering method.@footnote 1@ The use of Nb and W as effective dopants is reported for the first time. Metallic targets were used exclusively, and the dopant concentration was easily controlled using a second sputtering power supply. As a result of the cathode and gas flow geometry, the sputtering is conducted in metal mode, and the target and doping materials are free from oxidation during the deposition process. Film resistivities achieved with the various dopants will be reported. For In@sub 2@O@sub 3@:Mo, a resistivity of 1.6x 10@super -4@ @ohm@-cm and a mobility of 80 cm@super 2@/Vs were achieved for Mo concentrations in the range 0.5-5.0% as measured by ICP. XPS analysis indicates Mo with a +6 valence state. The dependences of film resistivity on substrate temperature during preparation and film temperature during measurement will be presented and discussed. Different dominant scattering mechanisms can be seen in different films. Reasonably transparent films of CuAlO@sub 2@ will be reported. And remarkably, semi-transparent films of InN having sheet resistances of 12 @ohm@/square have also been prepared. A scaled-up linear cathode 50 cm in length is under construction, and we expect to report results for ZnO:B deposited using this source. @FootnoteText@ @footnote 1@A. E. Delahoy, S. Y. Guo, C. Paduraru, and A. Belkind, J. Vac. Sci. Technol. A 22 Jul/Aug 2004.

4:00pm **TF-ThA7 High Efficiency CIGS Thin Film Solar Cells***, **K. Ramanathan,*** National Center for Photovoltaics **INVITED**

This paper will present the current staus of solar cells fabricated from CuInGaSe@2@(CIGS) polycrystalline thin films. CIGS thin film solar cells are considered as an excellent option for power generation at low cost. The technology has matured to the point of commercial production. We will highlight the special properties of CIGS materials and the 3-stage growth process developed at NREL. We have achieved a world-record solar cell efficiency of 19.3% at NREL. As the device efficiencies have increased and the confidence in the repeatability has grown, more attention is given to basic science of junction formation, surface properties of absorber films, and electronic properties of interfaces. We shall review our work in this area and also our collaborations with our industrial partners.

4:40pm **TF-ThA9 High Stability a-Si:H Films Deposited using Cluster-Suppressed Triode Plasma CVD*, K. Koga*,** *N. Kaguchi, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

Reduction of a total volume of amorphous silicon particles below 10 nm in size (clusters) incorporated into a-Si:H films is the key to suppression of light-induced degradation of the films, since the films containing the less volume of clusters show the higher stability.@footnote 1@ In order to realize such reduction, we have deduced a sticking probability s of clusters to a stainless steel mesh from an experiment for which gas containing clusters has been passed through a series of eight meshes. Most clusters are trapped with the first two meshes, indicating s~1. Based on the result, we have employed a cluster-suppressed plasma CVD reactor@footnote 2@ together with a triode discharge for which clusters are trapped with a mesh placed at 18 mm above a substrate. The light-induced degradation of the film qualities has been evaluated using a n@super +@Si/a-Si:H(1µm thick)/Ni Schottky solar cell. The initial and stabilized fill factor FF of the Schottky cell is 0.60 and 0.56, respectively. The degradation ratio of 6.7% is significantly low compared to the ratio of 17% for device quality films deposited using a conventional diode discharge. The stabilized FF= 0.56 surpasses the initial FF= 0.53 for the diode discharge. We will also present experimental results obtained using an "improved version" of the cluster-suppressed triode plasma CVD reactor. @FootnoteText@ @footnote 1@K. Koga, N. Kaguchi, M. Shiratani and Y. Watanabe, J. Vac. Sci. Technol. A 22, (2004) to be published.@footnote 2@M. Shiratani, K. Koga, M. Kai, and Y. Watanabe, Thin Solid Films 427, 1(2003).

Thin Films
Room 303C - Session TF-FrM
In-Situ/Ex-Situ & Real-Time Monitoring

Moderator: C.H. Stoessel, Consultant

8:20am **TF-FrM1 Real-time and Spectroscopic Second Harmonic Generation as a Tool to Probe Surface Processes during Amorphous Silicon Film Growth*, I.M.P. Aarts*,** *J.J.H. Gielis, C.M. Leewis, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

We have explored the capability of second harmonic generation (SHG) to probe surface and interface processes during the growth of amorphous silicon-based thin films such as hydrogenated amorphous silicon (a-Si:H). The a-Si:H thin films are deposited under ultrahigh vacuum conditions by means of a hot wire source on fused silica substrates. Real-time spectroscopic ellipsometry has been used to monitor the thickness evolution and the optical properties of the a-Si:H films. SHG has been observed during in situ experiments on as-deposited films for various input and output polarizations configurations. Although SHG is surface and interface specific for isotropic media such as a-Si:H, interpretation in the present case is complicated because not only interference effects have to be taken into account but also the macroscopic origin of the SHG is not straightforward to determine. The experimental data has therefore been analyzed with a complete optical model that takes into account interference effects of both the fundamental and the SHG radiation as well as two nonlinear polarizing sheets in which the SHG signal is generated. These sheets are positioned at the surface and at the interface between the film and the substrate. Further understanding of the SHG signal has been obtained by performing spectroscopic SHG measurements, which showed two distinct resonance peaks at photon energies of 1.2 and 1.4 eV. After exposing the a-Si:H film to oxygen the SHG signal is quenched, indicating that the corresponding resonance peaks involve transitions with dangling bond states. In addition, real-time observation of the SHG signal during film growth and dosing experiments have already revealed that SHG is sensitive to nucleation and relaxation processes at the surface and/or interface region during and after growth of these silicon-based films.

8:40am **TF-FrM2 MultiChannel Mueller Matrix Ellipsometry for In-Situ and Real Time Analysis of Thin Films and Surfaces*, R.W. Collins*,** *C. Chen, I. An, N.J. Podraza,* University of Toledo **INVITED**

A dual rotating compensator multichannel ellipsometer has been applied for real time Mueller matrix spectroscopy (2 to 5 eV) of anisotropic surfaces and thin films. The sequence of optical elements for this instrument is denoted PC@sub 1@SC@sub 2@A, where P, S, and A represent the polarizer, sample, and analyzer. C@sub 1@ and C@sub 2@ represent the first and second compensators that rotate at frequencies of 10 and 6 Hz, respectively, synchronized for a 5:3 ratio. At this ratio, the 2n@omega@ frequencies where n = 1, ..., 8, 10, 11, 13, and 16, and where @omega@/2@pi@ = 2 Hz, are present in the detected irradiance waveform for the most general sample Mueller matrix. The associated 25 experimental dc, cosine, and sine Fourier coefficients are determined for a given pixel of the photodiode array detector by integrating the waveform 36 times per optical cycle. Spectra in the 16 Mueller matrix elements can be determined from spectra in the 25 non-zero coefficients acquired in a single 250 ms optical cycle and from instrument calibration data obtained in advance. In high speed Mueller matrix measurements, this research has focused on weakly anisotropic surfaces and thin films that push the instrument to its limits. These include the (110) Si surface and thin films having an oriented columnar microstructure in which case the weak anisotropic optical response can be over-determined from analyses employing separate 2x2 blocks of the Mueller matrix. As a result, detection of anisotropy is definitive, and the co- and cross-polarization ellipsometric angles @psi@@sub pp@, @psi@@sub ps@, and @psi@@sub sp@ can be determined to within an accuracy of 1 part in 10@super 4@.

9:20am **TF-FrM4 Analysis of Ti and TiN Thin Film Nucleation, Coalescence, and Growth by Rotating Compensator Multichannel Ellipsometry*, C. Chen,*** The Penn State University*; B. Hong,* Sungkyunkwan University, Korea*; P. Sunal, M.W. Horn, R. Messier,* The Penn State University*; R.W. Collins,* University of Toledo

Real time spectroscopic ellipsometry has been applied in the rotating-compensator configuration to characterize the nucleation, growth, and optical properties of titanium and titanium nitride thin films deposited by magnetron sputtering on silicon wafers with thermally-grown silicon oxide and nitride overlayers. The ellipsometer used in this study incorporates recent instrumentation advances for a wide spectral range (1.5 to 6.5 eV), including a dual Xe/D@sub 2@ source with an intervening iris for spectral flattening. The real time ellipsometric spectra collected throughout film deposition on the smooth wafer substrates are analyzed in terms of a transition from a one-layer to a two-layer optical model. This transition simulates the overall thin film structural evolution including nucleation, coalescence, and surface roughening during growth. In the initial stages, the spectra are particularly sensitive to smoothening that occurs during coalescence. In the case of Ti deposition on SiO@sub 2@ covered Si wafers, for example, this effect is maximized within a narrow deposition parameter window of Ar sputtering gas pressure and plasma power. In this case, 15-20 Å thick Ti clusters coalesce, yielding surface roughness only a monolayer in thickness after ~100 Å of Ti bulk layer deposition. The evolution of the optical properties of the Ti layer with cluster size during nucleation and with bulk thickness during growth provides additional information on the structure of the film and its electronic properties. Finally, insights from these studies can be used to direct the fabrication of alternating multilayer and nanocomposite films for hard-coating applications.

9:40am **TF-FrM5 Comparative Ellipsometric Study of Liquid Helium Thin Films on Au, Cs, HOPG and Rb Substrates*, T. McMillan*,** *P. Taborek, J.E. Rutledge,* University California Irvine

We have developed a modulated null ellipsometer with sub-monolayer resolution to measure adsorbed liquid helium thin films at temperatures from 1.3 to 4.3 K. Measuring helium films pushes the limits of cryogenic ellipsometry due to helium's extremely small index of refraction. We have performed isotherms on substrates with a range of substrate potentials: Au is a representative strong substrate while Rb is an intermediate and Cs a weak substrate. These measurements will determine how the binding energy affects the superfluid transition. The ellipsometer allows us to explore effects that cannot be discerned solely from quartz crystal microbalance measurements, which are only sensitive to the normal fluid fraction of the film.

10:00am **TF-FrM6 Studies of Coupling and Ordering in Magnetic Thin Films with Polarized Neutron Reflectometry*, S.G.E. te Velthuis,*** Argonne National Laboratory **INVITED**

Traditionally neutron scattering has been an important tool for studying bulk magnetic materials. The success has been due to the high sensitivity of neutrons for magnetic moments, combined with their characteristics in relationship to wavelength and velocity. As the interest of the scientific community has shifted towards nanostructured materials, polarized neutron reflectivity (PNR) and scattering at grazing incidence have emerged as powerful methods for studying magnetic thin films. As will be illustrated by the presentation of several experiments, the depth dependent magnitude and orientation of the magnetization in a thin film can be determined with PNR. In the case of GaMnAs thin films knowledge about the magnitude of the magnetization provided understanding about the effect of temperature annealing in these films. Determination of the orientation of the magnetization of individual Fe layers in Fe/Cr[110] superlattices as was essential to the understanding of the magnetic coupling between the Fe layers spaced by Cr. Finally, PNR experiments performed with polarization analysis mapped out the evolution of individual magnetization vectors during the first order spin flop transition in a finite antiferromagnet, thereby confirming theoretical predictions about this magnetic phase transition.

10:40am **TF-FrM8 Real-time Optical Monitoring of Ammonia Decomposition Kinetics in InN Vapor Phase Epitaxy at Elevated Pressures*, N. Dietz*,** *M. Strassburg, V. Woods,* Georgia State University

Understanding the decomposition kinetics of the chemical precursors involved in nucleation and thin film growth processes is crucial for controlling the growth process. The growth of emerging materials heterostructures such as InN and related alloys requires deposition methods operating at elevated vapor densities due to the high thermal decomposition pressure in these materials. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has so far not been explored in chemical vapor deposition experiments. The extension of chemical vapor deposition (CVD) to elevated pressure opens an avenue for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures. In this contribution we present research results on the decomposition kinetics of ammonia in the laminar flow regime of a high-pressure flow channel reactor. Real-time optical UV absorption and fluorescence spectroscopy has been applied to study the gas phase chemistry as function of flow, pressure and temperature. Data are presented for the optical methods of real-time process monitoring to analyze the decomposition process as well as the initial stages of InN heteroepitaxy.

11:00am **TF-FrM9 In-Situ Real-Time FT-IR Spectroscopy During APCVD: The Effect of B and P Dopants on SiO@sub 2@ Deposition***, A. Effenberger, L.D. Flores,* ***J.E. Crowell,*** University of California, San Diego

In-situ FT-IR spectroscopy has been used to explore the chemical boundary layer (CBL) region formed during atmospheric pressure chemical vapor deposition. Infrared spectra are recorded in 22 second intervals while varying the precursor gas composition. Using TEOS and ozone precursors in combination with borates and/or phosphites, thin films of boro-, phospho-, or borophosphosilicate glass are deposited onto Si wafers at 725K. Gas phase intermediates containing SiOH and BOH functionalities have been observed, and their variation with chemical composition has been investigated. A partial least squares principle component analysis has been used to quantify the reactive chemical mixtures and to evaluate the effect of dopants on the chemical kinetics.

11:20am **TF-FrM10 Optimal Control on Composition and Optical Properties of Silicon Oxynitride Thin Films***,* ***E.C. Samano,*** *J. Camacho, R. Machorro,* CCMC-UNAM, Mexico

The desire to merge the most advantageous physical and chemical properties of both SiO@sub 2@ and Si@sub 3@N@sub 4@ in an optimum combination tailored to various applications in electrical, optical and optoelectronic thin films has pushed a continuous interest in the processing of SiO@sub x@N@sub y@ thin films. Inhomogeneous thin film filters have had an increasing importance in the industry as optical filters. Silicon oxynitride, SiO@sub x@N@sub y@, is a very interesting material for multiple applications, including graded refractive index films. The refractive index can be changed from pure silicon dioxide (1.47) to silicon nitride (2.4) by just varying the film composition. We report the growth of SiO@sub x@N@sub y@ films by reactive laser ablation using two different solid targets, Si@sub 3@N@sub 4@ and Si, in the ambient of N@sub 2@ and O@sub 2@ at various pressures, introduced separately in the growth chamber, as the film is monitored by real time ellipsometry. The oxidation rate in the films is studied for both targets. The composition of the films is in situ determined by AES and XPS. The evolution of the chemical bonding of the species in the film is done by FTIR. The SiO@sub x@N@sub y@ film stoichiometry, bonding character and optical properties are compared as a function of O@sub 2@ pressure while N@sub 2@ pressure is maintained fixed as either the Si@sub 3@N@sub 4@ or Si target is ablated.

11:40am **TF-FrM11 III Nitride-Based Optical Sensors Integrated with a TOF Mass Spectrometer for Aerosol Characterization.***, D. Starikov, N. Medelci, R. Pillai,* Integrated Micro Sensors Inc.*; A. Bensaoula,* ***C. Joseph****, Z. Mouffak,* University of Houston

Mass spectrometry is currently an essential aerosol characterization tool. For many important biochemical and biomedical applications it would be beneficial to perform optical characterization of the aerosol prior to mass spectrometry. Such characterization would include particle detection, evaluation of the particle size, shape, velocity, etc. Rugged multifunctional multi-wavelength solid-state optical sensors fabricated from III nitride based components have a miniature size and demonstrated high performance in detecting various important compounds. In this work integration of our miniature solid-state optical sensors based on III nitrides with a compact Time-of-Flight (TOF) mass spectrometer has been attempted. The sensors were tested ex situ by fluorescence, absorption, and scattering measurements performed on solutions of fluorescein, rhodamine, erythrosine, chlorophyll, pyrene, anthracene, alexa fluor, and red fluorescing microsphere fluorochromes. These measurements indicated that some of the compounds can be detected with a sensitivity as low as 4-5 ppm in a wide range of concentrations. After integration with an ORTOF mass spectrometer (Ionwerks Inc.), the sensors will be tested for detection and characterization of fluorescing and non-fluorescing aerosols. The sensitivity, dynamic, range, detection limits will be evaluated for various aerosol analytes.

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