Topical Conference on Renewable and Alternate Energy
Room 304 - Session EN-SuA

Renewable and Alternate Energy

Moderators: R. Ahrenkiel, University of Denver, G. Parsons, North Carolina State University

3:00pm **EN-SuA1 Scientific Challenges in Sustainable Energy Technology*, N.S. Lewis,*** California Institute of Technology **INVITED**

This presentation will describe and evaluate the challenges, both technical, political, and economic, involved with widespread adoption of renewable energy technologies. First, we estimate the available fossil fuel resources and reserves based on data from the World Energy Assessment and World Energy Council. In conjunction with the current and projected global primary power production rates, we then estimate the remaining years of supply of oil, gas, and coal for use in primary power production. We then compare the price per unit of energy of these sources to those of renewable energy technologies (wind, solar thermal, solar electric, biomass, hydroelectric, and geothermal) to evaluate the degree to which supply/demand forces stimulate a transition to renewable energy technologies in the next 20-50 years. Secondly, we evaluate the greenhouse gas buildup limitations on carbon-based power consumption as an unpriced externality to fossil-fuel consumption, considering global population growth, increased global gross domestic product, and increased energy efficiency per unit of globally averaged GDP, as produced by the Intergovernmental Panel on Climate Change (IPCC). A greenhouse gas constraint on total carbon emissions, in conjunction with global population growth, is projected to drive the demand for carbon-free power well beyond that produced by conventional supply/demand pricing tradeoffs, at potentially daunting levels relative to current renewable energy demand levels. Thirdly, we evaluate the level and timescale of R&D investment that is needed to produce the required quantity of carbon-free power by the 2050 timeframe, to support the expected global energy demand for carbon-free power. Fourth, we evaluate the energy potential of various renewable energy resources to ascertain which resources are adequately available globally to support the projected global carbon-free energy demand requirements. Fifth, we evaluate the challenges to the chemical sciences to enable the cost-effective production of carbon-free power on the needed scale by the 2050 timeframe. Finally, we discuss the effects of a change in primary power technology on the energy supply infrastructure and discuss the impact of such a change on the modes of energy consumption by the energy consumer and additional demands on the chemical sciences to support such a transition in energy supply.

3:40pm **EN-SuA3 Our Solar Power Future: The U.S. PV Industry Roadmap for 2030 and Beyond*, A.M. Barnett,*** University of Delaware*; R. Resch,* Solar Energy Industries Association **INVITED**

The next 10 years are critical for worldwide solar power development. Actions by industry and government will determine whether solar power is catapulted to a new level and whether the United States will regain its position at the forefront of solar power development. Investment decisions over the next decade for research, new manufacturing, and creating new markets will determine where solar power will thrive-and where it will merely survive. Solar power can provide great value in residential and commercial grid-connected applications, for individual consumers and businesses, as well as for utilities and the communities they serve. Our goals for 2030 are solar power system costs of $2.33 per watt, solar electricity prices of 3.8 cents per kilowatt-hour (kWh) delivered to the customer, installed solar power generation of 200 gigawatts (GW), and direct employment of 260,000 people.

4:20pm **EN-SuA5 Hydrogen and Chemicals from Fossil and Renewable Fuels by Autothermal Reforming*, L.D. Schmidt,*** University of Minnesota **INVITED**

Autothermal reactors have great promise for hydrogen and chemicals production because they have reactor residence times of 10-3 seconds and require very simple reactors. We describe the production of hydrogen and olefins from fossil fuels from methane to diesel and from renewable fuels such as ethanol and biodiesel in millisecond reactors. For successful vaporization and mixing of heavy fuels the use of fuel injectors for rapid vaporization and mixing is essential to suppress flames and carbon formation. For ethanol to hydrogen we obtain 80% selectivity to hydrogen at nearly 100% conversion of ethanol and oxygen for an ethanol-air feed. By adding water we obtain 110% (H2 from ethanol and water) in a single stage reactor and 130% H2 selectivity in a staged reactor where a cooler section undergoes the water gas shift reaction. For biodiesel (the methyl ester of C18 fatty acids from soy oil), we can obtain 80% H2 selectivity at C/O=0.8 and 80% selectivity to olefins at C/O=1.5. At higher C/O ratios the ester linkage also survives to produce olefinic esters. Modeling with detailed surface and homogeneous chemistry is used to simulate and understand these processes.

5:00pm **EN-SuA7 Fuel Cells from the Viewpoint of a Skeptical Optimist*, T. Zawodzinski,*** Case Western Reserve University **INVITED**

Fuel cells have been the subject of hype and backlash of late. The hype took various forms, including the 'We'll have a product next year' variety as well as inflated estimates system efficiency, simplicity, etc. Hopes have been dashed because of failure to adequately anticipate the difficulty of some technical and practical problems and from the short duration over which present-day configurations have been tested. The backlash has evolved from reaction to not meeting promises as well as from the realization of the aforementioned problems. Also, fuel cells are linked in many minds to the Hydrogen Economy, which has its own set of detractors. After reviewing these promises and pitfalls, this talk will discuss the current state of development of fuel cells, highlighting technical state of the art. Significant achievements and substantial activities to address some of the major challenges posed by the combination of cost, reliability and performance/functionality factors will be highlighted. By presenting a realistic assessment of these aspects, we hope to leave people with 'reasons to believe' in the promise of fuel cell technology in some applications

Advanced Surface Engineering
Room 201 - Session SE-MoM

Nanocomposites and Coatings with Enhanced Thermal Stability

Moderator: J.M. Schneider, RWTH Aachen

8:20am **SE-MoM1 John Thornton Memorial Award Lecture: Understanding of the Preparation and Properties of Superhard Nanocomposites***, **S. Veprek**[1]*, Technical University Munich, Germany **INVITED**

Since the first report on the strong enhancement of hardness to 60-70 GPa in the Ti-Si-N system by Li Shizhi et al.,@footnote 1@ followed by the publication of the generic design concept,@footnote 2,3@ a large number of papers were published on this and similar systems which have led to some misunderstanding and controversies regarding the suitable deposition techniques and conditions, the maximum achievable value of hardness, the mechanism of the hardness enhancement, thermal stability and others. So far, plasma induced deposition techniques, such as glow discharge CVD, reactive sputtering and vacuum arc evaporation were used to prepare thin films of such materials. In my lecture I shall try to answer some of the open questions. First it will be shown how to differentiate between the superhard nanocomposites and coatings in which the hardness enhancement is due either to energetic ion bombardment during deposition or to solution hardening. The focus will be on the recent results regarding the spinodal nature of the phase segregation in this system, and on the thermodynamic and kinetic conditions needed to complete it during the deposition to obtain superhard nanocomposites with high thermal stability. The high hardness enhancement achieved in these materials is associated with the formation of a nanostructure where few nanometer small crystals of a hard transition metal nitride are "glued" together by about one monolayer of silicon nitride, as reported in our earlier HYPERLINK "mailto:work.@footnote"work.@footnote 1,2@ This finding was recently confirmed by the work of Oden et HYPERLINK "mailto:al.@footnote"al.@footnote 5@ on the preparation of high-quality heterostructures where the highest hardness enhancement was achieved for one monolayer of Si@sub 3@N@sub 4@. The first principle DFT calculations by C. Stampfl et HYPERLINK "mailto:al.@footnote"al.@footnote 6@ lend further support to this concept and show that, as predicted (see references quoted in@footnote 4@), such nanostructure reaches the ideal strength. The unusual combination of a high hardness, high resistance against crack formation and high elastic limit is a simple consequence of the almost flaw-free nature of these nanocomposites@footnote 4@ and of a finite activation volume for the initiation of plastic deformation within an amorphous HYPERLINK "mailto:phase.@footnote"phase.@footnote 7@) In order to correctly describe the mechanical properties of these materials, a new constitutive material's model was elaborated that accounts for the pressure enhancement of elastic moduli and of the flow stress. To be able to quantitatively describe the plastic deformation under conditions of a pressure dependent flow stress, the von Mises yield criterion had to be expressed in terms of a critical deviatoric strain. This model was then implemented into an advanced Finite Element Method code and the behavior of the materials upon indentation was studied in some HYPERLINK "mailto:detail.@footnote"detail.@footnote 8@ An important result of this work is the strong stiffening for both, elastic and plastic deformation due to the increase of the elastic moduli and of the flow stress by the high pressure under the indenter which is not found in conventional materials. The lecture will conclude with a brief overview of the recent industrial applications. @FootnoteText@ @footnote 1@ S. Z. Li, Y. Shi and H. Peng, Plasma Chem. Plasma Process. 12 (1992) 287. @footnote 2@ S. Veprek and S. Reiprich, Thin Solid Films 268 (1995) 64. @footnote 3@ S. Veprek, S. Reiprich and S. Z. Li, Appl. Phys. Lett. 66 (1995) 2640. @footnote 4@ S. Veprek, M. G. J. Veprek-Heijman, P. Karvankova and J. Prochazka, Invited Review, Thin Solid Films 476 (2005) 1. @footnote 5@ M. Oden, invited paper at the 51st Int. Symp. of the American Vacuum Society, Anaheim, November 14 – 19, 2004. @footnote 8@ S. Hao, B. Delley, and C. Stampfl, School of Physics, The University of Sydney, to be published. @footnote 7@ M. J. Demkowicz and A. S. Argon, Phys. Rev. Lett. 93 (2004) 025505-1. @footnote 8@ R. G. Veprek, D. M. Parks, A. S. Argon, and S. Veprek, to be published.

9:00am **SE-MoM3 Effect of Momentum Per Arriving Atom on nc-TiN/a-Si@sub x@N@sub y@ Nanocrystalline Composite Thin Film Properties in a Pulsed DC Magnetron Sputtering System***, **P. Sunal**, M.W. Horn,* The Pennsylvania State University

The mid-frequency pulsed dc range of 50-250 kHz was used to co-sputter nanocrystalline-TiN/a-Si@sub x@N@sub y@ films. A combinatorial process was performed in a reactive nitrogen environment from pure Ti and Si targets. An asymmetric bipolar pulsing frequency affects the plasma properties and results in a change in the density and energy of arriving ions at the growing film surface. The plasma potential, electron density, and electron temperature have been determined using a Langmuir probe and used with ion specie results from an energy resolved mass spectrometer to calculate the momentum per arriving atom. Using nanoindentation, the reduced modulus and hardness of the films were characterized and related to the plasma properties during deposition. The momentum per arriving atom shows threshold values for changes in the morphology, which result in different mechanical properties. Finally, the plasma properties were studied against the sputter pressure. At higher pulsing frequencies, the plasma potential increases causing energetic bombardment which yields smaller nanocrystal diameters and a stronger (200) preferred crystallographic orientation. Oxygen contamination of the thin films leads to degradation of the film properties and was investigated by using a silicon nitride capping layer to hermetically seal the film before leaving vacuum.

9:20am **SE-MoM4 Columnar Growth, Nanostructure and Properties of TiC/a-C:H Nano-Composite Coatings***, **D. Galvan**, Y.T. Pei, J.Th.M. De Hosson,* University of Groningen, The Netherlands

TiC/a-C:H coatings were deposited through closed field unbalanced magnetron sputtering (CFUBMS) reactive deposition. Different acetylene gas flow and substrate bias values were employed to vary the coatings composition and nanostructure. To improve adhesion between substrate and coating a Cr-Ti/Ti-TiC graded interlayer was introduced. Various techniques were employed to study the formation of TiC particles within the a-C:H matrix, e.g. EPMA, XPS, grazing angle XRD and high-resolution transmission electron microscopy (HR-TEM). The investigations provide detailed information about the TiC particles volume fraction, particle size and their size distribution in different coatings. It turns out that the Ti content affects to a great extent the columnar features. It is influenced by processing parameters such as deposition temperature or ion flux to atom flux ratio (ion number). An explanation of this effect is provided based on the observed nanostructure and the deposition technique employed. The mechanical performance of coatings with various chemical compositions was investigated through nano-indentations, focused ion beam (FIB) and TEM observations. It was found that the C-enriched columnar boundaries are the locations of crack nucleation and propagation. The investigations confirmed that a coating of low elastic modulus favors the redistribution of the applied load over a larger area, delaying the onset of plastic deformation and subsequent coating failure in these systems. The influence of the toughness of the coatings on their tribological performance is discussed.

9:40am **SE-MoM5 Smart Nanocomposite Tribological Coatings with Chameleon Behavior***, **A.A. Voevodin**,* Air Force Research Laboratory **INVITED**

A review of a recent progress in developing new tribological materials for operating across multiple environments relevant to aerospace applications is provided. New coating materials were designed to rearrange their structure and chemistry on demand to adapt to variable surface conditions (environment humidity, temperature). These materials have been dubbed chameleon because of their ability to change their surface chemistry and structure to avoid wear. The chameleon coating concept involves a nanocrystalline/amorphous nanocomposite structure, where individual phases are arranged to provide a high degree of mechanical and thermal stability and, at the same time, serve as nano reservoirs for tribological surface self-reconstruction. The stored materials are released from nanophase reservoirs in the process of wear and tribological surface chemistry and structure change to continuously reduce friction and wear. This surface response is triggered by changes in the operating environment and/or temperature. Several mechanisms are employed, including self-induced crystallization of amorphous dichalogenide phases, nucleation of nanograins of low melting point metals, formation of low melting point glassy ceramics, and change in the electron hybridization of carbon. These mechanisms were explored in sliding wear tests performed in controlled humidity air, dry nitrogen, and vacuum, as well as at high temperature in air.

[1] **John A. Thornton Memorial Award Winner**

10:20am **SE-MoM7 Optimization of Multilayer Wear-resistant Thin Films Using Finite Element Analysis**, ***R.K. Lakkaraju***, *F. Bobaru, S.L. Rohde,* University of Nebraska

Extensive research has been carried out by researchers on the growth and characterization of multilayer protective coatings, but the design of these coatings still remains largely empirical. In this regard, recent progress has been made in developing a design approach for optimizing multilayer coating structure before deposition which would help in saving time and material. In pursuit of optimal design, finite element analysis using a plane strain, hertzian contact model was developed to investigate the stress/strain behavior within the layers of the system. The present study looks to find optimal thicknesses of individual layers in the multi-layer coating-substrate system. First test case is a multiobjective optimization of a multilayer system performed by minimizing the strain discontinuities at the coating/substrate interface and the stresses developed in top layer, under combined normal and tangential load conditions. Another option is a single objective optimization (minimizing the strain discontinuity) by constraining the stress values below yield strength. We discuss the use and efficiency of optimization algorithms such as genetic algorithm and gradient based routines used in the present work, and the preliminary results are compared to pin-on-disk wear results of empirically designed coatings.

10:40am **SE-MoM8 Investigation on the Thermal Cycling Behaviour of Graded and Multilayered Lanthanum Zirconate as EB-PVD Thermal Barrier Coating**, *K. Bobzin, E. Lugscheider,* ***N. Bagcivan,*** Surface Engineering Institute (IOT) RWTH Aachen, Germany

Thermal cycling behavior of thermal barrier coatings (TBC) is essential for the increase of efficiency of gas turbines. Traditionally Yttria partially stabilized Zirconia (YPSZ) coatings are used as TBCs on turbine blades. One approach within the collaborative research center (SFB) 561 "Thermally highly loaded, porous and cooled multilayer systems for combined cycle power plants" is to develop innovative TBCs to increase the overall efficiency of the power plant from 58% up to 65%. Investigations on some materials with perovskite, spinelle and pyrochlore structure have shown a great potential of Lanthanum Zirconate (pyrochlore) as thermal barrier coating. In this work Lanthanum Zirconate has been developed as TBC using electron beam physical vapour deposition (EB-PVD). TBCs deposited by EB-PVD show a columnar grain microstructure. A columnar grown TBC is able to balance the difference in thermal expansion between base material and TBC by the relative movement of the single columns. Two different coating architectures have been developed for the TBCs. First a multilayered TBC consisting of YPSZ and Lanthanum Zirconate has been deposited. In the second approach a graded TBC with a transition from YPSZ to Lanthanum Zirconate has been deposited by EB-PVD. The thermal cycling behavior of these coatings on Inconel Alloy 600 has been investigated by a thermal cycling test at 1050°C. Additionally the coatings have been characterized by x-ray diffraction (XRD), scanning-electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and nanoindentation. The results of thermal cycling test show an increase of number of cycles before fatigue from 1380 cycles for YPSZ to 3390 cycles for graded YPSZ/Lanthanum Zirconate and 4140 cycles for multilayered YPSZ/Lanthanum Zirconate.

11:00am **SE-MoM9 Established Protective Cutting Tool Coatings for Difficult Machining Operations**, ***K. Bobzin***, *M. Maes, C. Pinero,* RWTH Aachen University, Germany **INVITED**

This paper presents a review of the most important thin coatings developed for the protection of cutting tools. Special attention was given to the development of promising coatings for difficult machining operations. Because of the increasing of the complexity in the aircraft and nuclear industry and the elevated operating temperatures, super alloys were developed from simple nickel-chromium matrix to multi-element, multi-phase systems. These new nickel-based super alloys are specially favored for their exceptional thermal resistance and ability to retain mechanical properties at elevated temperatures. However, they are classified as difficult-to-machine materials due to their high shear strength, work hardening tendency, highly abrasive carbide particles in the microstructures, strong tendency to weld and form built-up edges. Also, their tendency to maintain a high strength at the elevated temperatures generated during machining because of their low thermal conductivity constitutes an important challenge. Nowadays, TiAlN is well known because of its excellent overall performance in cutting operations. Also crystalline Al@sub 2@O@sub 3@ shows a high potential for the protection of cutting tools due to its very good chemical and thermal properties. However an adequate coating system for machining super alloys was not found yet. In order to obtain the appropriated properties combination in a single coating system, different TiAlN + @gamma@-Al@sub 2@O@sub 3@ coating system combinations were deposited on cemented carbide cutting inserts and characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Surface energy of the coated samples was measured. Tribological and chemical properties were analyzed at room and high temperatures.

11:40am **SE-MoM11 Multifunctional SiAlON Ceramic Coatings for High Temperature Applications**, *J.I. Krassikoff, D.J. Frankel, T.A. Dunn, D.R. Southworth,* ***R.J. Lad,*** University of Maine

SiAlON ceramics possess oxidation resistance, high strength, and thermal shock resistance, which make them extremely attractive for applications in 1000-1500°C oxidation environments. We have investigated well-defined SiAlON thin films deposited by rf magnetron co-sputtering of Al and Si targets in Ar/O@sub 2@/N@sub 2@ mixtures. By precisely controlling film architecture at the nanometer level, coating structures having homogenous, gradient, or multilayer compositions that span the full range of O/N and Al/Si ratios have been synthesized, and their chemical, thermal, and mechanical properties have been characterized. Nitride-rich SiAlON film compositions are extremely wear resistant, yet they become oxidized during thermal treatments in air between 1000-1500°C. Compositionally graded coatings with oxide-rich terminations show improved oxidation resistance. Similarly, Al@sub 2@O@sub 3@/Si@sub 3@N@sub 4@ laminate structures exhibit low wear and chemical stability at high temperature. Photolithographically patterned thin film metal resistors embedded at the SiAlON/substrate interface have been used to quantify the oxygen penetration rates through the SiAlON film structures during isothermal annealing and thermal cycling experiments. Accelerated testing consisting of rapid thermal cycling in various reactive environments was accomplished using a microfabricated heater platform. The role of film stress on resulting mechanical properties was investigated using microfabricated cantilever structures.

Thin Films

Room 306 - Session TF+EM-MoM

Thin Films for Photovoltaic and Energy Applications

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

8:20am **TF+EM-MoM1 Hydrogen - The World of Tomorrow?**, ***G.N. Richter***, Chevron Fellow Emeritus **INVITED**

We have all heard of the coming world of hydrogen, and how it will become our energy carrier of choice, both clean and efficient, a major input for many chemical processes and, perhaps, our saviour. I am sure that this is coming, and it will bring a major change to many things we do. It will take a revolution to bring this about and it won't be until some time in the future. The question isn't if it will happen, but when will it come and what is needed to bring it about? Others at this meeting are telling us of the uses of hydrogen, its promises and its behaviour. But, there are also important questions to ask about where will the hydrogen come from and the infrastructure needed for us to be able to use it. It is the difficulty in answering these questions that is holding back the revolution. And it is these points that I would like to discuss with you today. Not the promises we have all heard, but how we can get to this "promised" land, as well as some of the things we might all do to get there sooner. What are the needs and opportunities for all of us to address?

9:00am **TF+EM-MoM3 Carbon Nanotube Catalyst for PEM Fuel Cells**, ***J. Narayanamoorthy***, *S. Durairaj, J. Choi,* Wayne State University

Carbon nanotubes have unique properties for future fuel cell applications such as diverse electrical properties, large surface area to volume ratio, chemical inertness, etc. The role of carbon nanotubes for the polymer electrolyte fuel cell has been investigated. First, the morphological, electrical, and mechanical role of the carbon nanotubes in the catalyst layer was studied. There was minimal cracking and maximal interconnect in the layer with carbon nanotubes. The resistance of the catalyst layer reduced due to the presence of carbon nanotubes and mechanical properties also showed good improvement. Further, carbon nanotubes themselves were employed as catalyst in place of noble metals and were optimized by tuning the electronic properties of carbon nanotubes. In this presentation, we will discuss the correlation between catalytic activity and the electronic structure of carbon nanotubes.

9:20am **TF+EM-MoM4 Growth of CIGSS Thin Film Solar Cells on Flexible Stainless Steel Substrates of Various Thicknesses**, ***A. Kadam***, *A. Jahagirdar, N.G. Dhere,* University of Central Florida

The article presents the effect of surface roughness and thicknesses of stainless steel(SS) substrates on the growth behavior of CuIn@sub 1-x@Ga@sub x@Se@sub 2-y@S@sub y@(CIGSS) absorber thin film solar cells. The work was carried out on 430 grade SS of thicknesses 25 µm, 50 µm and 127 µm. Surface roughness gradually decreased from 254 Å for 25 µm to 62.3 Å for 127 µm substrate. Thinner foil has higher surface roughness as it required more processing steps. Deposition sequence was Mo/SS/Mo/CIGSS/CdS/i:ZnO/ZnO:Al/Ni/Al. Mo back contact and Cu-Ga-In metallic precursors were deposited by DC magnetron sputtering. Mo was deposited on both the sides of SS to prevent the reaction of selenide and sulfide gases with SS during processing. Mo was deposited in a three-layer sequence. Mo layer deposited at low DC power and high argon gas pressure develops tensile stress while that deposited at high power and low pressure exhibits compressive stress. Tensile layer was sandwiched between two compressive layers to reduce the overall stress and to build the thickness of 500 nm. Identical parameters were used for deposition of metallic precursors on all three substrates. The elemental stack was selenized at 400@super o@C for 10 minutes followed by sulfurization at 475@super o@C for 20 minutes. CdS, n-type hetero-junction partner was deposited by chemical bath deposition. Window bilayer of i:ZnO and ZnO:Al were deposited by RF magnetron sputtering and Ni/Al contact fingers were deposited by e-beam evaporation. The crystal structure, surface morphology, chemical variation and cell efficiency were studied using the characterization technique such as x-ray diffraction, scanning electron microscopy, Auger electron spectroscopy, transmission electron microscopy, current-voltage and quantum efficiency measurement to bring out the variation in the growth behavior and cell efficiency on substrates having varied physical properties.

9:40am **TF+EM-MoM5 Surfactant-assisted Growth of CdS Thin Films for Photovoltaic Applications**, ***C.L. Perkins***, *F.S. Hasoon,* National Renewable Energy Laboratory

A common non-ionic surfactant, Triton X-100, was used to modify the chemical bath deposition (CBD) of CdS "buffer" layers on Cu(In,Ga)Se@sub 2@ (CIGS) thin films. X-ray photoelectron spectroscopy and Auger electron spectroscopy data demonstrate that films produced with the surfactant have about the same levels of impurities as films grown without it. It was found that Triton X-100 allowed the use of CdS layers that were 3-4 times thinner than those used normally in high efficiency CIGS-based devices, with no loss in cell performance. For these thin CdS layers and relative to devices made without the surfactant, average absolute cell efficiencies were increased from 10.5% to 14.8%, or by a relative 41%. Visual inspection of the CdS depositions reveals one possible mechanism of the surfactant's effects: bubbles that form and adhere to the CIGS surface during the chemical bath deposition are almost completely eliminated with the addition of the TX-100. Thus, pinholes and thin areas in the CdS layers caused by poor wetting of the substrate surface are sharply reduced, leading to large increases in the open circuit voltage in devices produced with the surfactant.

10:00am **TF+EM-MoM6 Surface Energies and Surface and Grain Boundary Nanochemistry of Cu(In,Ga)Se@sub 2@**, *C. Lei, D. Liao, A. Hall, I.M. Robertson,* ***A. Rockett***, University of Illinois

A combination of angle-resolved photoelectron spectroscopy, atomic force microscopy, and analytical high-resolution transmission electron microscopy including nanoprobe energy dispersive spectroscopy (EDS) and angular darkfield imaging have been used to characterize the surfaces and grain boundaries in a wide variety of Cu(In,Ga)Se@sub 2@ epitaxial single crystal and polycrystalline thin films. We have observed the formation of a wide variety of nanoscale and microscale voids in polycrystalline grain boundaries and in heteroepitaxial interfaces. It is argued that these are Kirkendall voids. Likewise, trapped internal voids within grains are observed in dislocation cores and at twin termination boundaries. These have been analyzed and a Wulff construction developed to characterize the surface energies in the material. The results show that the polar metal-terminated (112) planes are the lowest energy surfaces, followed by the Se-terminated (112) planes. These results are consistent with the surface morphology of growing epitaxial layers of various orientations, indicating that the surface faceting is a largely equilibrium rather than kinetically-determined result. Other planes are stable when covered by a surfactant layer of Cu@sub 2@Se, which occurs naturally when the film is deposited in an average Cu-rich condition. Grain boundaries are also found to exhibit faceted growth. Surprisingly, in spite of these surfaces being polar, no chemistry change is observed with nanoprobe EDS in the grain boundaries relative to the bulk grains for films grown at high temperatures. For low temperature depositions (below 450°C), non-equilibrium grain boundary compositions are observed. Clean metal-terminated (112) surfaces are shown to have Fermi energies higher in the energy gap when treated in various ways than the corresponding Se-terminated surfaces. The results are related to solar-cell device performances, the primary application of these materials.

10:20am **TF+EM-MoM7 Preparation and Characterization of Transparent Conducting ZnTe:Cu Back Contact Interface Layer for CdS/CdTe Solar Cell**, *U. Avachat,* ***N.G. Dhere***, University of Central Florida

This paper presents preparation and characterization of transparent conducting ZnTe:Cu back contact interface layer for CdS/CdTe thin film solar cells for multijunction thin film PV applications. Polycrystalline ZnTe:Cu thin films were grown by Hot Wall Vacuum Evaporation technique. Hot wall set up was developed to obtain highly stoichiometric films with better material yield and thickness uniformity. 500 nm ZnTe:Cu films were prepared on glass and characterized for stoichiometry, structural properties and optical transparency by electron probe microanalysis, optical transmission spectroscopy and X-ray diffraction technique respectively. Highly stoichiometric ZnTe:Cu films were obtained on glass with optical transparency in the range of 70-80 % in near IR region. X-ray diffraction patterns revealed face-centered cubic phase of ZnTe with preferred {111} orientation. CdS/CdTe solar cells were completed with configuration, CdS/CdTe/ZnTe:Cu/ZnO:Al/Ni-Al and CdS/CdTe/ZnTe:Cu/ITO/Ni-Al. ZnO:Al and ITO thin film layers were deposited by RF magnetron sputtering and Ni-Al contact fingers were deposited by e-beam vacuum evaporation through metallic mask. Completed CdS/CdTe solar cells were characterized for their I-V characteristics using current voltage measurements.

10:40am **TF+EM-MoM8 CuPc:C60 Blend Film: A Photoemission Investigation**, ***L. Lozzi***, University of L'Aquila and INFM-CNR, Italy; *V. Granato,* University of L'Aquila, Italy; *S. La Rosa,* Sincrotrone Trieste Scpa, Italy; *S. Santucci,* University of L'Aquila and INFM-CNR, Italy

Recently a strong research effort has been devoted to study the application of organic-inorganic multiplayer films for the preparation of photovoltaic devices. Generally these devices are composed by a multilayer of an organic film which is the active layer, a charge acceptor (to reduce the electron-hole recombination probability) and the two metallic contacts to collect the charges (as ITO, Au and Al). The most used compounds are Copper Phthalocyanine (CuPc), as organic layer, and the C60, as electron acceptor. An improved system, showing an higher efficiency, can be prepared depositing, between the metallic contacts, a blend of active layer and charge acceptor. With this design one of the most important parameter, the exciton diffusion length (which is quite small in the organic systems), becomes less important because it is obviously much higher then the CuPc-C60 distance when these molecules are bonded. The realization of these blend films determines the strong reduction of the luminescence of the CuPc film, but it is not clear if in this blend film there is the formation of bonds between CuPc and C60 molecules or if its electronic structure is simply the sum of the electronic states of the two single compounds. In this contribution we will show the results obtained using soft X-ray photoemission spectroscopy on CuPc:C60 blend films, with different concentrations. These films have been deposited in ultra high vacuum by thermal evaporation. We will show a variation of the HOMO states as a function of the concentration ratio. This HOMO level moves towards the Fermi level, influencing the interface properties with the metallic contacts. The intensity and position of this level is strongly influenced by the CuPc:C60 ratio. This result could be related to the variation of the optical properties of these films.

11:00am **TF+EM-MoM9 Silicon Thin Films from Trichlorosilane for Electron Beam Recrystallized Solar Cells**, ***C. Groth***, *K. Ong,* Hamburg University of Technology, Germany

The project's aim is to produce polycrystalline thin film solar cells on low cost substrates, especially on float glass. The chemical processing is entirely dry, which leads to high efficiency and throughput. There is no size limitation using this sequence of processing; even the in-line production of complete solar panels is feasible. An intermediate Tungsten (W) layer of approximately 1 µm is used to maintain mechanical stability at high temperatures. Furthermore, it is used as diffusion barrier during the recrystallisation process and serves as back surface reflector and electrical contact. Two deposition processes are currently under investigation: DC-magnetron sputtering and plasma enhanced chemical vapour deposition

(PECVD) using tungstenhexafluoride (WF@sub 6@) as precursor. Both processes are using substrate temperatures of ~400 °C. Analysis using XRD (x-ray diffraction) shows formation of @alpha@-W for sputtered layers while PECVD layers consist of @alpha@- and @beta@-W, depending on the process parameters. The silicon (Si) basis with a thickness of 15 µm is deposited by PECVD directly from trichlorosilane (SiHCl@sub 3@) as precursor at high rates of ~200 nm/min. Substrate temperature during the process is ~550 °C. RF frequencies of 13.56 MHz are used in both PECVD processes. P-doping of the basis is done in-situ using borontrichloride (BCl@sub 3@). The nanocrystalline silicon film is recrystallised by a line-shaped electron beam at high velocities of about 60 mm/s. This leads to grain sizes of up to several 100 µm. A PECVD deposited amorphous silicon layer will be used as hetero emitter to complete the solar cell.

11:20am **TF+EM-MoM10 Plasma-Assisted Co-Evaporation of Thin Films for Photovoltaic Applications***, S. Kosaraju, J.A. Harvey,* ***C.A. Wolden,*** Colorado School of Mines

This presentation describes the development of plasma-assisted co-evaporation (PACE) and its application to the formation of @beta@-In@sub 2@S@sub 3@ and InN thin films. The former is an alternative window layer for copper indium diselenide based devices and the latter is a potential absorber. In PACE metals are supplied by conventional thermal evaporation, while the chalcogen or nitrogen gas precursors are activated by an inductively coupled plasma (ICP) source. The performance of the ICP source to activate both H@sub 2@S and N@sub 2@ was measured and optimized using a combination of optical emission spectroscopy and mass spectrometry. Transport modeling was used to quantify the flux distributions of both the co-evaporated metal and the reactive species from ICP source impinging upon the substrate. The source geometries were positioned asymmetrically so that the influence of composition and absolute rate could be ascertained from a single deposition experiment in a combinatorial approach. Model predictions were compared and validated using measurements of film thickness, composition, and quality. Through the deposition of @beta@-In@sub 2@S@sub 3@ and InN it was demonstrated that PACE provides substantial improvements in both materials utilization and substrate temperature reduction. For the case of @beta@-In@sub 2@S@sub 3@ it was observed that film quality was highly sensitive to the S/In ratio. The buffer layer was formed as low as 100 °C, and it was found that both the morphology and optical band gap were strong functions of temperature. In the case of InN the most important parameter was the excitation of nitrogen in the ICP source. It was shown that the introduction of argon was beneficial to nitrogen activation as evidenced by measurements of crystal quality and electronic properties.

11:40am **TF+EM-MoM11 Anomalously High Seebeck Coefficient Observed in V@sub 2@O@sub 5@ Thin Films***,* ***S. Iwanaga****, N.T. Nguyen, R.B. Darling, F.S. Ohuchi,* University of Washington

Vanadium oxides, especially vanadium pentoxide (V@sub 2@O@sub 5@), have gained recent attention for a wide range of applications such as ion storage layers in solid-state batteries, windows for photovoltaic cells, and electro- and photo-chromic devices. Various transport properties have been investigated in the past; however, its thermoelectric properties have not been well characterized. Recently, we observed an anomalously high Seebeck coefficient from sol-gel deposited V@sub 2@O@sub 5@ thin films. Seebeck coefficients of between - 500 to - 700 µV/K were measured, with corresponding electrical conductivities ranging from 0.005 to 0.1 @ohm@@super -1@ cm@super -1@. Unlike conventional materials, the Seebeck coefficients and electrical conductivity act in parallel, suggesting that the carrier concentration increases while maintaining a high Seebeck coefficient. This peculiar transport characteristic appears to be related to polaron hopping. The power generation of the film was further estimated by current-voltage (I-V) measurements to assess the thermoelectric performance of the films. The I-V measurements were performed while applying a temperature gradient to the film by applying a current source in such a way that the thermopower current was suppressed by applying the current in the opposite direction. The I-V characteristics at different applied @DELTA@T were thus obtained, from which the output power (load characteristic, P) was calculated from the I-V data.

Thin Films
Room 306 - Session TF+NS-MoA
Focused Beam Processing & Fabrication

Moderator: J.D. Fowlkes, University of Tennessee

2:00pm **TF+NS-MoA1 Beam-Induced Nano-Structuring for Advanced Mask Repair*, T. Liang,*** Intel Corporation **INVITED**

Photomask repair is a process of editing local pattern structures by adding or removing materials in order to restore a defective mask to good lithographic condition and, in many instances, it is an enabling step for yielding a defect-free mask. Beam-induced nano-structuring has been developed for such process with the use of photons, ions and electrons. However, it has become ever more challenging to repair advanced photomasks because of the limited extendability of these technologies to meet the critical defect specifications and tight edge placement. Specifically, the use of aggressive optical proximity correction structures, resolution enhancement techniques, such as phase-shifting, and entirely new types such as EUV reflective masks has placed a great need for stringent lateral and vertical dimensional control. A capable repair process removes the defect with sufficient placement precision while at the same time preserves the optical integrity of the repaired site. This essentially requires also a damage-free process. Mask shops have put ever increasing emphasis and effort in mask repair at the back end of the production line to fix every defect possible in order to restore an otherwise defective mask. This invited talk will present an overview of advanced mask repair and the lithographic requirements, followed by an assessment of four repair technologies by comparing their respective uniqueness and limitations. The discussion of underlying mechanisms for different repair processes will provide an insight to the fundamental capabilities and ways for further improvements. Detailed descriptions will be given for examples representing binary Cr-on-glass, phase-shifting and EUV masks including repair qualification. I will present our recent progress in electron beam mask repair development and discuss future directions in mask repair using nano-structuring technologies to support the aggressive lithography roadmap

2:40pm **TF+NS-MoA3 Electron Beam Induced Processing Techniques for Advanced Lithography Mask Repair*, D.A. Smith,*** University of Tennessee, Knoxville*; J.D. Fowlkes,* University of Tennessee, Knoxville, US*; T. Liang,* Intel Corporation*; P.D. Rack,* University of Tennessee, Knoxville

Producing defect-free photomasks for semiconductor applications is a critical and challenging operation. Enabling nano-processes are being developed for mask repair to meet the defect requirements for advanced 193nm and EUV lithography. To this end, we are investigating electron beam induced deposition (EBID) and etching (EBIE) techniques for mask repair involving material deposition and removal, respectively. The EUV masks are typically composed of multi-layer Mo-Si on a quartz-like substrate, capped with a Ru etch stop layer with an overlaying TaBN absorber layer. For material removal, an etchant vapor such as XeF2 or NF3 is flowed over the mask surface in an SEM in the presence of an electron beam. The electron beam interacts with the etchant gas to produce an electron induced etch effect, allowing material removal at a controlled rate with nano-scale precision. Repair operations involving deposition are typically carried out with a precursor gas such as cyclopentadienylplatinum (IV)-trimethyl (CpPtMe3) which dissociates under an electron beam and adsorbs to the substrate. This presentation will demonstrate the results of a study involving the optimal operating conditions for controlled etching and deposition, including an analysis of the sidewalls, roughness, and spontaneous etching. Monte-Carlo based computer simulations of the material deposition will also be employed to describe the effects of varying system parameters such as operating voltage, gas pressure, current and time.

3:00pm **TF+NS-MoA4 Reduction of Laser-Induced Roughness in a-Si:H Surfaces for Vacuum Compatible Lithography*, R.N. Jacobs,*** US Army RDECOM CERDEC Night Vision and Electronic Sensors Directorate, 22060*; E.W. Robinson, A.J. Stoltz, J.H. Dinan,* US Army RDECOM CERDEC Night Vision and Electronic Sensors Directorate*; L.G. Salamanca-Riba,* University of Maryland, College Park

A vacuum compatible lithography technique has recently been demonstrated, whereby amorphous hydrogenated silicon (a-Si:H) films are used as a resist. Following plasma deposition of the a-Si:H film, poly-Si patterns are generated on the surface by excimer laser exposure through a projection mask. Development is then carried out by hydrogen plasma etching for which etch selectivities of over 1000:1 have been achieved for a-Si:H and poly-Si regions.@footnote 1@ However the rms roughness induced by excimer laser irradiation can be well over 10 times that of the as-deposited a-Si:H surface. This is problematic because the roughness may be transferred to underlying device layers during subsequent pattern transfer plasma etching. We have developed a step-wise laser irradiation procedure that results in a reduction of surface roughness by an order of magnitude to a level of ~1 nm (rms). This value is approximately equal to the surface roughness in the as-deposited a-Si:H film. The irradiation procedure uses multiple pulses with progressive increases in the energy density, in contrast to single high energy density pulses used previously. Transmission electron microscopy and Fourier transform infrared spectroscopy are used to understand and confirm the mechanism behind this process. Our data suggests that the observed reduction in roughness is due both to smaller grain sizes and to a slow rate of H removal from the film surface. While useful for a-Si:H vacuum-lithography processing, our results also hold significance for other applications of laser processed a-Si:H, even where different film properties may be desired. @FootnoteText@ @footnote 1@R.N. Jacobs, A.J. Stoltz, J.H. Dinan, and L. Salamanca-Riba, J. Vac. Sci. Technol. B, 22 1071 (2004).

3:20pm **TF+NS-MoA5 Maskless, Direct-Write Nanolithography using Electron Beam-Induced Deposition*, S.J. Randolph,*** University of Tennessee, Knoxville*; J.D. Fowlkes,* University of Tennessee, Knoxville, US*; P.D. Rack,* University of Tennessee, Knoxville

Several groups have investigated electron beam-induced deposition (EBID) as a nanoscale direct-write fabrication technique. The EBID process is similar to focused ion beam processing; however deleterious damage associated with ion implantation is mitigated when using an electron beam. Our group has been investigating this technique as a tool for rapid nanoscale device prototyping as well as for device and lithography mask repair. More recently, we have investigated EBID as a technique to be coupled with a massively parallel electron beam lithography concept-the so-called Digital Electrostatic E-beam Array Lithography (DEAL) system. The goal is to develop an alternative ultra-thin resist scheme for the DEAL low energy electron beam lithography system. We have developed a single layer and bilayer resist scheme using a tetraethylorthosilicate (TEOS) and tungsten hexafluoride precursors to deposit SiO@sub x@ and tungsten resist layers. In this presentation our experimental procedure and EBID system will described and the DEAL lithography concept briefly reviewed. The fundamental EBID process will be explained, and we will describe the relevant EBID parameters that affect the single and bilayer EBID resist schemes. The effects of secondary, backscattered, and forward scattered electrons on the resolution and exposure requirements will also be explained, and dose requirements for optimum exposure as a function of beam energy will be illustrated. Pattern transfer of sub-100 nm features requires excellent control of etch selectivity and profile control. The effects of RIE parameters such as pressure, power, and chemistry as they are related to etch selectivity and profile will also be presented.

3:40pm **TF+NS-MoA6 Focused Ion Beam Sculpting of Curved Shapes in Metals and Amorphizable Solids*, D.P. Adams,*** *M.J. Vasile,* Sandia National Laboratories

We describe how focused ion beams can be used to sculpt predetermined micron-scale, curved shapes in a variety of initially planar solids. Using a vector-scanned focused Ga ion beam system, we sputter different shapes including hemispheres, paraboloids and sine waves having dimensions from 1-50 microns. Ion sculpting is accomplished by varying pixel dwell time (i.e., dose) within individual boustrophedonic scans. The pixel dwell times determined for a given shape account for the material-specific, angle-dependent sputter yield, Y(theta), the beam current and the ion beam spatial distribution. We highlight new results that show how this sculpting technique can be applied to a large set of materials. Using appropriate sets of dwell times, we sculpt semiconductors (Si, C) amorphized by the high-energy beam, and single crystal metals (Au, W) that remain crystalline with ion exposure. The ion-milled features, in most cases, match the intended shape with milled feature depths repeatedly within 5% of intended values. Finally, we describe techniques that minimize the deleterious effects of redeposition. This includes a method that determines the optimal range of pixel dwell times and research of gas-assisted FIB sculpting techniques.

4:00pm **TF+NS-MoA7 Focused Electron and Ion Beam Processing and Fabrication*, J. Melngailis,*** University of Maryland*; I. Utke,* EMPA, Thun, Switzerland*; P. Hoffmann,* EPFL, Lausanne, Switzerland **INVITED**

Beams of electrons and ions are now fairly routinely focused to dimensions in the nanometer range. Since the beams can be used to directly alter material, they represent direct nanofabrication tools. We will focus here on direct fabrication rather than lithography which is indirect in that it uses the intermediary of resist. In the case of both ions and electrons material addition or removal can be achieved using precursor gases. In addition ions can also alter material by sputtering (milling), by damage, or by implantation. Many material removal and deposition processes employing precursor gases have been developed for numerous practical applications, such as mask repair, circuit restructuring and repair, and sample sectioning. In many cases the minimum dimensions at which these processes can be realized are considerably larger than the beam diameters. The detailed atomic level mechanisms responsible for the precursor gas activation have not been studied in detail in most cases. We will review the state of the art and level of understanding of direct ion and electron beam fabrication and point out some of the unsolved problems. We will present recent results on beam deposited contacts to carbon nanotubes, nanowires and nanofibers.

4:40pm **TF+NS-MoA9 Sub-Micron Features Using a Focused Ion Beam and Novel Resist Structures*, M.H. Ervin,*** U.S. Army Research Laboratory

Typically, sub-micron features are written with an e-beam lithography tool. However, e-beam tools are very expensive and availability is an issue. A method for writing sub-micron features (e.g. short gate-length contacts) using a focused ion beam (FIB) is described. It is not just a matter of milling a pattern into any resist. To avoid sputtering the substrate, the mill has to be incomplete, and the partially milled resist may be cross-linked due to the ion irradiation damage. The cross-linked resist is then resistant to solvent development or plasma ashing. This might make it useful as a negative resist, but for positive resist applications write times would be problematic. Instead, two metal films are deposited on top of the resist. The top layer (e.g. Au) is cut through by the FIB to form the pattern, and the underlying layer (e.g. Ti) is the backstop layer which prevents the FIB Ga ions from penetrating through to the resist. The backstop layer is then selectively wet etched. The etch is allowed to produce an undercutting of the pattern layer features for good lift-off. Similarly, the underlying resist can be plasma ashed to expose the substrate. One has to be careful with the ashing temperature to prevent blistering of the resist/metal layers. Subsequent metallization and lift-off can produce features below a quarter micron. Of course, if the substrate is vulnerable to resist solvents, one could omit the resist entirely if the backstop layer can be used to provide lift-off at the end. Another potential advantage for sensitive substrate materials, is that the substrate is never irradiated with ions or electrons as is the case in e-beam lithography.

Thin Films
Room Exhibit Hall C&D - Session TF-MoP
Aspects of Thin Films Poster Session

TF-MoP2 Effects of Annealing Gas on Characteristics of HfO@sub 2@ Deposited by ALD for MIM Capacitors*, S.-W. Jeong, H.J. Lee, K.-S. Kim, M.-T. Yoo,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea*; T. Noguchi, J. Jung, W. Xianyu,* Samsung Advanced Institute of Technology, Korea

Research on the insulating films in metal-insulator-metal (MIM) capacitors has focused on ways to increase the dielectric constant of insulator to improve the packing density of integrated RF capacitors. High-k oxide (e.g., Ta@sub 2@O@sub 5@) has been suggested as an alternative material to replace SiO@sub 2@ and Si@sub 3@N@sub 4@. However, reliability problem caused by leakage current may limit the application of Ta@sub 2@O@sub 5@. Properties of HfO@sub 2@ grown on the Si substrate shows a dielectric constant which is comparable to that of Ta@sub 2@O@sub 5@. Further, the characteristics of HfO@sub 2@ more stable than those obtained from Ta@sub 2@O@sub 5@, suggesting that we may use HfO@sub 2@ film as insulator in MIM capacitor. In this work, we report the physical and electrical properties of ALD-deposited HfO@sub 2@ film (11-12 nm) annealed at various gases (N@sub 2@, O@sub 2@, N@sub 2@O). HfO@sub 2@ films were annealed at 400, 600, 800 °C using a rapid thermal processor for 1 min. Top and bottom metal electrodes were Pt and Pd, respectively. The electrical characterization indicates that HfO@sub 2@ MIM capacitors fabricated at 800 °C under O@sub 2@ ambient show the most desirable electrical properties, such as a high capacitance density of ~16.9 fF/µm@super 2@, a low leakage current of 2.7*10@super â?"4@ A/cm@super 2@ at -5 V, low-voltage coefficients of capacitance, and good-frequency dispersion properties. In addition, better properties were obtained from the samples annealed using N@sub 2@O than those of samples treated using N@sub 2@. These results indicate that oxygen content has certain role(s) on the electrical properties of ALD-deposited HfO@sub 2@ film. These results, as well as further investigation of physical properties of the samples using XPS, will be presented at the conference.

TF-MoP3 The Annealing Effect on the Diamond-Like Carbon Protective Antireflection Coating*, **W.S. Choi**, K. Kim, J. Yi, B. Hong,* Sungkyunkwan University, Korea

Diamond-like carbon (DLC) film has many advantages like diamond film beside it has wide band gaps and its refractive index can be adjusted variably so the film can be utilized as protective coating for IR windows and anti-reflective coating for solar cells. In this study, DLC films were prepared by RF-PECVD (Plasma Enhanced Chemical Vapor Deposition) method on silicon substrates using methane (CH4) and hydrogen (H2) gas. We examined the effects of the post annealing temperature and the annealing ambient on tribological and optical properties of the DLC films. The films were annealed from 300 to 900oC in steps of 200oC by RTA equipment in different ambient. The thickness of the film was observed by a scanning electron microscope (SEM) and surface profiler. The structure and surface morphology of the films were examined using Raman spectroscopy, X-ray diffractometer and atomic force microscopy. The hardness and depth profile of the DLC film were measured with nano-indentor and Auger electron spectroscopy, respectively. The optical properties of DLC thin film were investigated by UV/VIS spectrometer, Fourier transform infrared spectroscopy (FT-IR) and ellipsometry. And also, we have checked their carrier life time.

TF-MoP5 Metalorganic Chemical Vapor Deposition and Characterization of Zr-silicate Gate Dielectrics*, J. Kim, **S. Lee**, K. Yong,* POSTECH, Korea

Zirconium silicate [ZrSi@sub x@O@sub y@] film, demonstrating good thermal stability in direct contact with Si, is a very promising candidate to replace SiO@sub 2@ (k=3.9) gate dielectrics. Zr-silicate films were deposited by injecting tetrakis-diethylamido-zirconium [Zr(NEt@sub 2@)@sub 4@] and tetra-n-butyl-orthosilicate [Si(O@super n@Bu)@sub 4@] precursors all together into metal-organic chemical vapor deposition (MOCVD) reactor. The growth rate was about 1 nm/min at 450~500 @super o@C. High-resolution TEM image of Zr-silicate films showed an atomically flat interface of silicate/silicon even in ultra thin films and showed smooth surface with RMS (root mean square) value of 0.5 nm. The Zr/(Zr+Si) ratio was average 0.2 for the bulk film, indicating a Si-rich composition. However at the silicate/silicon interface, it shows a higher Zr concentration than Si, implying a Zr-rich composition at the interface. Zirconium silicate films with ~30 % ZrO@sub 2@ were amorphous up to 800 @super o@C and above 900 @super o@C, phase separation of the films occurred into ZrO@sub 2@ and Zr-silicate phases. Amorphous silicates are desirable in order to avoid dislocations and grain boundaries, which provide pathways for diffusion of dopants from the electrode to the substrate and may exhibit high leakage paths. ZrSi@sub x@O@sub y@ exhibited a leakage current density of 1.6 x 10@super -4@ A/cm@super 2@ at a gate bias of 1 V for an equivalent oxide thickness of 4.3 nm and showed very low hysteresis volatage (delta VFB) below 0.02 V, which indicates the low impurities and defect contents in Zr-silicate films.

TF-MoP6 Isotopically Concentrated Silicon Film Formation by Chemical Vapor Deposition*, **H. Yamamoto**,* Japan Atomic Energy Research Institute, Japan*; H. Ohba,* Japan Atomic Energy Research Institute*; M. Sasase,* The Wakasa-wan Energy Research Center, Japan*; K. Yamaguchi, K. Shimura, S. Shamoto, A. Yokoyama, K. Hojou,* Japan Atomic Energy Research Institute

Isotopically concentrated silicon (@super 30@Si) film has been attempted to form by means of chemical vapor deposition. The natural isotope @super 30@Si can be transmuted into stable @super 31@P by the capture of a thermal neutron. If the @super 30@Si enriched layer is formed on the @super 28@Si or natural Si substrate, the enriched layer can act as "donor doping layer" by the transmutation. However, it is hard to obtain plenty of enriched @super 30@Si, since its natural abundance is only 3.1%. Recently, a method for highly efficient enrichment of @super 30@Si in a form of @super 30@SiF@sub 4@ has been established by Yokoyama et al.@footnote 1@ In the present study, the @super 30@Si enriched film (~several tens nm) was deposited on natural Si substrate by using RF plasma (13MHz, 300W) from gaseous mixture of SiF@sub 4@ and H@sub 2@ diluted with Ar. The optimum condition of Si deposition has been investigated by using natural SiF@sub 4@. Obtained film was characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). XPS results showed that an impurity phase appeared in the deposited film depending on the H@sub 2@/SiF@sub 4@ gas flow rate ratio and temperature during deposition. For example, the film contained ~10at.% of fluorine in the case of the gas ratio of 2~4 at 250°C. Even though the fluorine content decreased drastically with the increase of the gas ratio up to 10, it still remained at this temperature. The fluorine was not observed in the sample deposited at 400°C. Results of the other analyses will be also presented and discussed. @FootnoteText@ @footnote 1@A.Yokoyama, H.Ohba, et al., Appl.Phys.B 79 (2004) 883-889.

TF-MoP7 SiN Single Passivation Layer Grown by Linear Antenna Type Inductively-Coupled-Plasma Chemical Vapor Deposition for Top-Emitting Organic Light Emitting Diodes*, **H.-K. Kim**, M.S. Kim, K.-S. Lee, S.H. Jeong, K. Kim,* Samsung SDI

Thin film single passivation layers (SiH@sub x@:H) for top-emitting organic light emitting diodes (TOLEDs) were deposited at substrate temperature of 40°C by using linear antenna type inductively-coupled-plasma chemical vapor deposition (ICP-CVD). It was found that the deposition rates were mainly determined by SiH@sub 4@ flow ratio at low temperature. Even at the low substrate temperature of 40°C, SiN@sub x@:H films showed a good moisture resistance and transparency of 10@super -5@g/m@super 2@/day and 92% respectively. In addition, current-voltage results showed that the SiN@sub x@:H deposition process produced negligible plasma damage, which was generally observed by plasma-related deposition processes.

TF-MoP8 Effect of Hydrogen Dilution on Microstructure of In Situ Polycrystalline Si Film Grown by Catalyzer Enhanced Chemical Vapor Deposition*, **M.S. Kim**, H.-K. Kim,* Samsung SDI

The effect of hydrogen dilution on microstructure of in situ polycrystalline Si (poly-Si) films grown by catalyzer enhanced chemical vapor deposition (CECVD) has been investigated. It was shown that microstructure of the Si films grown at low substrate temperature (<300 °C) in CECVD was strongly affected by hydrogen dilution ratio (H@sub 2@/SiH@sub 4@). In addition, a secondary ion mass spectroscopy (SIMS) depth profile of the in situ poly-Si film grown by CECVD at SiH@sub 4@/H@sub 2@ (1/40 sccm) exhibited much lower hydrogen concentration than dehydrogenated amorphous Si film grown by conventional plasma enhanced chemical deposition (PECVD). These results indicated that the CECVD technique is a promising candidate to grow high quality in situ poly-Si films on glass or flexible substrate for low-temperature poly-Si (LTPS) and flexible displays.

TF-MoP9 Irradiation Effect of Nitrogen Ion Beam on Hydrogenated Amorphous Carbon Films, ***Y. Watanabe***, *S. Katoh, N. Kitazawa,* National Defense Academy, Japan

Hydrogenated amorphous carbon (a-C:H) thin films were deposited on silicon single crystal substrates from toluene vapor using rf plasma at room temperature. After deposition, the a-C:H films were irradiated with a nitrogen ion beam and effects of nitrogen ion beam irradiation on surface morphology and composition were studied. Nitrogen ion irradiation was performed using a nitrogen ion beam of 0.2 to 1.5 keV for 10 min under the constant ion current density at room temperature. Surface morphology was observed by atomic force microscopy (AFM). Changes in composition and carbon-nitrogen bonding states were analyzed by X-ray photoelectron spectroscopy (XPS). Carbon structures were examined by Raman spectroscopy. AFM observations revealed that the film surface became smooth after nitrogen ion beam irradiation and notable difference in surface smoothing is hardly observed between 0.2 and 1.5 keV ion irradiation. XPS studies showed that nitrogen was absorbed near the surface of the a-C:H films after nitrogen ion irradiation and combined with carbon, resulting in carbon nitride formation. Depth profiles obtained by XPS showed that 1.5 keV nitrogen ion irradiation is more effective for carbon nitride formation than 0.2 keV ion irradiation. Carbon structures did not change remarkably after nitrogen ion irradiation. These results show that irradiated nitrogen ions are absorbed into the a-C:H films to form carbon nitride layers near the surface. The effect of the nitrogen ion energy on surface morphology and nitrogen implantation will be discussed.

TF-MoP10 Fabrication of Micropatterned Mesoporpous Silica Films on a Flexible Polymer Substrate Through a Pattern Transfer and Subsequent Photocalcination, ***A. Hozumi***, *M. Inagaki, Y. Yokogawa, T. Kizuki,* AIST, Japan; *N. Shirahata,* NIMS, Japan

Mesoporous silica (MPS) have attracted much attention due to their advanced applications. In order to fabricate microdevices from such nanoporous materials, they must be formed into microstructured thin films on certain substrates. In particular, such microfabrication on polymeric surfaces has been attracting more and more attention to fabricate flexible microdevices. In this study, we report a novel way to fabricate MPS microstructures on the flexible polymer substrate based on a pattern transfer method. First, fluoroalkylsilane (FAS) self-assembled monolayer (SAM)-covered Si substrate was photolithographically micropatterned. Next, the second SAM, e.g., aminosilane (AEAMPS) SAM was site-selectively formed onto lithographically defined patterns through a liquid phase process. The substrate was then immersed in a solution consisting of tetraethoxysilane, cetyltrimethylammonium chroride, hydrochloric acid and water. As evidenced by AFM, surfactant-silica composite film was preferentially deposited on the FAS-SAM regions, while undesirable deposition was not observed on the AEAMPS-SAM regions. In order to transfer the micropatterns to the polymer substrate, they were attached firmly to the polymer surface. Subsequently, the polymer substrate was heated to its glass transition point and was kept at this temperature for 1 hour under the pressure of 2~4 MPa. AFM, EDS and XRD confirmed that the micropatterns were successfully transfered to the polymer substrate without distortion their morphologies and nanostructures, since the adhesion of the micropatterns and the FAS-SAM surface was very weak. Finally, on the basis of photocalcinationt, the micropatterns were exposed to172 nm vacuum UV light for 3 hours at 10 Pa to eliminate surfactant molecules in order to obtain nanopores. The resulting MPS micropatterns adhered very tightly to the polymer substrate and never peeled off even after a tape peeling test.

TF-MoP11 XPS and FTIR Characterization of C60 States in C60 Doped Conducting Polymers, ***H. Kato***, *S. Takemura, K. Iwasaki, N. Nanba, T. Hiramatsu,* Kanto Gakuin University, Japan; *O. Nishikawa, M. Taniguchi,* Kanazawa Institute of Technology, Japan

Conducting polymer polythiophene (PT) film incorporated with C60, highly functional molecule, was prepared by electrochemical doping and diffuse injection methods. Charge transfer and interaction between the doped dye molecule and PT polymer chains were investigated by XPS analysis of the core-level energies and spectral profiles of the atomic components. Vibration states of the doped dye molecule and the polymer backbone were also investigated by FTIR RAS and FTIR transmission in order to examine the dopant-chain interaction in the hybrid films. The XPS spectral profile of the electrochemical doping sample was different from that of the casting sample, which reflects the different dopant-chain interaction in polymer films. It is known that C60 is a highly symmetrical molecule with HOMO fivefold (hu) and LUMO threefold (t1u) enables various valence values to be possible filling the degenerate LUMO levels with different number of electrons. The higher binding energy peaks of C 1s reflect the valence values of C60. FTIR transmission measurement clarified that C60 molecules were doped in the polymer film by both methods of electrochemical doping and casting because characteristic peaks due to the vibrational modes of C60 were observed. The C60 originated peaks were also observed in the FTIR RAS spectra. The peaks due to C60 were differently observed in the spectra of electrochemical doping and casting samples reflects the different doping states of C60. The results of XPS and FTIR suggests the controllability of conductive state of PT by changing dopant valence values by electrochemical doping methods. XPS core-level analysis of S 2p was composed of several peak components. The energy position of the main peak is almost positioned in the reference value. The lower energy and the higher energy components reflect the charge transfer between polymer chain and C60 molecule. The present work supported by "High-Tech Research Center" Project aided by MEXT.

TF-MoP12 XPS Characterization of Electrochemical Growth of Conducting Polymer on Oxidized Si Surface, *H. Kato,* ***S. Takemura***, *N. Takakuwa, K. Ninomiya, T. Watanabe, N. Nanba, T. Hiramatsu,* Kanto Gakuin University, Japan

Electrochemical growth of conducting polymer polythiophene (PT) film on oxidized Si wafer was closely investigated by XPS. Initial stage of polymer growth was investigated by analyzing the core-level energies and spectral profiles of the atomic components. Oxidized Si surface was also closely characterized by XPS by using curve-fitting of Si 2p and Si 2s core-level spectra to determine precisely the Si covalent states of surface layers. The purpose of the present work is to clarify the interface between an organic upperlayer and oxidized Si sublayer which is an interesting issue from practical point of view in wet fabrication techniques. The XPS spectrum of Si 2p and Si 2s of the oxidized substrate surface was composed by 5 peaks which correspond with Si valence values, such as Si, Si+, Si2+, Si3+, SiO2. The core-level energy positions of those different states were determined by XPS. The Si wafer was prepared through several stages of cleaning process. The surface roughness was reduced and the STM image of nano-scale orederd surface was obtained although the surface layers were oxidized investigated by FTIR RAS and XPS measurements. Electrochemical PT growth at initial stage was implemented on the oxidized Si substrate. Obtained XPS spectra of Si 2p and 2s showed that the Si+ peak grew associated with polymer deposition. This experimental fact reflects the interface linkage between organic polymer chain and Si oxidized layer. The bonding between organic and inorganic species will be also discussed. The present work supported by "High-Tech Research Center"Project aided by MEXT.

TF-MoP13 Controlled Synthesis and Magnetic Properties of Iron Oxide Particles Formed by Thermal Decomposition of Rapidly Expanded Supercritical Solutions, *S. De Dea, D. Graziani,* ***D.R. Miller***, *R.E. Continetti,* University of California, San Diego

Films of iron oxide fine magnetic particles were synthesized by rapidly expanding a supercritical solution (RESS) of ferric acetylacetonate (FeAA) and CO@sub 2@ onto a hot silicon wafer. The temperature of the substrate was set at a value such that thermal decomposition of the solute would occur at the silicon surface with subsequent formation of iron oxide particles in an oxidizing atmosphere. We present the details of the RESS apparatus and initial data on the FeAA/CO@sub 2@ system and the deposited thin films. In the RESS process particle morphology and composition can be controlled by adjusting process parameters such as pre-expansion temperature, pressure and composition of initial solution, temperature of the substrate, nozzle to substrate distance, and expansion chamber pressure and composition. In the process design and utilization of RESS it is very important to acquire accurate solubility data and then to monitor the composition of the expanding solution. For this purpose a spectroscopic view cell was introduced in the RESS system, prior to the expansion, to allow both equilibrium solubility as well as on-line concentration measurements. Obtained solubility data will be presented and compared with predicted solubility from the Peng-Robinson equation of state. The deposited particles were analyzed with SEM, XRD, EDX and a SQUID based magnetometer. It was found that smaller nanoparticles were formed when the RESS expansion was into the vacuum. The effect of the supersonic expansion jet structure on particle morphology will be discussed. EDX and XRD showed that complete decomposition of FeAA occurred at the silicon surface and that the particles consisted of a mixture of crystalline Fe@sub 2@O@sub3@ and Fe@sub 3@O@sub 4@. Magnetization measurements were performed at different temperatures and they showed that the particles have ferromagnetic properties. Results

for the coercive field as well as saturated and remanent magnetization will be presented.

TF-MoP14 Growth of Novel NaCdF@sub3@ Thin Films by Pulsed Laser Deposition for Advanced Ferroelectric Applications, ***T. Aburada,*** *C.T. Nelson,* University of Virginia; *R.W. Smith,* University of Nebraska-Omaha; *S.B. Qadri,* US Naval Research Laboratory; *J.M. Fitz-Gerald,* University of Virginia

Ferroelectrics are an important class of materials in a variety of applications including, non-volatile random access memories.@footnote 1@ Recent computer simulations have predicted that NaCdF@sub 3@ has a ferroelectric ground state.@footnote 2@ Moreover, NaCdF@sub 3@ is predicted to have a large energy band gap and be transparent in the UV spectrum, thus having potential for use in electro-optic applications.@footnote 2@ Thin films of NaCdF@sub 3@ were grown by Pulsed Laser Deposition (PLD) on Si (100) substrates using a high purity NaF and CdF@sub 2@, 1:1 molar fraction, starting target in a high vacuum chamber. A KrF excimer laser (@lambda@ = 248 nm) was used to deposit films as a function of growth temperature, system pressure, and laser energy. All films exhibited a large degree of roughness along with pronounced surface irregularities, as evidenced by Scanning Electron Microscopy (SEM) images. X-ray Diffraction (XRD) data showed that the films consist of two binary phases: CdF@sub 2@ and NaF, closely matching the stoichimetries of the starting target constituents. Although XRD analysis indicates the absence of the ternary NaCdF@sub 3@ phase, it is important to point out that oxide peaks are not observed. This is a significant hurdle to overcome in producing these materials. Compositional measurements by Energy Dispersive X-ray Spectroscopy (EDXS) indicate that the atomic fraction of Na to Cd is lower in the deposited thin film than in the initial target material. A comparison of the XRD spectra of the deposited film and the target reveals a decrease in the NaF phase in the films. With the large band gap associated with NaF, KrF irradiation is not the optimum choice due to its relatively low energy of 5eV. @FootnoteText@ @footnote 1@J.S. Horwitz, K.S. Grabowski, D.B. Chrisey, R.E. Leuchtner, Appl. Phys. Lett. 59 (13), 23 (1991)@footnote 2@ C. Duan, W.N. Mei, J. Liu, W. Yin, J. R. Hardy, R.W. Smith, M.J. Mehl, L.L. Boyer, Phys. Rev. B 69, 033102 (2004).

TF-MoP15 Low Temperature Formation of High-Quality SiO@sub 2@ Thin Film using UV Light-Excited Ozone, ***A. Tosaka,*** National Institute of Advanced Industrial Science and Technology, Japan; *T. Nishiguchi,* Meidensha Corporation, Japan; *H. Nonaka, S. Ichimura,* National Institute of Advanced Industrial Science and Technology, Japan

Fabrication of high quality SiO@sub 2@ film at low temperature is required for a gate dielectric film in thin film transistor for future display devices. We have developed an oxidation system using highly concentrated ozone excited by KrF laser light (248 nm) since it is expected that ozone molecules exposed to 248 nm light readily decompose into excited oxygen atoms, O(@super 1@D), and oxygen molecules. It was revealed that the UV excited ozone results in SiO2 film growth more than 3.6 nm thickness at 70 °C within 10 min., sufficiently thick as a barrier oxide. The growth rate behavior shows that there are two oxidation mechanisms and the activation energy is almost zero (0 to 5 min.) and 0.14 eV (after 5 min.), respectively. The low activation energy is due to the reaction between highly-reactive O(@super 1@D) and the silicon surface layers whose electric state is UV-excited. The current density (J)-electrostatic field (E) characteristics of the SiO@sub 2@ film show the ideal tunneling current properties, indicating that the KrF laser light irradiation does not induce defects in the film. Details reaction mechanism of O(@super 1@D) with silicon in terms of the density of excited oxygen atoms will be also discussed.

TF-MoP16 Influences of the Dopant Concentration and Thermal Treatment on Optical and Electrical Properties of C-oriented Aluminum-Doped Zinc Oxide Films, *S.-Y. Kuo,* National Applied Research Laboratories, Taiwan; ***W.-C. Chen,*** National Taiwan Normal University, Taiwan; *C.Y. Su,* National Applied Research Laboratories, Taiwan; *C.-P. Cheng,* National Taiwan Normal University, Taiwan

Transparent and conductive Al-doped zinc oxide (ZnO:Al, AZO) thin films with highly preferential c-axis orientation have been prepared by the sol-gel technique. Structural, electrical and optical properties were performed by XRD, AFM, SEM, four-point probe, photoluminescence (PL) and UV-VIS transmission measurements. The influence of dopant concentration and thermal treatment on the microstructure as well as on the electrical and optical properties of the thin films is investigated. It was found that the FWHM of XRD patterns reach a minimum at annealing temperature of 750 @super o@C, which is consistent with the results of SEM images. Room-temperature PL spectra show two main peaks centered at about 380 nm (UV) and 520 nm (green). The variation of UV-to-green band emission was greatly influenced by annealing temperatures. The minimum sheet resistance of 10@super 5@ @ohm@/sq. was obtained for the film doped with 2 wt.% Al, annealed at 650 @super o@C. Meanwhile, all AZO films are very transparent, between 85 and 95 % transmittance, within the visible wavelength region. The optical absorption edge was found to blueshift with increasing doping concentration as well. Possible causes to the above will be given and discussed. These results indicate that AZO thin films might be a promising candidate for future photonic applications.

TF-MoP18 Electrical, Optical and Structural Properties of Arsenic-doped (Zn,Mg)O Films, ***J.-M. Erie,*** *Y.J. Li, H. Kim, K Ip, S.J. Pearton, V. Cracium, D.P. Norton, J. Chen, F. Ren, I. Kravchenko,* University of Florida

Zinc oxide is an attractive compound semiconductor for transparent electronics, UV light emitting diodes (LEDs) and laser diodes (LDs). It possesses a direct band gap of 3.37eV, a large exciton binding energy of 60 meV and a high theoretical saturation velocity. However, the formation of p-type material with a high hole carrier density remains a major challenge. Recent efforts have focused on ZnO p-type doping with group V anions, namely N, P or As. In this work, the synthesis and properties of As-doped (Zn,Mg)O thin films grown by pulsed laser deposition are reported. Epitaxial (Zn,Mg)O films doped with 0.02-0.2 at % As are grown using a single ablation target synthesized with high-purity zinc arsenide as the source of arsenic. The structure and phase formation are characterized as a function of growth temperature and oxidation conditions. Both oxygen and ozone are explored as oxygen source gases. Film properties are characterized using Hall measurement, photoluminescence, scanning electron microscope, and X-ray diffraction. This work was supported by the National Science Foundation, Air Force Office of Scientific Research, the Department of Energy, and the Army Research Office. The authors would also like to acknowledge the Major Analytical Instrumentation Center, Dept. of Materials Science and Engineering, University of Florida.

TF-MoP19 Fe(001) Thin Films for Novel Applications, ***C.A. Meserole,*** *G.L. Fisher, D.J. Hilton, R.D. Averitt, D.J. Funk, A.J. Taylor,* Los Alamos National Laboratory

The electrical and magnetic properties of thin iron (Fe) films have sparked significant scientific interest. Our interests are two-fold. First, Fe(001) films are ideal targets for a newly developed ultrafast x-ray diffraction instrument designed to understand complex behavior, such as melting or solid-solid phase transitions, in shock-loaded materials. The instrument utilizes an intense laser pulse to initiate a shock wave in the sample and x-ray diffraction to study the material's response. This target/instrument combination will allow for directly comparing experimental data to published molecular dynamics simulations of a shock wave propagating along the [001] direction in an Fe crystal. Second, we have discovered a novel application for thin Fe films, which generate picosecond, broadband terahertz frequencies after intense femtosecond pulse excitation by a Titanium:Sapphire laser. The terahertz emission provides a direct measure of the induced ultrafast magnetization change. Film thickness not withstanding, the criteria for samples used in both experiments are identical due to the similarities of the experiments. For example, the substrate must permit the epitaxial growth of continuous single/monocrystalline films, yet must be transparent to a pump laser. Fe(001) films grown on MgO(001) substrates make ideal samples for both experiments. Issues such as generating a specific crystallographic orientation in the Fe film, film growth mode, substrate preparation and surface contamination, are discussed, along with an overview of the applications for these films.

TF-MoP20 Electron Cyclotron Resonance Remote Plasma Enhanced Atomic Layer Deposition of Ruthenium Thin Films, *E.-J. Lee, B.-Y. Kim, S.K. Park, H.-D. Kim, J.-W. Park,* ***M.-G. Ko,*** Hanyang University, South Korea

As the silicon process migrates to small device geometries, new deposition process technology will be required to solve the problems obtained with high trench capacitor and ultra thin gate oxide. Attempts to deposit material with atomic level control, atomic layer deposition as a technique which can be available good film uniformity and excellent step coverage have been reported. Ruthenium is a noble metal has low electrical resistivity, high chemical inertness, thermal stability and hardness. Especially, ALD of ruthenium thin films using the metal electrode for trench DRAM capacitor have been researched because the films have not only excellent uniformity also high work function energy of deposited films. In this study, ruthenium thin films prepared by high density plasma ALD with

Ru(EtCp)@sub2@ as ruthenium precursor and NH@sub3@ gas as plasma ion source from room temperature to 400°C. ECR remote plasma as high density plasma ion source has over 10@super12@ /cm @super3@ ion density, therefore, ligands of precursor gas can be removed easily. Ruthenium thin films was grown to self-limited reaction process to be ranged from 250°C to 290°C deposited by conventional ALD on 44 nm thick TiN/ 4 nm thick Ti / 100 nm thick SiO@sub2@ / p-type (100) Si wafer. This result reveals that ALD process depends on chemical limited reaction with surface atom and precursor gas, furthermore, this temperature region possess sufficient energy to adsorb ruthenium precursor gas on substrate. Conventional ALD of ruthenium thin film deposited with oxygen and argon mixed gas as a reaction gas is formed ruthenium and ruthenium oxide, however, high-density remote plasma enhanced ALD of ruthenium deposited using NH@sub3@ as a plasma gas is formed only ruthenium films by low angle HRXRD (High Resolution X-ray Diffraction) peaks. Ruthenium thin films deposited by HDPALD have surface morphology of 10 ~ 12 Å, and electrical resistivity of 11 ~ 15 µm cm.

TF-MoP22 Experimental AES and Computer Model Based Elemental Depth-Profile Analysis of Tungsten Carbide Doped Diamond Like Carbon Films*, **J.A. Carlson**, J. Abou-Hanna, J. Lozano,* Bradley University

Tungsten-doped diamond-like carbon (DLC) coatings, with a thickness of approximately three microns, have been magnetron sputtered onto 52100 steel with chromium and chromium/tungsten carbide dual interlayers using a Hauzer Techno Coating HTC 1200 4 UBM system. The process gas for the deposition is acetylene. The deposition chamber uses a two degree of freedom rotational system to rotate parts to be coated so that eventually each portion of the part will experience the full impact of the target. Depending on the speed of the rotation, the rotation pattern may take several minutes to repeat. At certain intervals during deposition, the acetylene flow is linearly altered to change characteristics throughout the film. AES sputter depth profiling analysis shows a spatial dependency on the depth profile which is likely attributable to the fixture rotational system. AES depth profiling also reveals trace amounts of titanium within the DLC and within the interlayers. The presence of titanium has further been confirmed with EDS/SEM analysis. Furthermore, AES shows significant amounts of oxygen in the area of the interlayer/substrate interface. Lastly, in addition to the experimental data, mathematical models are presented that were used to predict film chemistry, film thickness, and film structure.

TF-MoP23 Improvement of Surface Roughness in Indium Tin Oxide (ITO) Anode for Organic Light-Emitting Diode (OLED) by Water Vapor Injected Radio Frequency Sputtering*, **K.-S. Lee**, D.-G. Kim, H.-K. Kim,* Samsung SDI

We report on improvement of surface roughness in indium tin oxide (ITO) anode which was grown by water vapor injected rf sputtering method, for use in organic light-emitting diode (OLEDs). It is shown that ITO films prepared by water vapor injected rf sputtering have very smooth surface (Rms 20.Å, PtV 174Å), low resistivity (0.00019 Ω/square), and high transmittance (~ 96%). Scanning electron microscopy (SEM), atomic force microscopy (AFM), and x-ray diffraction (XRD) examination results show that film surfaces of ITO were mainly influenced by the preferred orientations in ITO anode films. In addition, secondary ion mass spectroscopy (SIMS) result clearly shows that OH content in ITO film was increased by water vapor injection. OLED with ITO cathode prepared by water vapor rf sputter method show lower turn on voltage as compared to that of OLED with ITO films prepared by rf sputtering without water vapor. Based on SEM, AFM, and XRD results, we describe a possible mechanism to explain improved electrical and surface properties of ITO films prepared by water vapor injected rf sputtering.

TF-MoP24 Characteristics of Indium Zinc Oxide Top Cathode Layer Prepared by Box Cathode Sputtering for Top-Emitting Organic Light-Emitting Diodes*, H.-K. Kim, **D.-G. Kim**, K.-S. Lee,* Samsung SDI

We report on plasma damage-free deposition of indium zinc oxide (IZO) cathode layers for top-emitting organic light-emitting diodes (TOLEDs) by using a box cathode sputtering (BCS) technique. A sheet resistance of 42.6W/Â£ and average transmittance above 88% in visible range were obtained even in IZO layers deposited by the BCS at room temperature. The TOLED with IZO top cathode layer grown by the BCS shows electrical characteristics comparable to TOLED with only thermally evaporated Mg-Ag cathode. In particular, it is shown that the TOLED with the IZO top cathode layer deposited by the BCS has very low leakage current density of 1X10@super -5@mA/cm@super 2@ at reverse bias of -6V. This suggested that there is no plasma damage caused by the bombardment of energetic particles during IZO sputtering process. Based on current-voltage, x-ray diffraction (XRD), high-resolution electron microscopy (HREM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) examination results, possible mechanisms to explain plasma damage-free sputtering of the BCS system are suggested.

TF-MoP26 Fabrication of Long Lengths of Flexible High Temperature Superconductor Thin Film Tapes for Electric Power Applications*, **V. Selvamanickam**, Y. Chen, X. Xiong, Y. Li, Y. Xie, Y. Qiao, J. Reeves, P. Hou, M. Gardner, T. Salagaj, K. Lenseth,* SuperPower

High Temperature Superconductors (HTS) have immense potential in electric power applications such as cables, motors, generators, and transformers. The zero-resistance property of HTS can be beneficially used to transmit up to 10 times more power in cables, and reduce the size and weight of rotating machinery and transformers by half. SuperPower is scaling up the so-called second-generation HTS conductors which are based on thin film tapes of epitaxially grown superconducting films. Flexible metal substrates such as Hastelloy are used and highly biaxially-textured oxide buffer templates are deposited by ion beam assisted deposition and magnetron sputtering. The buffer layers are comprised of a multilayer stack of oxides, each layer comprising of about 10 to 100 nm. Y-Ba-Cu-O superconducting films are then deposited on the buffer stack in thickness of 1 to few microns by metal organic chemical vapor deposition (MOCVD). Overlayers of silver and copper films are used to complete the conductor. SuperPower has established Pilot-scale facilities for producing long lengths of high-performance second-generation HTS thin film tape conductors. We have scaled up the processes to 100 m lengths with critical currents exceeding 100 A at 77 K. In this presentation, we will discuss the recent advances in scale up several thin film process technologies, associated equipment and process control techniques to fabricate second-generation HTS thin film tapes for electric power applications. Prototype electric power devices fabricated with these HTS thin film conductors will also be presented.

TF-MoP27 Flexible Gas Barrier Coatings Based on Roll-to-Roll Symmetric Magnetron Sputtering*, **C.-S. Wang**, K. Sasaki,* Kanazawa University, Japan*; S.-F. Chen,* National Taipei University of Technology, Taiwan*; T. Hata,* Japan Science and Technology Agency

Superior gas and water vapor barrier coatings on polyethylene terephthalate substrate were prepared by roll to roll symmetric magnetron sputter technique. It has considerable attention that electronic devices such as flat panel displays, electronic paper and solar cell are to be flexible. In general, replacing the substrate from glass to plastic film, the gas permeability is so high that the oxygen and water vapor through the film damage the device. In this work, a new roll-to-roll coater for 300 mm web width combined with asymmetric magnetron sputtering has been developed to produce flexible gas barrier coating with high productivity. Three pairs of symmetric magnetron sputtering cathodes were sited on the both side of the substrate to realize subsequent coating of different layers and low-temperature deposition. On the other hand, the gas barrier coatings composed of 4 layered silicon oxynitride and oxide anti-reflection coatings have been investigated to improve resistance of the oxygen and moisture permeability. As experiments, the gas barrier properties were strongly depended on the film density and thickness and indicated that the gas barrier properties of 4 layered coatings were superior to single layer. The results show the transmission rate of water vapor bellow 0.07 cc/m@super 2@-day-atm and the oxygen transmission rates as low as 0.2 cc/m@super 2@-day-atm, moreover, an average transmittance rate of 98% in the range of visible spectrum has been measured. These competitive values of the coating can be actualized a high throughput of up to 1 m/min at economic coating cost.

TF-MoP28 Sputtering of Y3Al5O12:Cr Thin Films for Temperature Sensor Applications*, **Y. Deng**, P.D. Rack,* University of Tennessee

Phosphor materials can be used as a temperature sensor by monitoring the phosphor decay time. Chromium-doped yttrium aluminum garnet (Y3Al5O12:Cr, or YAG:Cr) powders have been used in phosphor thermometry as its decay time has been well calibrated from room temperature to 600 Celsius. While powder paints are useful in some applications, these paints can flake and peel under some harsher environments. To ameliorate this problem, we are exploring the properties of YAG:Cr thin films. In this work, YAG:Cr thin films were sputter deposited in a combinatorial fashion to rapidly determine the optimum chromium concentration. The photoluminescence (PL) properties were correlated to the chromium concentration and an optimum concentration of 0.7 atomic percent was determined. Subsequently, a design of experiments was conducted to study the effects that the substrate temperature, substrate bias, and oxygen flow rate have on the YAG:Cr thin film PL and crystallinity.

An optimum sputtering condition was found. Finally, temperature dependent PL intensity was measured as a function of temperature to understand the thermal quenching phenomenon.

TF-MoP29 Film Properties of Transparent Conductive Oxide Films Deposited from Either ZnO- In@sub2@O@sub 3@or ZnO-SnO@sub2@ Systems with Additional Ga@sub2@O@sub3@ Impurities*, K. Tominaga, D. Takada, Y. Sukeda, Y. Nishimura, T. Moriga, I. Nakabayashi,* Tokushima University, Japan

Recently transparent conductive oxide films with smooth surface are expected. Lower deposition temperature is also expected for the TCO in polycarbonate substrate. For these applications, amorphous transparent conductive films are expected to be one of adequate materials. Amorphous films can be deposited in the system of ZnO-In@sub 2@O@sub 3@, or ZnO-SnO@sub 2@. Therefore we deposited those films, and investigated the influence of the incorporation of Ga@sub 2@O@sub 3@ on the film properties for those systems. Transparent conductive oxide films deposited from either ZnO-In@sub 2@O@sub 3@ or ZnO-SnO@sub2@ systems with additional Ga@sub2@O@sub3@ impurities were deposited by facing target sputtering system. ZnO:Ga and In@sub2@O@sub3@ targets were used for ZnO-In @sub2@O@sub 3@ films, and ZnO:Ga and In@sub2@O@sub3@ for ZnO-SnO@sub 2@ films. Two targets were sputtered simultaneously in Ar gas at 1 mTorr, and electric current ratio @deruta@=I@sub Zn@/(I@sub Zn@+I@sub In@) or I@sub Zn@/(I@sub Zn@+I@sub Sn@) was adopted as a deposition parameter to change film composition. Discharge current of each target was changed from 0 to 80 mA in order to change the content ratio of Zn/(In+Zn) or Zn/(Sn +Zn) in the film. Compositional ratios in films were estimated by X-ray fluorescence analysis. We could deposit ZnO-In@sub 2@O@sub 3@ amorphous films between Zn/(Zn+In)=0.2-0.5 even at a temperature of 250 Â°C. Low resistivity of the order of 10@super -4@@ohm@cm was attained in amorphous phase. Optical transparency was good for all films. For the amorphous films, optical bandgap energy shifted to higher energy side with decreasing the resistivity. Homologous films were deposited between Zn/(Zn+In)=0.5-0.75. These films had higher resistivity and larger optical bandgap than those of amorphous films. Similar results were obtained for SnO@sub 2@:Sb and ZnO:Ga, although the film resistivities were higher than ZnO-In @sub2@O@sub 3@.

TF-MoP31 Palladium Oxide Composite Films Containing Palladium Metal Phase Fabricated by Reactive Ion Beam Sputter-Deposition*, T. Ichinohe, S. Masaki,* Tokyo National College of Technology, Japan*; K. Kawasaki,* TDY Co., Ltd., Japan

Palladium oxide (PdO) is known to be p-type semiconductor with 1.5-2.2 eV band gap, and generally formed by thermal oxidation over 400@super o@C. This study reports the relation between formation of PdO and the parameters of reactive ion beam sputter-deposition, such as various substrate temperatures, deposition rates, and oxygen flow rates. According to X-ray diffraction (XRD) study, PdO(002) mixed with Pd(100) was formed in the films at low substrate temperature (T@sub sub@). When T@sub sub@ was 200@super o@C, the XRD intensity of PdO(002) seemed to become higher than Pd(100), in other words, it was tended to show the ratio of their peak intensities (I@sub PdO@/I@sub Pd@) higher than 1 indicating that the formation of PdO was relatively dominant than that of Pd at T@sub sub@=200@super o@C. The intensity of PdO(002) decreased or sometime disappeared when the films were formed at T@sub sub@=400@super o@C. The optimal parameters of reactive ion beam sputter-deposition can lead to form palladium oxide films at low temperature.

TF-MoP32 Growth and Properties of CdTeO@sub x@ Films by Reactive rf Magnetron Sputtering: CdTeO@sub 3@ a High-quality Transparent Material for Solar Cell Applications*, S. Jiménez-Sandoval,* Centro de Investigación y de Estudios Avanzados del IPN, Mexico*; **J. Carmona-Rodríguez**, R. Lozada-Morales,* Benemérita Universidad Autónoma de Puebla, Mexico*; O. Jiménez-Sandoval, M. Meléndez-Lira, C.I. Zúniga-Romero,* Centro de Investigación y de Estudios Avanzados del IPN, Mexico

CdS/CdTe heterostrtuctures is one of the leading solar cell technologies nowadays. One of the current approaches is the use of thin (~ 100 nm thick) CdS layers to improve cell efficiency. However, as the thickness of the CdS layer is reduced there is a greater chance for the appearance of micro junctions between the p-type CdTe layer and the transparent conducting oxide used as front contact, reducing cell efficiencies. It has been recently suggested that the use of a highly resistive buffer layer could avoid micro shunt formation. In order to gain further insight on the formation of transparent CdTe-based materials, we report on the properties of CdTeO@sub x@ films grown by reactive rf sputtering and of films annealed after deposition. The films were grown under an argon flow of 12 sccm and using oxygen flows of 0, 3, 5, 7, 8, 9, 9.5, 10, 10.5 and 11 sccm. This range of oxygen flows was equivalent to oxygen partial pressures within the chamber from 6.7 x 10@super -5@ (3 sccm) to 1.1x10@super -4@ Torr (11 sccm). The substrate temperature was maintained at 400°C for all growths with deposition times of 35 minutes at 35 W of power applied to the 99.999% pure CdTe target. The X-ray diffraction results indicate that the structure of the films was a mixture of cubic/hexagonal phases, typical of CdTe films, for films grown with oxygen flows of up to 10.5 sccm. This structure, however, is no longer sustained when the oxygen flow reaches 11 sccm. At this point, the X-ray diffraction peaks narrow because the material reaches the stoichioimetry and structure of high-quality CdTeO@sub 3@. Accordingly, the bandgap increases from 1.50 to 1.67 eV as the oxygen flow increases from 3 to 10.5 sccm, and at 11 sccm the band gap jumps to 3.73 eV, becoming a transparent, highly resistive film. Annealing the films for two hours under an inert atmosphere at 450°C does not produce significant changes in the crystalline structure, optical properties or bandgap values.

TF-MoP34 Electron Beam Induced Processing of Nanoscale Features: Process Parameters, Simulated Growth, and Nanoscale Applications*, **P.D. Rack**,* University of Tennessee*; J.D. Fowlkes,* University of Tennessee, US*; S.J. Randolph,* University of Tennessee

The rapid and precise direct write growth of nanoscale features by electron beam induced deposition (EBID) requires the optimization of growth velocity while maintaining nanoscale feature dimensions. There is a vast and complex EBID parameter space includes the precursor gas pressure, the primary electron beam energy, the electron beam current, surface diffusion rates of adsorbed precursor species, thermal effects on desorption, and the cascade of electron species produced by inelastic scattering processes. These variables affect the probability of precursor dissociation and hence determine the feature growth velocity and the size of the structure through a series of complex, coupled nonlinear interactions. A dynamic computer simulation based on Monte Carlo calculation sequences was created to aide in the interpretation of experimental observations by simulating experimental growth conditions. In this presentation, we will describe the parameter space and illustrate some of the complex interactions and introduce a Monte Carlo growth simulation. Experimental observations will be correlated to the simulated results. Finally, several nanoscale devices grown with electron beam induced processing will be demonstrated.

TF-MoP35 Influence of Sputtering target Structure on the Deposited Film Properties*, C.F. Lo,* Praxair Surface Technologies - MRC

This study correlated sputtering targets and deposited film properties in physical vapor deposition (PVD). When the sputtering targets consist of multiple elements, in addition to sputtering parameters, distribution of the individual elements or the constitutional target structure will affect the deposited film properties. In this report, we investigated the influences of target structures, including inter-diffusion between W and Ti in W-10 wt% Ti, precipitate size of Si in Al-1 wt% Si and distribution of Al10Mo inter-metallic phase in Al-2 at% Mo, on the deposited film properties. The results indicated that the greater extent of inter-diffusion between W and Ti of the W-10 wt% Ti target, the higher the compressive stress of the deposited film. The larger the Si precipitates in the Al-1 wt% Si target, the larger the Si precipitates in the deposited film. The larger the Al10Mo inter-metallic phases in the Al- 2 at% Mo, the less but larger whiskers generated on the annealed films. These evidences suggest that, although the films are formed by re-arrangement of the bombarded atoms from the sputtered target, mirror effect from target to film exists via PVD.

TF-MoP36 Reactive Pulsed DC Magnetron Sputtering of Oxide Films*, M. Ye,* Applied Materials, Inc.

Reactive pulsed DC magnetron sputtering extends the capabilities of DC sputtering to the area of insulating thin films deposition. The occurrence of arcing can be avoided and the plasma can be stabilized by periodically discharging the poisoned regions of the target through target voltage reversals. By careful design of hardware and selection of appropriate operating conditions, successful processing of various oxide films (aluminum oxide, tantalum oxide, and titanium oxide, etc.) on Applied Materials 200mm Endura platform is demonstrated in this paper. The experimentally established hysteresis curves are compared with modeling analysis. Film characterization results, including deposition rate, film stress, composition, optical index of refraction, density, and roughness, are presented. The effects of oxygen flow rate are studied. It is shown that

amorphous films with low stress level, good adhesion, smooth surface and the right stoichiometry can be achieved. Oxide films have been used in a variety of applications, including semiconductor devices, optical films, and MEMS devices. Compared to other deposition methods, DC magnetron reactive sputtering proves to be a simple yet powerful and efficient way of depositing insulating thin films, in both manufacturing environment and R&D applications.

TF-MoP37 Synthesis and Characterization of SiN@sub x@ Films Deposited on Silicon by Reactive RF Sputtering@super *@, ***C. Mendoza-Barrera**, E. Valaguez,* UPIITA-IPN, México*; A. Garcia-Sotelo, V. Altuzar, M. Melendez-Lira, A. Mendoza-Galván,* Cinvestav-IPN, México*; S. Jiménez-Sandoval,* Cinvestav-IPN, México, Mexico

Silicon nitride SiN@sub x@ is a widely used compound in the area of sensors because its electric an optoelectronic properties when it is grew at temperatures lower than 400°C. Also it is employed as buffer layer to deposit films of metallic nanoparticles which are employed as seed for nanotubes grown. We report details of the deposition of SiN@sub x@ thin films by reactive R.F. sputtering on silicon along with results of their structural and optical characterization. The effect of substrate temperature and power intensity of the radiofrequency on films properties were evaluated. Radiofrequency power intensities between 100 and 300 W and substrate temperatures between 100 and 300 °C were studied. Structural and optical characterization were carried out by X-ray diffraction, energy dispersive of X-ray spectroscopy, atomic force microscopy and UV-Vis, Raman and ellipsometry spectroscopies. As expected results indicated that SiNx was produced with optical and structural properties depending on growth parameters. Results are discussed taking in account the stoichiometry obtained under the different growth conditions and the possibility of a porous structure of SiN@sub x@. @FootnoteText@ *Work partially funded by CONACyT-Mexico.

TF-MoP38 Optical and Charge Transport Properties of p-type (CdTe)@sub x@Cu@sub y@O@sub z@ Films: a Novel Material for Photovoltaics and other Optoelectronic Applications, ***S. Jiménez-Sandoval**,* Cinvestav-IPN, Mexico*; J. Carmona-Rodríguez,* Benemérita Univerisidad Autónoma de Puebla, Mexico*; O. Jiménez-Sandoval,* Cinvestav-IPN, Mexico*; R. Lozada-Morales,* Benemérita Universidad Autónoma de Puebla, Mexico*; M. Meléndez-Lira, C.I. Zúniga-Romero,* Cinvestav-IPN, Mexico

Cadmium Telluride is a technologically important semiconductor material for optoelectronic applications; more specifically, for photovoltaic applications and infrared detection. The search for CdTe-based materials that may improve some of the still difficult matters regarding CdTe-based technology is currently underway. This work reports the continuation of our previous work on Cu@sub x@Cd@sub 1-x@Te@footnote 1@ and on Cd-Cu-Te-O systems@footnote 2@ by presenting the structural, optical and electrical properties of (CdTe)@sub x@Cu@sub y@O@sub z@ films grown by reactive rf-magnetron co-sputtering; it is shown that the optical and charge transport properties may be tailored by changing the relative concentration of the four elements. The films were obtained by co-deposition from CdTe and Cu targets under a controlled oxygen flow rate of 11 sccm. The power applied to the Cu target was 0, 10, 20, 30, 40, and 50 W, for different runs. The X-ray diffraction patterns indicated that the films are a mixture of CdTe-type cubic/hexagonal phases; however, it was observed that the hexagonal phase was favored for higher copper concentrations. The chemical composition was analyzed by energy dispersive spectroscopy. The results indicated that the atomic concentration of Cd and Te has nearly identical values in all samples, and decreases as the copper concentration increases from zero to 25 at.%. For films grown with 40 and 50 W in the copper target x=y=z=0.25. The bandgap varied from 1.62 eV (no Cu) to 1.48 eV (25 at.% Cu), a value quite appropriate for the absorbing layer in a solar cell. The four probe method was useful to determine the p-type resistivity of the films grown with Cu powers of 20 W and above. The values obtained ranged from 1.6 x10@super 3@ to 6.5x10@super -3@ ohm-cm. @FootnoteText@ @footnote 1@ S. Jiménez-Sandoval, S. López-López, B.S. Chao, M. Meléndez-Lira, Thin Solid Films 342 (1999)1.@footnote 2@ S. Jiménez-Sandoval et al., To be published (2005).

TF-MoP39 Influence of Ga Doping Level on the Properties of ZnO-Gax Films prepared by Radio Frequency Magnetron Sputtering, *H.C. Pan, C.Y. Su, C.N. Hsiao,* National Applied Research Laboratories, Taiwan*; S.-P. Lin,* ***C.-S. Chiou**,* Yuan Ze University, Taiwan

Gallium doped zine oxide (GZO) thin films are prepared by radio frequency sputtering on the Corning glass using a co-sputtering technique varying sputtering power of Ga@sub 2@O@sub 3@ target as the Ga doping source. The structural, electrical and optical properties of the GZO films are investigated in terms of the deposition conditions such as the Ga@sub 2@O@sub 3@ content in the film, partial oxygen pressure (O@sub 2@ /Ar ratio), film thickness, working pressure and film thickness. The optical and the electrical properties of GZO films were investigated by spectrometer, Hall effect measurement, X-ray diffractometery (XRD), atomic force microscopy (AFM), conducting atomic force microscopy (CAFM) and X-ray absorption near-edge spectroscopy (XANES). The deposited GZO films at room temperature were polycrystalline with a hexagonal wurtzite structures and preferential orientation along (002) plane, regardless of the Ga content. The crystallinity and grain size of the IZO showed an increasing tendency as function of the film thickness. The resistivity of the GZO prepared with around 2 wt.% Ga content in film composition is about 8x10@super -4@ @ohm@-cm and depends on the Ga doping level. The average optical transmittance of a 30 nm-thick film in the visible region (400 nm ~ 700 nm) is about 85%. The optical band gap depends on the Ga doping level is in the range of 3.4 ~ 3.5 eV. Chemical change of different Ga doping level in zinc oxide films was investigated using XANES. Intensities of the peaks appearing at the same energy of ZnO in XANES spectra were decreased with the Ga doping level.

TF-MoP41 The Effect of Ion-beam Assisted Deposition on the Electrical Properties of Indium Zinc Oxide Thin Films Investigated by Conducting Atomic Force Microscopy, ***C.Y. Su**,* National Applied Research Laboratories, Taiwan*; H.C. Pan,* National Applied Research Laboratories*; M.H. Shiao, C.N. Hsiao, K.N. Lee,* National Applied Research Laboratories, Taiwan

Indium zinc oxide (IZO) thin films with 5 wt.% and 10 wt.% of zinc oxide were prepared as the anode layer for organic light emitting diodes (OLEDs). The film deposition process gave a significant influence on device characteristics, and considerable improvements due to the energetic ion bombardments during ion-beam assisted deposition (IAD) were obtained. These improvements are even over the conventional vacuum deposition results. The conducting atomic force microscope (CAFM) that was self-established from a commercial atomic force microscope at ITRC (Instrument Technology Research Center) was employed to investigate the surface morphologies and corresponding electrical properties. And the experiment results suggest that the IAD has the possibility of controlling two factors: the growth morphology and surface electrical properties of the IZO thin films. Including lower roughness (Rms changed from 2.15 nm to 1.50 nm) and higher conductivity (>10@super 3@ @ohm@@super -1@cm@super -1@). The IAD gave uniform surface coverage, which means the initial film growth topography consist of well-distributed small grains other than coagulated islands. The current images that were simultaneously scanned and captured with the topographic images indicate improvement of surface electrical properties from the nano-scale surface inspection of the IZO thin films. The basic principles and mechanisms of this CAFM system are also described.

TF-MoP42 Optical and Electrical Properties of Sc-doped ZnO Thin Films Prepared by RF Magnetron Sputtering, ***M.H. Shiao**,* National Applied Research Laboratories, Taiwan*; C.C. Jaing, Y.J. Huang,* Ming Hsin University of Science & Technology, Taiwan*; H.C. Pan, C.Y. Su, C.N. Hsiao, K.N. Lee,* National Applied Research Laboratories, Taiwan

Scandium-doped zinc (ZnO:Sc) oxide thin films were prepared on Corning 1737 glass by r.f. co-sputtering of ZnO and Sc@sub 2@O@sub 3@ targets at various deposition temperatures ranging from room temperature (RT) to 300°C and different oxygen partial pressures. Composition of the ZnO:Sc thin films was analyzed by energy dispersive X-ray spectroscopy (EDS), and the crystalline structure was examined by X-ray diffraction (XRD). Optical transmittance of the films was measured by a Perkin Elmer Lambda 900 spectrometer. Electrical resistivity, Hall mobility and carrier concentration were investigated by a Hall effect measuring system. Surface morphologies and corresponding electrical properties of ZnO:Sc thin films were observed by adopting a conducting atomic force microscope (CAFM). From experimental results, the deposited thin films showed good conductivity (@>=@ 10@super 2@ @ohm@@super -1@cm@super -1@) and high optical transmittance (@>=@ 85%) in the wavelength range of 400-800 nm. The resistivity of ZnO:Sc thin films increased and the preferred orientation was changed from (002) to (103) as the oxygen partial pressure increased.

TF-MoP43 Characteristics of High-k Gate Dielectric Formed by Oxidation of Multi-layered Metal Films Deposited Directly on the Si Substrate by Sputtering, ***M.T. You**, S.-W. Jeong, H.J. Lee,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea

Recently, we demonstrated that the oxidation of the Hf metal film deposited directly on the Si substrate by sputtering results in the HfSi@sub

x@O@sub y@/HfO@sub 2@ stack layer with excellent electrical properties and high thermal stability in direct contact with Si. In this work, we further investigated the physical and electrical properties of high-k oxide films obtained by the oxidation and annealing of the multi-layered metal films (e.g., Hf/Zr/Hf, Zr/Hf/Zr, etc.) Thin metal films with the typical thickness of 1-2nm were deposited on the Si substrate alternately by rf-magnetron sputtering. Oxidation was performed at 500°C for 120min using the conventional furnace under O@sub 2@ ambient. Post oxidation annealing was done at several temperatures (i.e., 500, 700, and 900°C) for 90sec using a rapid thermal processor(RTP) under either N@sub 2@ or O@sub 2@ ambient. Data of HF C-V, I-V and Fowler-Nordheim tunneling (FNT) electron injection were analysed. TEM and XPS techniques were used to investigate the structural changes of the high-k films due to post oxidation annealing. The multi-layered high-k oxide films were formed after oxidizing the multi-layered metal films deposited directly on the Si substrate. The subsequent RTP annealing at high temperature (700°C) not only results in the poly-crystallization of the multi-layered high-k oxide films, but also causes the inter-diffusion of either Hf or Zr, resulting in the multi-layered high-k gate oxide. For example, HfSi@sub x@O@sub y@/HfO@sub 2@/intermixed-layer(IL)/ZrO@sub 2@/intermixed-layer(IL)/HfO@sub 2@, films were formed, if the Hf/Zr/Hf metal films were oxidized and subsequently annealed. The inter-diffusion of metal atoms improves electrical properties in general. In addition, the data obtained from the FNT electron injection either from the gate electrode or from the Si substrate indicate that the defect density changes depending on the annealing conditions.

TF-MoP44 Characterization of Barium Zirconium Titanate Thin Films as Tunable Materials Prepared by rf Magnetron Sputtering*, **W.-A. Lan,*** National Tsing Hua University, Taiwan, R.O.C.*; T.-B. Wu,* National Tsing Hua University, Taiwan, R.O.C., Republic of China

There are a large number of perovskite structure ABO@sub 3@ ceramics with nonlinear dielectric properties being studied. For Ba(Zr@sub x@T@sub 1-x@)O@sub 3@ (BZT), with increasing the Zr content, the dielectric constant decreases and the leakage current is reduced by suppressing the formation of Ti@super 3+@ and hopping conduction. The Zr@super 4+@ ion is chemically more stable than the Ti@super 4+@ and has a larger ionic size to expand the perovskite lattice and shifts the ferroelectric-to-paraelectric phase transition temperature toward room temperature. In this work, the sputtered BZT ferroelectric thin films with different Zr substitution under several deposition conditions were investigated. The BZT thin films were deposited by rf sputtering using a 2 inch target. The test structure was made in M-I-M structure. The bottom electrode is (001)-textured LaNiO@sub 3@ (LNO) conductive oxide which was deposited on the Pt/Ti/SiO@sub 2@/Si substrate by rf sputtering with a thickness of 200nm. The Ba@sub x@(Zr@sub y@Ti@sub 1-y@)O@sub 3@ targets were prepared by solid state mixing method using single phase calcined powders x of BaZrO@sub 3@ and (1-x) Ba@sub 2@TiO@sub 4@. The mixing ratio , x, were 0.15, 0.2, 0.25. The sputtering was conducted under different rf-sputtering power, substrate temperature, Ar/O@sub 2@ ratio and target stoichiometry. The deposition time was controlled at 1 hour to study the effects of sputtering conditions. Platinum top electrode of 75 nm thick was deposited by rf sputtering at room temperature. Lift-off process was used to defined the pattern in circles with different radius. The crystalline phases of the films were examined with x-ray diffraction. Cross-sectional morphologies and thickness of the films were examined by field emission SEM. The dielectric properties of the films were measured with 4192A from 1 kHz to 1MHz. The voltage dependence of dielectric constant and loss tangent was measured with 4284A at 1 MHz.

TF-MoP45 Electrical and Optical Characteristics of MIS Structure using the a-C and a-C:H Films Grown by Closed-Field Unbalanced Magnetron Sputtering*, **Y.S. Park**, B. Hong,* Sungkyunkwan University, Korea

With extreme hardness of diamond and synthetic diamond-like carbon (DLC), carbon based materials were used mainly as a cutting tool coating and as an abrasive material. Since then, carbon based materials have been expanded into the market of electronics, optics and acoustics as well as coatings due to excellent electrical properties. Amorphous carbon (a-C) and hydrogenated amorphous carbon films were deposited on p-type silicon and glass substrates by a closed-field unbalanced magnetron (CFUBM) sputtering method. We have investigated the effect of various DC bias voltages on microstructure, electrical conductivity and optical properties. The samples were characterized with Raman spectroscopy, XPS, electrical resistivity, current-voltage (I-V) and capacitance-voltage (C-V) curves, UV-visible and FT-IR. The a-C and a-C:H films prepared by CFUBM sputter in this study show good conducting properties.

TF-MoP47 Thermochromic La@sub 1-x@Sr@sub x@MnO@sub 3@ (x = 0.1, 0.175, and 0.3) Smart Coatings Grown by Reactive Pulsed Laser Deposition*, **M. Soltani**, M. Chaker,* INRS-Energie, Matériaux et Télécommunications, Canada*; X.X. Jiang, D. Nikanpour,* Canadian Space Agency, Canada*; J. Margot,* Université de Montréal, Canada

Thermochromic Sr-doped LaMnO@sub 3@ thin films exhibit a metallic-to-insulator phase transition from low to high temperature. The transition temperature can be controlled by varying the concentration of Sr@super 2+@ ions dopant in the films. Using a reactive pulsed laser deposition (RPLD) process, we have successfully fabricated thermochromic La@sub 1-x@Sr@sub x@MnO@sub 3@ (LSMO) smart coating at relatively low deposition temperature (about of 500 °C), and without post-annealing. Silicon (100) and sapphire (1000) were used as substrates in order to study the substrate effect on the deposited films. The RPLD of LSMO films was performed in a background gas mixture of Ar and reactive O@sub 2@, from three La@sub 1-x@Sr@sub x@MnO@sub 3@ targets with different Sr doping concentrations (i.e. x = 0.1, 0.175, and 0.3). It was found that the deposited LSMO films perfectly adhere to the wurtzite Al@sub 2@O@sub 3@ as well as to the cubic Si substrate. Their perovskite structure was confirmed by X-ray diffraction (XRD). The composition of LSMO coatings was investigated by X-ray photoelectron spectroscopy (XPS) analysis of the La, Sr, Mn, and O bands. The metal-to-insulator phase transition of LSMO-coated sapphire was investigated by measuring the temperature dependence of the sheet electrical resistivity using the standard four-point probe technique. At room temperature, a thermal coefficient of resistance (TCR) about -1.5 % per °C was achieved in these films. Finally, the potential applications of these thermochromic smart coatings will be discussed.

TF-MoP48 TiN and TiO@sub2@:Nb Thin Film Preparation using Hollow Cathode Sputtering with Application to Solar Cells*, **S.Y. Guo,*** Energy Photovoltaics, Inc.*; W.N. Shafarman,* University of Delaware*; A.E. Delahoy,* Energy Photovoltaics, Inc.

Hollow cathode sputtering has found many applications for deposition of functional thin films. In particular, excellent TCOs, including In@sub 2@O@sub 3@:Ti, have been produced by reactive-environment hollow cathode sputtering.@footnote 1@ Recently, we have investigated titanium-based thin films using similar methods. TiN is well known for its excellent conductivity, inertness, and good optical reflectivity at long wavelengths. These properties make it a potential IR-reflective back contact material suitable for ultra-thin CIGS solar cells. Using a pulsed power, linear hollow cathode source, TiN films on Mo-coated glass were achieved by adopting a combination of four critical parameters. Two of these were the passing of nitrogen through the cathode cavity and magnetic field assistance. Electrical and optical properties of the films were measured. The optical emission spectrum of the Ar/N@sub 2@/Ti plasma and film XRD measurements will be reported. The effect of deposition parameters such as nitrogen flow rate, pressure, substrate bias and substrate temperature have also been studied. CIGS solar cells have been successfully fabricated on TiN and a conversion efficiency of 11.7% has so far been achieved. Transparent and somewhat conductive TiO@sub 2@ films doped with Nb were also prepared. The electrical and optical properties of these films will be reported. @FootnoteText@ @footnote 1@ A.E. Delahoy and S.Y. Guo, J. Vac. Sci. Technol. A, Jul/Aug 2005.

TF-MoP49 Optical Constants of (CdTe)@sub 1-x@Al@sub x@x Thin Films*, J. Jimenez Montecinos,* UAM-Azc., Mexico*; **A. Mendoza-Galvan,*** Cinvestav-IPN, Mexico*; M. Zapata-Torres,* CICATA-IPN, Mexico*; S. Jimenez-Sandoval, M. Melendez-Lira,* Cinvestav-IPN, Mexico

We have prepared (CdTe)@sub 1-x@Al@sub x@ thin films by R.F. co-sputering in order to evaluate their capability as a photovoltaic material. CdTe and Al were employed as targets. Samples were deposited on commercial glass substrates at substrate temperature of 400 °C. The aluminum content was controlled through the R.F. power intensity applied on the aluminum target. Samples were characterized by X-ray diffraction and EDX. Surface morphology, monitored by atomic force microscopy, showed a dependence with preparation details. A blue band gap shift is clearly observed by absorption spectroscopy as function of aluminum content of the films. Raman spectroscopy present a FHMW increase and small shift toward high wavenumbers in the LO CdTe-like mode. From ellipsometry measurements we obtained the pseudo dielectric function obtaining information about the critical points. Ellipsometry results also shown the shift in critical point energies as function of aluminum content. @FootnoteText@ @footnote 1@ Work partially funded by CONACyT-Mexico.

TF-MoP50 Inhomogeneous Rarefaction of the Process Gas in a Direct Current Magnetron Sputtering System*, **F.J. Jimenez**, S.D. Ekpe, S.K. Dew,* University of Alberta, Canada

The interactions between energetic particles and the sputter gas in a magnetron sputtering system have strong effects on the growth, structures and properties of the film. These interactions result in inhomogeneous rarefaction of the gas in the space between the target and substrate, and affect the transport of particles towards the substrate. A hybrid Monte Carlo and fluid model is developed to simulate 3-dimensional gas rarefaction due to the sputtering of metals in Argon, Neon and Krypton. The governing equations are solved iteratively in a 3D space with a non-uniform grid (octree). Collision events between the sputtered particles and the process gas are assumed as the dominant source of gas heating, however, the effect of the reflected neutrals is also included in the model. Gas rarefaction profiles have been predicted for different process conditions. Results compare well with experimental results. The location of the highest rarefaction depends strongly on pressure, power, target material and location of the substrate plane relative to that of the target. The extent of rarefaction depends further on the thermal conductivity of the gas. Materials with high sputtering yield, like Silver, show more rarefaction than those with low sputtering yield, like Tungsten and Aluminum. Tungsten, as a result of a higher target to gas mass ratio, shows more of the effect than Aluminum. For a 75 mm target at 300 W and 10 mTorr a rarefaction of about 65% is obtained for the sputtering of Aluminum in Argon gas, with the substrate plane located at 10 cm in front of the target.

TF-MoP51 Influence of Flux Anisotropy on Microstructure of Sputter Deposited Cr Films*, **S.Yu. Grachev**, J.-D. Kamminga, G.C.A.M. Janssen,* Netherlands Institute of Metals Research, the Netherlands

Sputter deposition is widely used to produce metal and compound thin films. The immanent feature of sputter deposition is that the arriving flux possesses a wide angular distribution. The flux distribution at the coated surface is influenced by the pressure of sputtering gas and by the tilt/rotation of the substrate. It is known, that the anisotropy of the flux distribution can become a source of anisotropic microstructure and, as a consequence, the anisotropy of film properties. In our study we concentrated on the influence of the flux anisotropy on the microstructure of Cr films. There are several sources for anisotropy in the Hauzer HC 750 industrial deposition system we used. First, the elongation of the target (600x120mm@super 2@) induces a flux distribution with arriving angles up to 60° to the substrate normal. This flux distribution results in strong anisotropy of the surface morphology and in-plane crystallographic texture. Second, we tilted the substrate around an axis parallel to the target elongation. This introduced anisotropy in the perpendicular direction. As a consequence, the in-plane texture of the film was turned by 90° with respect to the texture in films grown on substrates parallel to the target. Planetary rotation around axes parallel to the target elongation was also studied. The tilt of the columnar microstructure of samples on tilted substrates is dependent on Ar pressure. At low Ar pressure the tilt is close to the substrate tilt (43° for 45° substrate tilt). The tangent rule predicts the inclination of 26.5°. The discrepancy is attributed to the complicated flux angular distribution from the elongated target. At higher Ar pressure the tilt of the columnar structure was smaller due to the smearing out of the flux distribution.

TF-MoP52 Plasma Diagnostics of Inductively Coupled Plasma Assisted Magnetron Sputtering for Reactive Deposition of MgO*, **J. Joo**,* Kunsan National University, Korea

Real time process diagnostics for reactive deposition of MgO were done to optimize high deposition rate and high transparency of the deposited films in rectangular (5 inch x 25 inch) target system. Inductively coupled plasma was adopted to enhance reactivity of oxygen for low temperature deposition of MgO. Using bipolar pulse power supply at 150 kHz, depositiion rate of 30 nm/min was achieved with 500 W pulse and 300 W of ICP power, which gave 90% of UV/VIS transparency(300 nm - 800 nm). For more intelligent feedback control, several real time diagnostics including OES, discahrge voltage and current waveform, QMS were carried out. With aid of ICP, metal ion signal showed very strong correlation with the reactivity of the plasma.

Thin Films
Room 306 - Session TF-TuM
Atomic Layer Deposition - Oxides

Moderator: H. Kim, Pohang University of Science and Technology, Korea

8:20am **TF-TuM1 Atomic Layer Deposition of Titanium Oxide Thin Films using O@sub 3@ for MIM Capacitor of Next Generation Memory Devices***, **S.K. Kim**, K.M. Kim, C.S. Hwang,* Seoul National University, Korea

TiO@sub 2@ films were deposited using a travelling-wave type ALD reactor on a bare-Si (100) wafer, sputtered and ALD Ru, and sputtered Pt electrodes at a wafer temperature of 250°C. TiO@sub 2@ thin films was grown using Ti(OC@sub 3@H@sub 7@)@sub 4@ and O@sub 3@ as the precursor and oxidant, respectively. The dielectric constants of these TiO@sub 2@ films are 83 between 100 for the films on Ru electrodes. Crystalline structure of TiO@sub 2@ films on various substrates was investigated to understand the origin of higher k values of TiO@sub 2@ films on Ru substrates. XRD results of TiO@sub 2@ films on various substrates show that the TiO@sub 2@ films on Si and Pt substrates have anatase structure whereas the films on Ru substrates have rutile phase grains. This means that the growth of rutile TiO@sub 2@ is related to the kind of substrate. The growth of rutile TiO@sub 2@ on Ru substrate is induced by the formation of RuO@sub 2@, which has almost identical ion arrangements in its rutile structure, at the TiO@sub 2@/Ru interface. For the application of the material and ALD process to DRAM devices, TiO@sub 2@ films were grown on contact hole structured Ru electrodes and the dielectric properties of Ru/TiO@sub 2@/Ru 3-D capacitor were investigated. The conformity in film thickness and dielectric properties over the entire structured surface was confirmed by capacitance variation vs. hole surface area experiments. Also, addition of Al as an acceptor in TiO@sub 2@ films was tried to improve the leakage properties of TiO@sub 2@ films due to a rather high leakage current density of TiO@sub 2@ films. Although toxeq. of doped-TiO@sub 2@ films is smaller than that of undoped-TiO@sub 2@ films, leakage current density of doped-TiO@sub 2@ films is much lower than that of undoped-TiO@sub 2@ films.

8:40am **TF-TuM2 Characteristics of Atomic Layer Deposited TiO@sub2@ Films and its Photocatalytic Activity***, **D.H. Kim**, R. Pheamhom,* Chonnam National University, South Korea

Titanium dioxide has many attractive physicochemical properties and thus lends itself to various applications such as optical coatings for anti-reflection, high dielectric layers for electronic devices, biocompatible coatings for biomaterials, and photosensitive layers for photocatalysts and solar cells. In this work, tetrakis(dimethylamido) titanium (TDMAT) has been evaluated as a possible precursor for TiO@sub 2@ ALD using H@sub 2@O@sub 2@ as a counter-reactant. We have explored the effects of deposition temperature, reactants pulse and purging time on the film growth rate to optimize the ALD process for TiO@sub 2@ preparation using TDMAT. Self-limiting reaction was possible, as supported by saturated film growth rate and the linear property of the film growth depending on the number of cycles. Film growth rate, surface morphology, crystallinity, and conformality on the deposition temperature along with the photocatalytic activity of the ALD TiO@sub 2@ in decomposing methylene blue in aqueous solution will be presented.

9:00am **TF-TuM3 Atomic Layer Deposition of SrTiO@sub 3@ Films Having a High Thickness- and Cation-Composition Conformality Over a Severe Contact Hole Structure***, **O.S. Kwon**, S.W. Lee, C.S. Hwang,* Seoul National University, Korea

SrTiO@sub 3@ (STO) thin films were grown on Si wafer and Ru-coated Si wafers, respectively, by an atomic-layer-deposition (ALD) technique using conventional metal organic precursors, Sr(C@sub 11@H@sub 19@O@sub 2@)@sub 2@ (Sr(thd)@sub 2@) and Ti(Oi-C@sub 3@H@sub 7@)@sub 4@ (TTIP) as Sr- and Ti-precursors, respectively, with a remote-plasma activated and thermal H@sub 2@O vapor as oxidant. Although the each precursor exhibited ALD reaction with the remote-plasma activated H@sub 2@O vapor, STO exhibited quite different deposition behavior with the bubbling temperature of Sr(thd) @sub 2@. The cation stoichiometry of STO films was dramatically improved when the bubbling temperature of Sr(thd) @sub 2@ < 200°C (melting temperature of Sr(thd) @sub 2@) irrespective of the type of oxidants. Furthermore, cation composition conformality over the severe contact hole structure (0.13µm opening diameter with an aspect ratio of 8) was highly improved when the Sr(thd)@sub 2@ bubbling temperature was 180°C. The thickness step coverage over the entire contact hole was >95%, and the variation of cation composition was very small (< 3%). The different degree of oligomerization of Sr(thd)@sub 2@ with the bubbling temperature was supposed to be the reason for these phenomena. Electrical properties of STO films grown by ALD were highly dependent on the amount of oxidant. Leakage current density of STO films with lower oxidant supply was too high to measure the dielectric properties. The high leakage property was directly related to the binding energy shift into high binding energy direction of Sr 3d peak position in the XPS analysis. The leakage current density of STO films with sufficient oxidant was reduced and the binding energy shift of Sr 3d peak was reduced. Equivalent oxide thickness < 1nm and leakage current density < 10@super -6@A/cm@super 2@ at 1V were obtained by the optimized two step deposition and post-annealing processes.

9:20am **TF-TuM4 Selective Atomic Layer Deposition (ALD) for Fabrication of Metal and Oxide Nanotubes***, **J.Y. Kim**,* Kookmin University, Korea, Rep. of Korea*; D. Jeong, S. Won, H. Shin, J. Lee,* Kookmin University, Korea

In this study, we have fabricated various metal and oxide nanotubes using selective atomic layer deposition (ALD). We easily control the nanotubes shape and make high aspect ratio nanotubes by selective ALD using SAMs such as OTS(octadesyl-tetrachlorosilane). We avoid unnecessary deposition on top of nanotemplates such as poly-carbornate, which results in stand alone nanotubes without connection. The selective ALD is performed on sacrificial nanotemplates with pore sizes of 30 - 200nm. The template were commercial available polycarbonate (PC) and anodic aluminum oxide (AAO) with various hole sizes and thicknesses. After deposition, template was removed by wet etching. We successfully obtain metal (Cu,Co) and oxide(ZrO2,TiO2) single material nanotubes. In addition, metal/oxide double wall nanotubes are fabricated by sequential ALD process. We make metal oxide nanotubes and measure various properties using high resolution-transmission electron microscope (HR-TEM), field emission-scanning electron microscope (FE-SEM), selective area electron diffraction (SAED) patterns, X-ray diffractionmeter (XRD). We also characterize electrical properties of the nanotubes using conducting-atomic force microscope (AFM). The authors gratefully acknowledge the financial support through center for nanostructured materials technology by Korean ministry of science and technology (03K1501-02410).

9:40am **TF-TuM5 Laterally Graded Films and Multilayers Using Atomic Layer Deposition with a Slit Doser and Substrate Translation***, **F.H. Fabreguette**, S.M. George,* University of Colorado

Laterally graded multilayers have a bilayer spacing that continuously changes versus spatial position. These graded multilayer structures are important for x-ray collimation and x-ray focusing. Recently, optimized W/Al@sub2@O@sub3@ superlattices grown using atomic layer deposition (ALD) displayed an excellent x-ray reflectivity (XRR) of 96% at @lambda@=1.54 Å. To obtain laterally graded W/Al@sub2@O@sub3@ multilayers, the normal conformality of ALD must be circumvented by preventing ALD on the entire substrate. Laterally graded multilayers can be fabricated using a slit doser to localize reactant delivery in a viscous flow gas stream. The substrate is then translated relative to the slit doser with a magnetic linear translator. Since the viscous flow entrains the reactants and moves them downstream, substrate translation upstream of the slit doser prevents ALD on the entire substrate. A laterally graded Al@sub2@O@sub3@ ALD film was initially demonstrated by translating the substrate relative to the slit doser during Al@sub2@O@sub3@ ALD reaction cycles. Variable angle ellipsometry and XRR quantified a varying Al@sub2@O@sub3@ film thickness grown on a Si(100) wafer with a length of 6 inches. Changes in leakage current density and capacitance confirmed the Al@sub2@O@sub3@ thickness gradient. In addition, a laterally graded ZnO/Al@sub2@O@sub3@ multilayer was grown and characterized using XRR. The angle of the first Bragg peak revealed a bilayer spacing that changed as expected versus spatial position.

10:00am **TF-TuM6 Coating Nanoparticles by Atomic Layer Deposition in a Rotary Fluidized Bed Reactor: Al@sub 2@O@sub 3@ ALD on ZrO@sub 2@***, **J.A. McCormick**, A.W. Weimer, S.M. George,* University of Colorado at Boulder

Ultrathin and conformal Al@sub 2@O@sub 3@ films have been grown by atomic layer deposition (ALD) on ZrO@sub 2@ particles with diameters of 60 nm and 400 nm using sequential exposures of trimethylaluminum and H@sub 2@O. This Al@sub 2@O@sub 3@ ALD on gram-scale quantities of high surface area ZrO@sub 2@ nanoparticles was performed in a novel rotary fluidized bed reactor. The rotary fluidized bed reactor consisted of a stainless steel porous metal cylinder that rotated inside a vacuum system. The nanoparticles were contained inside the porous metal cylinder and the

gaseous reactants and products could easily diffuse through the porous walls without particle loss. A magnetically coupled rotary motion feedthrough rotated the porous metal cylinder and provided a fluidization-like mixing between the particles and the reactants. The Al_2O_3 ALD films were deposited on the ZrO_2 nanoparticles at 180°C with a growth rate of 1.8 Å/cycle. The composition of the Al_2O_3 ALD coating was verified using Auger electron spectroscopy, x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Transmission electron microscopy and BET surface area analysis were utilized to determine the conformality of the Al_2O_3 ALD coating and to check for particle coalescence. The Al_2O_3 ALD film uniformly coats the primary ZrO_2 particles and there was no evidence for any particle coalescence.

10:20am **TF-TuM7 The Atomic-Layer-Deposited HfO_2 Gate Dielectric Films; Chemistry of Interface and Electrical Performances***, T.J. Park, M.J. Cho, S.H. Hong, M.H. Seo, J.H. Kim, J.H. Park,* ***C.S. Hwang,*** Seoul National University, Korea **INVITED**

HfO_2 thin films were deposited on HF-dipped Si wafers at temperatures ranging from 250 to 300°C using an atomic-layer-deposition technique with N-containing $Hf[N(CH_3)_2]_4$, $Hf[N(CH_3)(C_2H_5)]_4$ or $Hf[N(CH_3)(_2H_5)]_3[OC(CH_3)_3]$ and H_2O or O_3 as the precursor and oxidant, respectively. A thin interfacial SiN_x layer was spontaneously formed at the HfO_2/Si interface during film growth. This interfacial SiN_x layer played a critical role in improving the thermal stability and interfacial trap (D_{it}) property. D_{it} of < 5 x 10^{10} $cm^{-2}eV^{-1}$ near the mid-gap energy states was obtained from most of the process conditions but it usually suffer from the degradation by high temperature post-deposition annealing (PDA) at temperatures > 800°C. The adoption of O_3 oxidant reduced carbon impurity concentration and made the film more amorphous compared to the films grown using H_2O as oxidant. Although ozone was effective in reducing the impurity concentration, the higher concentration slightly deteriorated the dielectric performance. Investigation of the interface states using X-ray photoelectron spectroscopy revealed that the excessive oxygen incorporated during the film growth made the interfacial sub-oxide species (SiO, Si_2O_3 and silicate) and SiO_2 coordinate more with oxygen. This was further confirmed by the MOSFET performance comparison fabricated with HfO_2 gate dielectrics using different O_3 concentration. An electron effective mobility of ~ 65% of the MOSFET with SiO_2 as gate dielectric was obtained from the stoichiometric HfO_2 gate dielectric film. The effective mobility from the MOSFET with the oxygen excess HfO_2 film was only ~ 45 %.

11:00am **TF-TuM9 Atomic Layer Deposition for the Modification and Stabilization of Localized Surface Plasmon Resonance Nanosensors***,* ***J.W. Elam****, M.J. Pellin,* Argonne National Laboratory*; A.V. Whitney, R.P. Van Duyne, P.C. Stair, G.C. Schatz, S. Zou,* Northwestern University

Noble metal nanoparticles serve as optical biosensors and chemosensors because of the localized surface plasmon resonance (LSPR) effect. The optical properties of LSPR sensors are strongly influenced by the size, shape and dielectric environment of the nanoparticles. Atomic layer deposition (ALD) can deposit dielectric films with atomic layer precision onto a variety of substrates including noble metals. Consequently, the optical properties of LSPR sensors can be tailored using ALD coatings. In this study, ordered arrays of Ag nanoparticles were coated with ALD Al_2O_3 and the resulting changes in the physical properties of the nanoparticles were explored. Initial experiments examined the nucleation and growth of ALD Al_2O_3 on flat Ag surfaces using quartz crystal microbalance and ellipsometry measurements. Surprisingly, these measurements demonstrated that the Al_2O_3 ALD proceeds on Ag without any nucleation delay. Next, ordered arrays of Ag nanotriangles fabricated using nanosphere lithography were coated using ALD Al_2O_3 at 50 °C. Optical absorption measurements revealed a 6 nm red shift in the LSPR peak for an Al_2O_3 thickness of only 1.6 Å. The LSPR peak continues to red shift with increasing Al_2O_3 thickness up to ~600 Å. These changes are explained well by theoretical analysis using finite element electrodynamics. The Ag nanotriangles were also examined using atomic force microscopy and scanning electron microscopy and these measurements demonstrated that the ALD Al_2O_3 conformally coats the nanotriangles while preserving their initial shape. Preliminary experiments reveal that thin ALD Al_2O_3 layers significantly improve the thermal stability of Ag nanoparticles while retaining strong Raman enhancement, suggesting that ALD coatings will broaden the range of applications for LSPR nanosensors.

11:20am **TF-TuM10 Atomic Layer Deposition (ALD) of Nickel Films Using Amidinate Precursors***,* ***V.R. Pallem****, K. Kim, J.S. Park, R.G. Gordon,* Harvard University

Atomic layer deposition (ALD) of nickel thin films was demonstrated by using new nickel-amidinate precursors. Here we present a dozen nickel N,N'-Dialkyl-2-alkyl/aryl-amidinate derivatives as potential precursors for ALD. Their physical properties (volatility, thermal stability and chemical reactivity) were tuned by altering the alkyl groups. Nickel-bis(N,N'-di-tert-butylacetamidinate) showed the best overall properties as an ALD precursor. With NH_3 as a reducing agent at 270°C, self-limiting growth was achieved at a rate of 0.4 Å/cycle. Analyses of the deposited films showed only nickel. Nickel films grown on silicon nitride substrate had resistivity of 81 µΩ-cm. Post-deposition annealing of nickel films on HF-last silicon showed the formation of nickel silicide.

Thin Films
Room 306 - Session TF-TuA
Atomic Layer Deposition - Metals

Moderator: S. Rossnagel, IBM

2:00pm **TF-TuA1 Materials Available by ALD*, R.G. Gordon,*** Harvard University **INVITED**

Atomic later deposition (ALD) can deposit pure thin films with precisely-controlled, uniform thickness and composition over large areas and on aggressive topologies. ALD is a vapor deposition process based on sequential self terminating surface reactions where the precursor vapors are injected separately in pulses added to a flowing carrier gas, separated by a purge of excess precursor vapor. Each pulse and purge sequence constitutes an ALD half-cycle. Ideally, each half-cycle adds a uniform new layer of material and then the reaction stops even if more precursor vapor arrives at the surface. This self-terminating character results in ALD's uniformity, conformality and precise thickness control. To achieve ALD's unique characteristics, ALD precursors must have very specific properties: high reactivity with surfaces (but not with themselves), high thermal stability, along with adequate volatility. In addition, their reaction byproducts must not react with the deposited films. Precursors with metal-nitrogen bonds have been found to be particularly effective for ALD of metal oxides, nitrides, silicates, phosphates and pure metals: dialkylamides of Al, Sn, Ti, Zr, Hf, Nb and Ta; dialkylamide-alkylimide mixed ligand compounds of Nb, Ta, Mo and W; dialkylacetamidinates of Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Ru, Co, Ni, Cu, Bi, Y, La and the other lanthanide metals. Examples of the materials made from these precursors include high-k dielectric insulators HfO@sub 2@, HfON, HfSiON and LaAlO@sub 3@; electrical conductors of Cu; conducting Cu diffusion barriers of WN and TaN@sub x@; metals Co and Ru that promote strong adhesion between Cu and nitride diffusion barriers; magnetic metals Fe, Co and Ni and their magnetoresistive combinations with Al@sub 2@O@sub 3@ or MgO; photonic crystals of high-dielectric constant material Ta@sub 3@N@sub 5@; insulating AlN for passivating Ge surfaces; conformal silica layers for insulation in microelectronics, and for optical interference filters and nano-optical devices.

2:40pm **TF-TuA3 Ru ALD and Applications for Advanced Devices*, H. Lee,*** *S.J. Lim, W.J. Maeng, H. Kim,* POSTECH, South Korea

Ru has good properties such as low resistivity, high thermal stability, and nobility. Thus, the atomic layer deposition (ALD) of Ru has been required for many applications in nanoscale device fabrication including memory capacitor electrode, Cu electroplating seed layer, and CMOS gate electrode with the scaling of devices. Although ALD of Ru has been reported by several groups previously, there are still crucial problems to be solved including the poor nucleation and practical limitation caused by the use of oxidant as a reactant. To address these problems, we have performed comparative studies using different Ru precursors including cyclopentadiel, pentadienyl, and carbonyl based precursors on various practically important substrates including Si, SiO@sub 2@, Ta@sub 2@O@sub 5@, TaN, and TiN. Also, plasma enhanced ALD using hydrogen and nitrogen plasma has been performed. Very low resistivity (as low as 10µ@ohm@cm) Ru with excellent conformality was obtained and the in situ plasma treatment produced promising results to enhance nucleation behavior. The microstructure of Ru layer as well as interface between Ru and substrates and chemical and electrical properties have been characterized. The results will be discussed focusing on the future semiconductor device applications including electrode and Cu electroplating seed layer.

3:00pm **TF-TuA4 Atomic Layer Deposition of Ruthenium on Organic Self Assembled Monolayers for Work Function Tuning*, K.J. Park,*** *D.B. Terry, G.N. Parsons,* North Carolina State University

Ruthenium is of interest for advanced metal/oxide/ semiconductor (MOS) transistor gate electrodes to reduce poly-silicon depletion and as a nucleation layer for copper interconnects. Patterned self assembled monolayers have previously been used to impede nucleation during ALD processing. In this work, metal atomic layer deposition was achieved on self-assembled monolayers, where the tail groups were chosen to promote, rather than impede nucleation, and the effect of the monolayer on the work function of the metal in an MOS capacitor is characterized. Specifically, Ru was deposited using bis-(cyclopetandienyl) ruthenium and oxygen onto HfSiO@sub x@, SiO@sub 2@, and onto 3-aminopropyltriethoxysilane (APTES) and undecenyl tricholosilane (UDS) monolayers formed on HfSiO@sub x@. Self-limiting atomic layer deposition was achieved at temperatures between ~310° and 350°C, corresponding to ~1 Å per deposition cycle. Capacitance vs. voltage (CV) with various thicknesses of dielectric was measured at 1MHz using p-type silicon substrates with doping levels of 1.5x10@super 18@ cm@super -3@, to determine the effective workfunction (@PHI@@sub m,eff@) of the ALD metal. The organic monolayer undergoes some reaction and modification during the metal ALD step, however CV measurements show relatively stable behavior at room temperature, with large changes observed after a 400°C forming gas anneal, suggesting stability of the monolayer during deposition. Ru on untreated HfSiO@sub x@ gives @PHI@@sub m,eff@ = 4.7 eV, whereas the APTES treated surface shows an increase in @PHI@@sub m,eff@ to about 4.8 eV, and a decrease to about 4.2 eV for the UDS surface. The shifts are consistent with dipoles in the monolayers at the organic/dielectric interface. The ability to deposit metal by ALD onto organic surfaces will likely be useful for a variety of advanced organic device structures.

3:20pm **TF-TuA5 Quartz Crystal Microbalance Measurements of W ALD Nucleation on Al@sub 2@O@sub 3@*, R.A. Wind*,** *F.H. Fabreguette, S.M. George,* University of Colorado

Nucleation phenomena can critically affect the growth of nanolaminates using atomic layer deposition (ALD). A good example is W/Al@sub 2@O@sub 3@ nanolaminates where the nucleation of W ALD on Al@sub 2@O@sub 3@ limits the minimum thickness of a continuous and ultrasmooth W nanolayer to ~25 Å. Quartz crystal microbalance (QCM) studies can measure the mass gain per cycle (MGPC) during ALD with a precision of ~0.4 ng/cm@super 2@. QCM investigations of W ALD nucleation on Al@sub 2@O@sub 3@ reveal complex behavior. During optimum nucleation conditions, WF@sub 6@ exposures lead to mass gain but Si@sub 2@H@sub 6@ exposures produce no measurable mass gain for the first 2 cycles. After 3 cycles, the MGPC for both reactants increases and reaches a maximum after 8 cycles for WF@sub 6@ and after 12 cycles for Si@sub 2@H@sub 6@. The total MGPC exhibits a "ringing" behavior and a second maximum is observed before reaching the steady state growth rate. For different reactant exposures, the positions of the first and second maxima in the MGPC shift to a longer number of cycles. Modeling of these QCM results is in agreement with three-dimensional W island growth that produces a maximum in the MGPC. This maximum corresponds to the largest W surface area prior to the coalescence of the W islands. The existence of these W islands is confirmed by atomic force microscope (AFM) measurements. The changing ratio of the WF@sub 6@ and Si@sub 2@H@sub 6@ MGPCs is consistent with distinct growth regimes. These different ratios suggest that the relative density of reactive surface sites evolves as W islands are created, grow, and coalesce prior to forming a continuous W film.

3:40pm **TF-TuA6 Novel ALD Reactor Design and Metrology Study for Tungsten ALD Process*, W. Lei,*** *L. Henn-Lecordier, G.W. Rubloff,* University of Maryland

We have developed a novel wafer-scale atomic layer deposition (ALD) reactor which incorporates small reaction volume for short cycle time, multi-mode operation for process flexibility, and in-situ chemical sensing for rapid process learning and control. A movable cap within the UHV chamber enables transfer and enclosure of the wafer within a 0.2 L mini-reactor. Operation is possible using steady-state flow with alternating gas species or using fill-and-pumpout cycling of each gas with pumpout acceleration by lifting the cap to employ the larger reactor volume as ballast. Downstream in-situ mass spectrometry (MS) provides direct process sensing. By integrating reaction product MS signal over each exposure, we are able to observe nucleation and linear film growth stages of ALD film growth and study nucleation kinetics under different process and initial surface conditions, which indicated the application of in-situ MS for advanced process control in ALD process. First wafer effects in in-situ MS sensing are apparent when a sequence of wafers are processed, particularly when time delays are introduced between wafers; this is attributed to concurrent reaction on mini-reactor walls, where different gas exposure history is encountered. Advanced process control can be improved by proper pre-process reactor treatment to reduce first wafer effect.

Plasma Science and Technology
Room 302 - Session PS+TF-WeM
Plasma Enhanced CVD and ALD

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

8:20am **PS+TF-WeM1 Developments of Plasma Copolymerization Technique for Deposition of low-k Films**, ***K. Kinoshita***, *A. Nakano, N. Kunimi, M. Shimoyama, J. Kawahara,* Mirai-Aset, Japan*; O. Kiso, Y. Seino, Y. Takasu,* Mirai-Asrc, Aist, Japan*; M. Komatsu,* Sumitomo Chem., Japan*; K. Nakamura,* Chubu University, Japan*; T. Kikkawa,* Hiroshima Univ., Japan **INVITED**

We have proposed the strategic concept of scalable low-k materials for ULSIs which can be used over two or three technology nodes.@footnote 1@ The major challenge to realize this concept is controlling the dielectric constant and mechanical strength. A plasma copolymerization technique has been developed for this purpose.@footnote 2@ Basic film properties will be determined by the matrix monomer, and modified by copolymerization with modification monomers. A narrow-gap CCP was employed to generate uniform discharge over the 300 mm wafer. A divinylsiloxane-bis-benzocyclobutene (DVS-BCB) was chosen as a starting matrix monomer. The dielectric constant of the polymerized DVS-BCB film was 2.78. Electron density of this polymerization plasma was about 1.5E10 cm@super -3@ as measured by surface wave probe technique.@footnote 3@ Modification monomers were chosen from the view points of the reactivity, the estimated dielectric constant of the monomers, and the vapor pressure. To increase film modulus, phenyl compounds with unsaturated functional groups were introduced. The copolymerization ratio corresponded to the film modulus.@footnote 4@ To reduce dielectric constant, aliphatic compound was introduced. However, copolymerization with DVS-BCB at 400 °C could not reduce the dielectric constant due to decomposition of aliphatic components. A process of low temperature deposition followed by annealing was examined with 2-dimethylvinylsiloxane-tricyclodecane (2DMVS-TCD). A dielectric constant of 2.48 was obtained by deposition at 300 °C followed by annealing at 400 °C. This work was supported by NEDO. @FootnoteText@ @footnote 1@ T. Kikkawa, Ext. Abst. ADMETA 2003: Assian session, Tokyo, 1-2, (2003) 4,@footnote 2@ J. Kawahara, et al., Technical Dig. IEDM 2003, 6-2, (2003) 143,@footnote 3@ K. Nakamura, et al., Proc. Int. Symp. Dry Process 2004, Tokyo, P-29, (2004) 169,@footnote 4@ N. Kunimi, et al., Proc. IITC2004, San Francisco, 8.5, (2004) 134.

9:00am **PS+TF-WeM3 Amorphous Carbon Thin Films Deposition by Pulsed Substrate Biased PECVD using a CH@sub 4@-CO@sub 2@ Gas Mixture**, ***G. Gottardi***, *N. Laidani, L. Calliari, M. Filippi,* ITC-Irst (Centro per la Ricerca Scientifica e Tecnologica), Italy*; R.S. Brusa, C. Macchi, S. Mariazzi,* Università di Trento, Italy*; M. Anderle,* ITC-Irst (Centro per la Ricerca Scientifica e Tecnologica), Italy

Various plasma-assisted deposition techniques and carbon bearing source materials have been investigated and can be used for the synthesis of a-C:H films. In particular, radio frequency (RF) plasma-enhanced chemical vapor deposition (PECVD) systems are the most common type employed, over a broad range of process conditions which are generally recognized to strongly influence the material properties. This research work intends to explore new perspectives in the hard carbon films production via PECVD, through the use of non-traditional gas precursors (CH@sub 4@-CO@sub 2@) and a voltage pulsing technology applied externally simultaneously to the film growth. The modulation of the substrate bias, when applied in a pulsed mode, provides in fact with more operative opportunities, broadening the process parameters set with respect to the conventional technology with a continuous bias and turning out to be much more effective in the densification and hardening of the material. A multi-technique approach has been used for a thorough characterization of the deposited films in order to highlight the effects of the gas precursor composition and of the ion bombardment due to the substrate bias on the chemical, structural and mechanical evolution of the material. In particular, the chemical composition and the structure were investigated with X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FT-IR) and electron energy loss spectroscopy (EELS). Positron annihilation spectroscopy (PAS) was performed for the detection of nano-scale open volume defects while nano-indentation and stylus profilometry techniques were used to evaluate the film hardness and internal stress.

9:20am **PS+TF-WeM4 Multi-hollow Plasma CVD Method for Depositing Cluster-free a-Si:H Films**, ***K. Koga***, *K. Bando, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

The three major limitations of a-Si:H solar cells are 1) light-induced degradation of cell efficiency, 2) a low deposition rate, and 3) a low cell efficiency. We have developed a multi-hollow plasma CVD method for depositing cluster-free a-Si:H films, since films incorporating less amount of a-Si:H nano-particles (hereafter refereed to as clusters) show better stability.@footnote 1@ For the method, powered and grounded electrode of 70 mm in diameter, which had 24 holes of 5 mm in diameter, were placed at a distance of 2 mm. Discharges were sustained in the holes using a VHF power source. A short gas residence time of ~ ms in the discharge regions suppressed growth of clusters and gas viscous force drives clusters toward the downstream region. Therefore, cluster-free a-Si:H films can be deposited on substrates set in the upstream region. Stability of the films against light soaking was evaluated with their defect density measured by ESR and a fill factor FF of a Schottky cell having a structure of Ni/a-Si:H/n type Si. The initial defect density of a film deposited at 0.12 nm/s is 3.5x10@super 15@cm@super -3@ and that after light soaking (7.5 hours under 2.4 SUN) is 3.7x10@super 15@cm@super -3@. The cell using a film deposited at 0.2 nm/s has a rather high stabilized FF of 0.50 and a small degradation ratio of 2.0 %. A higher deposition rate up to 0.66 nm/s can be obtained by utilizing a higher discharge power. Thus the multi-hollow plasma CVD method is effective in overcoming the three limitations for a-Si:H solar cells. @FootnoteText@ @footnote 1@K. Koga, N. Kaguchi, M. Shiratani and Y. Watanabe, J. Vac. Sci. Technol. A 22, (2004) 1536.

9:40am **PS+TF-WeM5 Proton/Deuteron Exchange in Functional Plasma Polymer Films (A Neutron and X-ray Reflectometry Study)**, *B.W. Muir,* ***C. Fong***, *J. Oldham, P.G. Hartley, K. Mc Lean,* CSIRO, Australia*; A. Nelson, M. James,* Australian Nuclear Science and Technology Organisation

The plasma polymer (PP) deposition of chemically reactive monomers is frequently used to provide a chemical handle on inert surfaces. The characterization of the surface and internal structure of these thin films is critical in establishing their efficacy in technological applications. X-ray and neutron reflectometry are techniques that have become increasingly important in the characterisation of thin-film surfaces and interfaces; it now being possible to obtain angstrom precision depth profiles of a films composition. In this study, we have investigated the physico-chemical properties of allylamine plasma polymer thin films using X-ray and Neutron reflectometry in air and aqueous environments. Correlation of X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) data with X-ray and neutron reflectometry measurements on the PP film versus air, has allowed the stochiometric composition of the film to be obtained. The mass density was found to be 1.305 g/cm@super 3@ and film thickness 27.8 nm which correlated well with AFM measurements. Interestingly, when neutron reflectometry measurements are performed in D@sub 2@O we observe a significant increase in the scattering length density of the film from 2.033 e@super -6@ Å@super -2@ in air to 3.81 e@super -6@ Å@super -2@ in D@sub 2@O. By performing contrast experiments in mixtures of D@sub 2@O/H@sub 2@O we have found that a significant proportion of the protons within the film exchange with deutrons from solution. The films were found to contain approximately 3.3% water and 30% of the protons in the film are capable of exhanging, indicating significant functionality within the plasma polymer film. The study demonstrates that rich physicochemical information can be obtained on nano-scale thin plasma polymer films in different environments by combining a number of surface analytical techniques.

10:00am **PS+TF-WeM6 Anisotropic Deposition of Cu and Ru in Trenches by H-assisted Plasma CVD**, ***M. Shiratani***, *T. Kaji, K. Koga,* Kyushu University, Japan

Previously we realized anisotropic deposition of Cu, for which Cu is filled preferentially from the bottom of trenches without being deposited on their sidewall, by H-assisted plasma CVD using Cu(HFAC)@sub 2@ as a source material.@footnote 1,2@ In this study, we have demonstrated anisotropic deposition of Cu from Cu(EDMDD)@sub 2@ and that of Ru from Ru(ACAC)@sub 3@. Ion irradiation to surface where deposition takes place, is the key to all of the anisotropic deposition processes, whereas deposition characteristics depend on materials. For Cu(EDMDD)@sub 2@ and Ru(ACAC)@sub 3@, the deposition rates on the bottom of trenches decrease with decreasing the trench width, while that for Cu(HFAC)@sub 2@ increases. These results suggest that anisotropic deposition by H-assisted plasma CVD using metal-complex has a potential to be applied to deposition processes of many kinds of metals, metal-oxide, and metal-

carbide. We will compare deposition characteristics for Cu and Ru and discuss the deposition mechanisms. @FootnoteText@ @footnote 1@ K. Takenaka, et al., Pure. Appl. Chem. 77(2005)391.@footnote 2@ K. Takenaka, et al., J. Vac. Sci. Technol. A22(4) (2004) 1903.

10:20am **PS+TF-WeM7 Metal ALD Challenges in Microelectronics Fabrication**, ***K. Leeser,*** Novellus Systems Inc. **INVITED**

As device geometries continue to shrink, limitations are encountered with conventional thin film processing techniques. Some of these applications have begun the migration towards atomic layer deposition (ALD) as a means of addressing these limitations. Initial applications have focused on dielectric deposition for DRAM and gate stack, but the migration from fab R&D to production has been slow. Current trends indicate that ALD applications of metallic compounds and elemental metals will actually enter mainstream production at a faster rate than their dielectric counterparts with substantial evaluation activity already at the 45nm node, especially for backend metallization. However, metal ALD process technology, applications, integration, and hardware design are more difficult than those required for dielectric ALD. This presentation will highlight and discuss these critical challenges with emphasis on non-tungsten applications.

11:00am **PS+TF-WeM9 Plasma-assisted Atomic Layer Deposition of TiN Films at Low Substrate Temperatures**, ***W.M.M. Kessels,*** Eindhoven University of Technology, The Netherlands, Netherlands; *S.B.S. Heil, E. Langereis,* Eindhoven University of Technology, The Netherlands; *F. Roozeboom,* Philips Research Laboratories, The Netherlands; *M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin films with a high conformality and with precise thickness control. The extension of the technique with plasma processes (i.e., plasma-assisted ALD) opens up new routes in ALD that are difficult to attain by pure thermal ALD, as for example depositing high-quality films at low substrate temperatures. This is an important issue for metallic films such as TiN. High quality films can be deposited by ALD using the halide precursor TiCl@sub 4@ and NH@sub 3@ but this process is only applicable at temperatures of 350-400 °C. Lower deposition temperatures are, however, necessary for compatibility with some high-k oxides, processes involving Cu to avoid CuCl formation, and for improved barrier properties. Therefore we have developed a plasma-assisted ALD process of TiN using TiCl@sub 4@ dosing alternated with H@sub 2@-N@sub 2@ plasma exposure. The plasma is generated with a remote ICP plasma source and has been characterized by electrical probe measurements and optical emission spectroscopy. In situ spectroscopic ellipsometry has been used to monitor the growth rate per cycle (0.6 Å/cycle at 400 °C) and from a parameter study it has been proven that the surface reactions are self-limiting. TiN films have been deposited for substrate temperatures between 100-400 °C and the material properties have been analyzed by several diagnostics. Some key observations are that the deposition rate decreases and the Cl content and electrical resistivity increase with decreasing temperature. Nevertheless, the Cl content and resistivity remain relatively low for an ALD process. Furthermore, some plasma-related aspects for the ALD process will be discussed, such as facilitated initial growth on different substrates, surface modification of the underlying substrate (nitridation by N radicals), and the influence of wall-recombination of radicals in high-aspect ratio structures.

11:20am **PS+TF-WeM10 Characteristics of HfN deposited by using Remote Plasma Enhanced Atomic Layer Deposition Method**, ***K.W. Lee,*** *S.J. Han, G.J. Kim, W.H. Jeong, H.T. Jeon,* Hanyang University, Korea

Metal oxide films with high dielectric constants (high-k) have been studied recently to overcome the current disadvantages of SiO@sub2@ material. This high-k oxide material also need to apply new gate electrode because of the problems of polysilicon/high-k gate stacks such as poly-Si depletion effect, Fermi level pinning, surface phonon scattering, high threshold voltages and channel mobility degradation in real devices. Current polysilicon as a gate electrode results in poor transistor performance. Due to these problems new metal gate materials are needed to solve these problems because the metal/high-k gate stack is very effective in screening the phonon scattering and improves the channel mobility. And the use of metal gate electrode eliminates poly-Si depletion effect and Fermi level pinning. Among the many candidates the refractory metal nitrides such as titanium nitride (TiN) and tantalum nitride (TaN) are considered as the solutions to replace current poly-Si gate electrode. HfN exhibits various advantages such as thermal stability, midgap work function(4.65eV), and low lattice mismatch(1.13) with HfO@sub2@ gate dielectric and is considered as one of the most suitable candidates as gate electrode. In this work we studied this HfN material with remote plasma enhanced atomic layer deposition(RPEALD) method with tetrakis-ethylmethylamino-hafnium (TEMAH), Hf[N(CH@sub3@)C@sub2@H@sub5@]@sub4@ as a Hf precursor and NH@sub3@ plasma as a reactant gas. This HfN gate electrode was deposited on the HfO@sub2@ gate oxide. After deposition, the physical and chemical characteristics were evaluated, and MOS capacitors were fabricated with the HfN electrode to measure the electrical properties. The interfacial layers of deposited the HfN/HfO@sub2@ and the TiN/HfO@sub2@ stacks were investigated by high resolution transmission electron microscope (HRTEM).

11:40am **PS+TF-WeM11 Plasma-Enhanced Atomic Layer Deposition for Compositionally Controlled Metal Oxide Thin Films**, *R.M. Martin,* ***K.M. Cross,*** *J.P. Chang,* University of California, Los Angeles

The need to replace SiO@sub 2@ by a higher dielectric constant material in fabricating smaller and faster metal-oxide-semiconductor (MOS) transistors is well recognized by the National Technology Roadmap for Semiconductors. Atomic layer deposition emerges as a viable chemical processing technique to enable the deposition of ultra-thin and highly conformal thin films, and the use of plasma allows greater flexibility in designing doped or alloyed thin films with controlled compostition. In this work, we discuss the atomic layer deposition of HfO@sub 2@ and Hf@sub 1-x@Si@sub x@O@sub y@ using an alternating, cyclical sequence of hafnium terta-tert butoxide and tetra ethyl ortho silicate as the chemical precursors and oxygen radicals generated from an oxygen plasma as the oxidant. Optical emission spectroscopy (OES) was used to identify and quantify the gas phase atomic species. The thicknesses of the films scaled linearly with the number of deposition cycles as determined by both ellipsometry and x-ray photoelectron spectroscopy (XPS) measurements. Thin film composition of Hf@sub 1-x@Si@sub x@O@sub y@ can be varied and controlled by the chemical sequences, as verified by XPS compositional analysis. Atomic force microscopy (AFM) was used to determine surface roughness of the deposited films as a function of the deposition chemistry sequence and film thickness. MOS transistors were fabricated with the PEALD deposited films and capacitance-voltage (C-V) and current voltage (I-V) measurements showed that the PEALD HfO@sub 2@ films had a dielectric constant of 25 and an equivalent oxide thickness of 12.5-15 Å. Device results of Hf@sub 1-x@Si@sub x@O@sub y@ will be discussed as a function of the Si concentration and the resulting interfacial composition.

Thin Films
Room 310 - Session TF+EM-WeM
In-Situ/ Ex-Situ & Real- Time Monitoring

Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am **TF+EM-WeM1 In-situ Infrared Absorption Spectroscopy of High-k Dielectrics Growth on Semiconductors**, ***Y.J. Chabal,*** *S. Rivillon, Y. Wang, K. Bratland, M.-T. Ho,* Rutgers University **INVITED**

Atomic Layer Deposition (ALD) is a particularly attractive method to grow a variety of heterostructures on semiconductors. It makes it possible for instance to deposit ultra-thin and near stoichiometric high-k dielectric metal oxides films one layer at a time in a highly conformal manner. For microelectronics applications, controlling the nature of the semiconductor/oxide interface and the oxide film itself is critical. For instance, formation of an interfacial SiO2 layer during metal oxide growth or incorporation of excess oxygen in the oxide is a major detriment to the performance of future MOSFETs. This talk discusses the use of in-situ infrared (IR) absorption spectroscopy to optimize silicon and germanium wafer pretreatments, to monitor interface formation during growth and to control the nature of metal oxides. For this work, a simple ALD reactor has been designed to be compatible with efficient transmission IR spectroscopy. The effects of surface chemical functionalization of H-terminated Si and Ge surfaces with Cl, NH3 prior to and thermal annealing after Al2O3 and HfO2 deposition have been investigated with emphasis on identifying the presence and bonding of oxygen at the interface. The mechanism for oxygen incorporation have been identified resulting in a much better control of the interface.

9:00am **TF+EM-WeM3 Real-time Sensing for Process Dynamics and Metrology in Tungsten Atomic Layer Deposition**, ***L. Henn-Lecordier,*** *W. Lei, G.W. Rubloff,* University of Maryland

Atomic layer deposition (ALD) has been investigated using a novel wafer-scale reactor which features an internal mini-reactor and in-situ mass spectrometry (MS) for chemical analysis during tungsten ALD using WF6

and SiH4. Downstream MS sampling system measures deposition kinetics directly and reaction product MS signal is used for real-time thickness metrology. MS signal reveals ALD reactant and product species in real time through ALD process cycle, with product generation and reactant depletion indicative of species consumption. Both the H2 product from SiH4 exposure and the SiF4 product from WF6 exposure show the kinetics of self-limiting adsorption/reaction on the surface, which enables process optimization to minimize cycle time. MS data also directly indicates the influence of process temperature and precursor dose on film growth, and can also been employed for process optimization. The integrated reaction product MS signal over each exposure, when plotted against ALD cycle number, reveals different stages of ALD film growth and provides a quantitative measure of film thickness. Our study demonstrated that integrated reaction product MS signal has a good linear relationship with ALD film thickness. This provides a promising approach to advanced process control in ALD manufacturing.

9:20am **TF+EM-WeM4 Twin Boundaries can be Moved by Step Edges during Film Growth***, **N.C. Bartelt**, W.L. Ling, K.F. McCarty,* Sandia National Laboratories*; C.B. Carter,* University of Minnesota

Considerable effort has been devoted to minimizing twins in a film's microstructure because they typically degrade a film's performance. Twins are generally believed to originate from the nucleation stage of film growth. That is, when film islands nucleate, not all of them contain the same stacking sequence of film layers. Twin boundaries then occur where islands with different stacking sequence impinge. Attempts to reduce the density of twins are usually based on minimizing their nucleation or by removing them by annealing. We track individual twin boundaries in Ag films on Ru(0001) using low-energy electron microscopy (LEEM). We find that twin boundaries can move readily during film growth but relatively little during annealing. The growth-driven motion of twin boundaries occurs as film steps advance across the surface -- as a new atomic Ag layer approaches an fcc twin boundary, the advancing step edge carries along the boundary, which intersects the film thickness. This process can produce twin-free regions that are over 10 Âµm wide. These observations show that there can be a close connection between morphological evolution and microstructural evolution in thin films. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000.

9:40am **TF+EM-WeM5 In-Situ Real Time Spectroscopic Ellipsometry Studies of the Growth of Amorphous and Epitaxial Silicon for Photovoltaic Applications***, **D.H. Levi**, C.W. Teplin, E. Iwaniczko, Y. Yan, T.H. Wang, H.M. Branz,* National Renewable Energy Laboratory **INVITED**

In-situ monitoring of material properties during thin film deposition provides researchers with a valuable tool for maximizing solar cell performance, while also enabling efficient exploration of deposition parameter space. In this presentation I will describe how our research team at NREL has utilized in-situ real time spectroscopic ellipsometry (RTSE) to maximize our productivity in two related projects. We are using hot wire chemical vapor deposition (HWCVD) for low-temperature (90 to 350@super o@C) deposition of very thin films of amorphous hydrogenated silicon (a-Si:H) for a-Si / crystal-Si (c-Si) heterojunction (SHJ) solar cells. We are also using HWCVD for low temperature (200 to 440@super o@C) deposition of epitaxial films of silicon (epi-Si) on c-Si substrates. We utilize RTSE as both an in-situ diagnostic and a post-growth analysis tool for SHJ solar cells and epi-Si films grown by HWCVD. RTSE enables precise thickness control of the 3 to 10 nm thick layers used in the SHJ devices, as well as monitoring crystallinity and surface roughness in real time. Post-growth analysis of the RTSE data has enabled us to determine the optical, electronic, and structural properties of the thin films used in the SHJ devices, as well as crystallinity vs. thickness in the epi-Si layers. This information has been used to fine-tune the deposition parameters to optimize device performance and epi-Si thickness. Using input from RTSE analysis we have achieved a photovoltaic energy conversion efficiency of 17% on an Al-backed p-type float-zone c-Si wafer. Epi-Si films have been grown as thick as 500 nm utilizing parameter optimization based on RTSE analysis.

10:20am **TF+EM-WeM7 Analytic First-Order Solution for the Simultaneous Determination of Complex Refractive Indices and Thicknesses of Thin Films Deposited on Substrates***, **I.K. Kim**, D.E. Aspnes,* North Carolina State University

The problem of the simultaneous determination of the complex refractive index = n + i@kappa@ and thickness d of an isotropic thin film deposited on an isotropic substrate from polarimetric data (the so-called nkt problem) has never been solved analytically for a general , although solutions are available for the case of a transparent film (@kappa@ = 0). Here, we present an analytic solution for arbitrary n and @kappa@ that is valid to first order in d/@lambda@, where @lambda@ is the wavelength of light. The solution requires a knowledge of the change of pseudodielectric function <@epsilon@>, or alternatively the relative change @Delta@@rho@/@rho@ in the complex reflectance ratio @rho@, and either the relative change @Delta@Rp/Rp or @Delta@Rs/Rs, where Rp and Rs are the reflectances for p- or s-polarized light. Ranges of validity are obtained by comparing results to those obtained numerically using the exact three-phase-model expressions, and a procedure is presented for improving the accuracy. Numerical evaluation of the exact equations, which proceeds by least-squares analysis, is facilitated by using the first-order solution as a starting point. Depending on the sample the first-order solution is more effective at some energies than others, emphasizing the need for multiwavelength measurements over finite energy ranges. The most effective ranges can be determined from the correlation coefficients obtained in the least-squares analysis. As previously noted, the highest correlation generally occurs between n and d, although under some situations a high correlation can also occur between @kappa@ and d. The results should be particularly useful for systems involving reversible configurations, such as the cyclic adsorption and desorption of gases on clean surfaces, where accuracy can be improved by modulation techniques.

10:40am **TF+EM-WeM8 Linear Nanomechanical Measurements using a Novel AFM Technique***, **P.M. Hoffmann**,* Wayne State University **INVITED**

Atomic Force Microscopy has been extensively used to study roughness, adhesion and mechanical properties of surfaces and thin films. However, commonly used AFM techniques suffer from a variety of problems inherent to the technique: Snap-in instabilities in static AFM and non-linearities in dynamic AFM measurements. Here we present a new AFM technique that avoids these problems and is capable of stable, linear measurements of many systems, including atomic scale contact mechanics and atomic friction on surfaces. I will introduce the technique and present recent results, especially the finding that continuum mechanics applies in atomic contacts even if the number of atoms in the contact becomes very low and the observation of friction due to a single atomic defect.

Thin Films
Room 306 - Session TF-WeM
Mechanical and Tribological Properties of Thin Films

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

8:20am **TF-WeM1 Mechanical Properties of Thin Films and Multilayers***, **F. Spaepen**,* Harvard University **INVITED**

Thin films and multilayers are ideal systems to study the dependence of the mechanical properties on various length scales: grain size, film thickness, layer thickness, compositional modulation and dislocation cell size. Special techniques are required to perform tensile tests on thin films, which can be free-standing, or in the case of metallic films less than 1 mm thick, supported on thin, compliant polymeric substrates, such as Kapton. These techniqes allow determination of stiffness, anelastic behavior, yield stress, work hardening and fracture, all of which depend in characteristic ways on the various length scales. The development of stress in a thin film during deposition can be studied by measuring the curvature of the substrate (usually by laser reflection, often in situ) or the average lattice parameter (by X-ray diffraction). The development of the stress is strongly affected by the evolution of the microsctructure. Interfaces play a particularly important role. For example, the trade-off between surface and grain-boundary energies provides the (tensile) strain energy in island coalescence. Examples will be given from metallic (Cu, Ag,..) and ceramic (YSZ) films.

9:00am **TF-WeM3 Evaluation of Applied Substrate Bias on Yttria-Stabilized Zirconia Thin Films***, **J.R. Piascik**,* University of North Carolina at Chapel Hill and RTI International*; J.Y. Thompson,* University of North Carolina at Chapel Hill*; C.A. Bower,* RTI International*; B.R. Stoner,* RTI International and University of North Carolina at Chapel Hill

Partially stabilized zirconia (PSZ), possesses a unique set of material properties. Due to its high toughness, excellent wear behavior, and thermal stability, PSZ, in the form of thin films, can be used for a variety of applications ranging from biomedical to thermal barriers. The objective of this research was to study environmental effects on film stress and model water absorption into the defect structure of films deposited with varying

substrate bias. Yttria (3 mol%)-stabilized zirconia (YSZ) thin films were deposited using radio frequency (RF) magnetron sputtering. YSZ thin films were deposited at a working pressure of 15mT, temperature of 150°C, and Ar/O2 gas ratio of 30:1. An applied substrate bias was varied (0 to 50W) to alter film density and structure. X-ray diffraction (XRD) showed that films increased in monoclinic phase percentage as a function of increasing substrate bias power. Wafer bow measurements indicate that initial film stress increased in a compressive direction (70 to 302MPa) as substrate bias was increased. Aging in ambient environments (25°C, 75% relative humidity) led to a significant increase in compressive stress (80MPa) for films deposited without substrate bias. Thermal treatment, to remove absorbed water, caused films to return to near-initial stress states. Once exposed to ambient conditions, measured stress was found to increase at a rate of 0.20MPa/min for the first 2hr of exposure then by approximately 2MPa/day for a period of 30 days. Films deposited with applied substrate bias displayed a reduction in this time-dependent phenomenon. Cross-sectional TEM allowed for high-resolution images to analyze film structure and defect density. A subsequent model is proposed, describing the incorporation of water vapor into structural defects in the deposited films. This work is supported through NIH-NIDCR R01 DE013511.

9:20am **TF-WeM4 Ion Beam Assisted Deposition of Cubic Zirconia***, X. Wang,* University of Nebraska-Lincoln*; I. Amirani, S. Varma,* University of Nebraska Medical Center*; D.W. Thompson,* University of Nebraska-Lincoln*; F. Namavar,* Universoty of Nebraska Medical Center*;* ***N.J. Ianno****,* University of Nebraska-Lincoln

Cubic zirconia's excellent wear properties and inertness make it an excellent choice for a range of applications. In this work we will show that ion beam assisted deposition (IBAD) of thin film single phase cubic zirconium oxide has been accomplished. Deposition is accomplished by electron beam evaporation from a pure zirconium oxide source in a low pressure oxygen ambient coupled with simultaneous argon ion beam bombardment of the growing film. We will show that by proper control of the deposition parameters the grain size can be varied in a continuous manner from micron scale at the film-substrate interface to the nanometer scale at the film surface. This microstructure results in a film with an extremely high hardness. The deposited films will be characterized by x-ray diffractometry, atomic force microscopy, interferometry, transmission electron microscopy and spectroscopic ellipsometry.

9:40am **TF-WeM5 Effects of TiO@sub x@ PVD Deposition Parameters on the Preferred Orientation and Adhesion of Pt Films on @gamma@-Al@sub 2@O@sub 3@***,* ***E. Derniaux****,* ONERA France*; P. Kayser,* ONERA France, FRANCE*; C. Gageant, C. Sanchez, D. Boivin,* ONERA France

PVD TiO@sub x@ films are studied in order to improve the adhesion of Pt/AlN/Pt piezoelectric transducers on @gamma@-Al@sub 2@O@sub 3@/NiCoCrAlY/superalloy components. Thick (2 µm) TiO@sub x@ films deposited by RF reactive cathodic sputtering on @alpha@-Al@sub 2@O@sub 3@ substrates were analysed by X-ray diffraction (XRD) and scanning electron microscopy equipped with X-ray spectroscopy (SEM/EDX). The influence of substrate temperature, O@sub 2@/(Ar+O@sub 2@) ratio in the plasma gas and annealing (1050°C, 1h, in air) on structural properties, morphology and chemical composition was observed. Thin (@<=@100 Å) TiO@sub x@ adhesion layers and Pt films were sputtered on @alpha@-Al@sub 2@O@sub 3@. The effects of TiO@sub x@ deposition parameters on the adhesion and the orientation of as-deposited and annealed Pt films were examined respectively by pull off test and XRD. Results showed the (111) preferred orientation and the good adhesion of Pt films. Finally, the selected TiO@sub x@ deposition parameters were applied on @gamma@-Al@sub 2@O@sub 3@/NiCoCrAlY/superalloy substrates. Adhesion properties of annealed Pt films on @gamma@-Al@sub 2@O@sub 3@ and TiO@sub x@/@gamma@-Al@sub 2@O@sub 3@ were evaluated, the results showed a drastic improvement of the pull off force (0 to 1000 kg.cm@super -2@) by using the TiO@sub x@ 'glue layer'. The adhesion layer led also to a higher (111) preferential orientation of the Pt films.

10:00am **TF-WeM6 Microstructure and Stress of Room Temperature Reactively Sputtered RuOx Thin Films***, J. Shi,* ***T.M. Klein****,* The University of Alabama

RuOx thin films were deposited at room temperature by reactive RF magnetron-sputtering using Ar/O2 discharges of varying O2 flow ratio (O2/Ar+O2) over the range 10% to 50%. With an increase of O2, the film texture changed from (110) to (101). Films deposited with a flow ratio >25% were determined stoichiometric. Apparent grain sizes, densities and hardnesses by nanoindentation were measured as a function of flow ratio. Deposition rate, resistivity and intrinsic stress trends with O2 flow ratio were similar. The intrinsic stresses in as-deposited films were all compressive and increased with addition of O2, except for the film sputtered at a flow ratio of 20% which was in biaxial tension. Stress-temperature behavior during a thermal cycle in air up to 500Âº C changed for films deposited at different flow ratios due to varying microstructure evolution. The film deposited at a flow ratio of 30% became nearly stress-free with a low resistivity value of 68 micro Ohm-cm after anneal which is promising for use in micro-devices.

10:20am **TF-WeM7 Synthesis of Carbon Films with Ultralow Friction in Dry and Humid Air***,* ***C.A. Freyman****, Y.F. Chen, B. Zhao, Y.W. Chung,* Northwestern University

In this paper, we present experimental strategies of how one can synthesize smooth carbon films using sulfur doping with ultralow friction coefficients (µ< 0.01) in dry and humid air, with relative humidity up to 50%. Auger studies show the absence of water adsorption after room temperature water exposure of 100,000 Langmuirs. Thermal desorption studies suggest the formation of water multilayers even at very low exposures, indicating that the surface is hydrophobic, consisting with water contact angle measurements. Results from quartz crystal microbalance studies at ambient pressures will also be discussed.

10:40am **TF-WeM8 Surface Modification of Si@sub 3@N@sub 4@ Probes for Adhesion and Wear Reduction***,* ***Z. Tao****, B. Bhushan,* The Ohio State University

Tip wear of Si@sub 3@N@sub 4@ probes used for atomic force microscope (AFM) can result in increase of tip radius, thus reducing the image resolution and introducing artifacts. Adhesion between the tip surface and sample is another source of image artifacts. In order to reduce adhesion and wear, perfluoropolyether (Z-TETRAOL) and Fluorinert@super TM@ will be deposited on the Si@sub 3@N@sub 4@ probe. The adhesion, friction, and wear of the uncoated/coated tips will be investigated. The humidity effects on the adhesion, friction, and wear of the uncoated/coated tips will be investigated as well. The influence of the coating on the image resolution will be discussed.

11:00am **TF-WeM9 Ultra-Hard Al-Si Nanocomposites Synthesized by High-rate Co-evaporation***,* ***D. Mitlin****, C. Ophus,* University of Alberta, Canada*; V. Radmilovic, T.J. Richardson, U. Dahmen,* Lawrence Berkeley National Laboratory

We used high rate co-evaporation to synthesize Al-Si nanocomposite films in the composition range of Al-1at%Si to Al-23at.%Si. Pure Al films were also synthesized using identical deposition conditions, and were used as a baseline. The Al-Si structures have a hardness as high as 4GPa (Al-23at.%Si), and display noticeable plasticity under nanoindentation (Al-12at.%Si). We used transmission electron microscopy (TEM) to analyze Al-12at.%Si and pure Al samples. The pure Al film had the expected grain size of upwards of one micrometer. The Al-Si film consists of a dense distribution of spherical nanoscale (10-30 nm) Si particles separating irregularly-shaped Al grains, many of which are also nanoscale (50-200 nm). This microstructural refinement is due to the Si particles disrupting the columnar growth of the Al grains by promoting re-nucleation. Additionally the particles also pin the Al grains which coarsen during deposition. X-ray diffraction results indicate that there is a marked decrease in the Al lattice parameter with increasing Si content. This effect is weaker after the samples have been stored at room temperature for six months. The structures' electrical resistivity remains near the level of pure Al for compositions up to 6.5at.%Si, but significantly increases at higher Si compositions. This work is the first step towards yielding Al-Si nanomaterials specifically optimized for integration into structural components of MEMS.

11:20am **TF-WeM10 Hard Coatings of Tungsten Nitride Grown by Reactive Sputtering and Laser Ablation***,* ***E.C. Samano****, A. Clemente, M.J. Oviedo, G. Soto,* CCMC-UNAM, Mexico

The search for materials showing chemical inertness and high hardness, elastic modulus and melting point is still intense. Transition metal nitride coatings are an alternative because they have been traditionally used as protective coatings against wear and corrosion. Due to the fact that refractory metals are hard materials with a high melting point, tungsten nitride coatings are an excellent choice. Their properties can be tailored by tuning the nitrogen content during film synthesis. The investigation on the relationship between thin film preparation conditions and mechanical properties for tungsten nitride films is not as well understood as other transition metal nitrides, like titanium nitride. We report the growth of tungsten nitride films grown by two different deposition methods, reactive

sputtering and laser ablation, in the ambient of N@sub 2@ at various pressures on stainless steel substrates. The composition of the films is determined by AES and XPS. The stoichiometry of the coatings grown by reactive sputtering are found to be W@sub2-x@N, 0@<=@x@<=@0.5, while those grown by laser ablation are W@sub2@N, WN and WN@sub2@. The mechanical properties of the films grown by both deposition methods are studied as a function of N@sub2@ pressure. The hardness of the deposited films resulted to be in the 25 to 35 GPa range.

11:40am **TF-WeM11 Electron Spectroscopic Studies of Friction Modifier Thin Films***, **K.C. Wong**,* University of British Columbia, Canada*; X. Lu,* Kelsan Technologies Corp.*; P.C. Wong,* University of British Columbia, Canada*; J. Cotter, D. Eadie,* Kelsan Technologies Corp.*; K.A.R. Mitchell,* University of British Columbia, Canada

Friction modifier (FM) thin films are important for controlling friction at the wheel-rail interface of trains. Products on the market have progressed to date largely by empirical development. Accordingly we have initiated a program to investigate how FM model systems are affected by tribological experiments that simulate wheel-rail contact using a rolling disk-on-disk setup adjusted for designated pressure and creepage. This paper will report spectroscopic characterizations (with XPS, Raman and SAM) and thermogravimetric analyses for FM materials (e.g. MoS2, graphite, BN, WS2, ZnO, MoO3, talc, SnO2, polytetrafluoroethylene, polyimide and polyamide) and water-based emulsion polymers as binders, where the studies are made as a function of coefficient-of-friction, number of rolling cycles and temperature.

Thin Films
Room 306 - Session TF-WeA
Fundamentals of Thin Films

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

2:20pm **TF-WeA2 PECVD Silicon Nitride Nucleation Kinetics Impact on Device Scaling*, A. Raviswaran*,** *P. Keswick,* Cypress Semiconductor

Plasma enhanced chemical vapor deposition of silicon nitride is a commonly used process in the microelectronics industry for etch stop and passivation layers. As the device dimensions continue to shrink along Moore's law, the silicon nitride thickness is also reduced to meet device requirements. So controlling the silicon nitride thickness and stoichiometry is critical as the gate length and contact width are affected by the thickness and etch rate of the silicon nitride layer used as etch-stop. The current study helps understand the initial stages of nucleation and growth of the PECVD silicon nitride and contributes significantly to better controlling the deposition of very thin silicon nitride layers used in device fabrication. Silicon nitride films with thickness ranging from 37 Å (deposition time of 1 sec) to 450 Å was deposited on Si wafers at 400 °C. Spectral data collected using an ellipsometer shows that as the thickness of the film increases, a transformation is observed in the spectral profile at about 200 Å thickness. AFM, SEM and cross section TEM show that the films are continuous (no 3D cluster growth) at 37 Å. In contrast to reports on LPCVD silicon nitride, the PECVD nitride deposition rate is found to increase with a reduction in deposition time and does not show an incubation time. The refractive index of these films is found to increase with a decrease in film thickness. XPS analysis shows that the thinner films are silicon rich. The 85 Å film with RI of 2.17 has a Si/N ratio of 0.947 and the 340 Å film with RI of 1.95 has a Si/N ratio of 0.928. Evaluation of hydrogen in the film by FTIR and HFS (in progress) will further help understand the impact of hydrogen on the nucleating film properties. The nucleation of a 2D Si-rich layer is attributed to high PECVD deposition rate (relative to surface diffusion) and lower bond strength of Si-H relative to N-H bonds in the reactant gases.

2:40pm **TF-WeA3 Transition Metal Diborides by CVD: Super-Conformal, Epitaxial, Diffusion Barrier, and Super-Hard Films*, J.R. Abelson,*** University of Illinois at Urbana-Champaign **INVITED**

Transition metal diborides are metallic ceramic materials with high electrical conductivities, refractory melting temperatures, and high hardness. Despite these attractive properties, the boride compounds have been overlooked in thin film science and technology relative to the carbides and nitrides. We employ the single-source, impurity-free precursors Hf(BH@sub 4@)@sub 4@, Zr(BH@sub 4@)@sub 4@ and Cr(B@sub 3@H@sub 8@)@sub 2@ to deposit stoichiometric thin films of HfB@sub 2@, ZrB@sub 2@, and CrB@sub 2@ by chemical vapor deposition. This talk highlights recent results on film microstructure, properties, and deposition mechanisms, which are analyzed using spectroscopic ellipsometry, line-of-sight mass spectroscopy, and trench coverage. Films grown at substrate temperatures of 200-300°C are diffraction amorphous and super-conformal in deep (20:1) trenches. The conformality is a consequence of site blocking which greatly lowers the precursor sticking coefficient. HfB@sub 2@ and ZrB@sub 2@ films are excellent diffusion barriers that prevent the mixing of Cu and Si during annealing up to 600°C. At growth temperatures @>=@ 500°C the films are crystalline and adopt a strong preferred orientation, including a normal texture on SiO@sub 2@ and pseudo-epitaxy on crystalline silicon (100) and (111) substrates. The latter may be good templates for heteroepitaxial growth of GaN, as previously reported. Amorphous HfB@sub 2@ can be crystallized by annealing at temperatures @>=@ 600°C. The post annealed films have an equiaxed, nanocrystalline structure with grain diameters of < 100 Å. Such films exhibit nanoindentation hardness as high as 40 GPa, exceeding the reported bulk value of 29 GPa. We create multilayered structures by periodically introducing a flux of atomic nitrogen during growth. This creates thin mixed phase layers that are softer; the ratio of hardness to modulus can be adjusted and the overall toughness increased.

3:20pm **TF-WeA5 Sputter Deposition of Silicon Oxynitride for Waveguide Applications*, J.G. Sandland,*** *A. Eshed, L.C. Kimerling,* Massachusetts Institute of Technology

Silicon oxynitride (SiON) is an ideal waveguide material because the SiON materials system provides substantial flexibility in composition and refractive index. SiON can be varied in index from that of silicon dioxide (n=1.46) to that of silicon-rich silicon nitride (n~2.3). This flexibility in refractive index allows for the optimization of device performance by allowing trade-offs between the advantages of low-index contrast systems and the benefits of high-index-contrast systems. We present sputter processing as an alternative to traditional CVD processing of SiON. We explore a co-sputtered deposition from a silicon oxide and a silicon nitride target, and reactive sputtering process from a silicon nitride target in oxygen ambient. Silicon nitride sputtered from a silicon nitride target is also investigated. Models were developed predicting the index and composition as function of deposition conditions. A materials study is provided that shows sputtered SiON to be a homogeneous material that gives good control of refractive index. Reactively sputtered SiON is shown to be Si-rich. These sputtered materials investigated for use as a core material in optical waveguides. Low loss waveguides are demonstrated for both co-sputtered and reactively sputtered depositions. Losses below 1 dB/cm are shown for co-sputtered deposition (n=1.65). These waveguide losses are then related back to our sputtering model, and silicon dangling bonds are shown to contribute to the losses in the waveguides.

3:40pm **TF-WeA6 ALD-like Deposition of High Quality SiO@sub 2@ Film at 200°C using Organic Silicon Source Gas and Highly Concentrated O@sub 3@ Gas*, T. Nishiguchi,*** *N. Kameda, Y. Morikawa, M. Kekura,* Meidensha Corporation, Japan*; H. Nonaka, S. Ichimura,* National Institute of Advanced Industrial Science and Technology, Japan

One of the technical issues to be solved to fabricate a high performance flexible poly-silicon (p-Si) TFT is the development of the technique of high-quality gate dielectric (SiO@sub2@) film formation even as low as 200 ° C. Although plasma enhanced CVD using an organic silicon source / O@sub 2@ gas is now widely used, the further reduction of impurity incorporation such as carbon and OH is required. Focusing on the high reactivity of O@sub 3@ to organic molecules even at low temperature, we have carried out an ALD-like process by supplying an organic silicon source gas and highly concentrated (100%) ozone (HC-O@sub 3@) gas to a vacuum (< 1 Pa) processing chamber alternately and cyclically. The SiO@sub2@ deposition rate on Si substrate was typically 1 nm per cycle in case of hexamethyldisilazane (HMDS) gas supply of 50 Pa and HC-O@sub3@ gas supply of 1,000 Pa at 200 ° C. As-deposited film was stoichimetric SiO@sub2@ with no Si-CH@sub3@ bond detected by infrared absorption spectroscopy. Leakage current through the film was satisfactory low, i.e. lower than 10@super -7@ A/cm@super 2@ for 3 MV/cm electric field application. However, a film deposited with a higher deposition rate contained a few wt. % Si-OH bonds and H@sub 2@O molecules. We have already confirmed that a UV-light irradiation to Si substrate through an O@sub 3@ atmosphere serves to enhance the chemical reaction at Si surface because of the generation of an excited state oxygen atom in gas phase as well as the temperature rise of uppermost Si region. We are now investigating that the usage of UV irradiation together is effective for achieving both high quality film formation and high deposition rate.

4:00pm **TF-WeA7 Strontium Oxide Template Monolayers by Surface Reactions of Metal-Organic Precursors with Si(100)*, A.C. Cuadra*,** *D. Skliar, B.G. Willis,* University of Delaware

The crystalline structure of strontium titanate (SrTiO@sub3@) consists of alternating 'sublayers' of SrO and TiO@sub 2@. Investigations by molecular beam epitaxy using elemental sources have shown that the heteroepitaxy of SrTiO@sub 3@ on Si(100) 2x1 surfaces can be nucleated with the SrO/Si(100) interface.@footnote 1@ This talk presents the experimental approach for monolayer growth of a SrO 'template' on a Si(100) 2x1 surface using strontium dipivaloylmethanate [Sr(dpm)@sub 2@] and water precursors as the sources of Sr and oxygen, respectively. To nucleate SrO on Si(100), the surface chemistry of the substrate must be tuned to direct the surface reactions of the strontium metal-organic precursor. Following native oxide desorption, dissociative chemisorption of H@sub 2@O is carried out in UHV to hydroxyl terminate Si(100) and initiate two-dimensional nucleation of the metal oxide while avoiding incubation periods common to the atomic layer deposition (ALD) of metal oxides. Metal oxide growth has been correlated to the concentration of hydroxyl groups on the substrate surfaces because they facilitate ligand exchange from the surface.@footnote 2@ Results show that thick SrO films with low carbon contamination can be grown on Si(100) and SiO@sub 2@ terminated with hydroxyl groups through wet chemical methods; this talk focuses on the initial SrO nucleation layer. In situ Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and reflection high energy electron diffraction (RHEED) are used to investigate the crystalline quality of the nucleation monolayers and to verify the epitaxial orientation of SrO films on Si(100) 2x1 surfaces. @FootnoteText@

@footnote 1@ G.Y. Yang, et al., Journal of Material Research, 17 (1), 204-213 (2002)@footnote 2@ R.L. Puurunen, Applied Surface Science, 245, 6-10 (2005).

4:20pm **TF-WeA8 Texture Evolution during Shadowing Growth of Ru Nanorods**, ***F. Tang***[1], *T. Karabacak, G. Churamani, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

A detailed study of texture evolution during oblique angle deposition of ruthenium vertical nanorods by dc magnetron sputtering is presented. The Ru nanorods have diameters less than 130 nm and lengths ranging from ~ 40 to ~ 480 nm. We used reflection high energy electron diffraction (RHEED) to characterize texture and demonstrated that RHEED can be a powerful tool to follow the growth front of texture evolution. The diffraction patterns showed that the nanorods developed into a strong vertical (100) texture unlike the usually observed (002) texture of conventional Ru films grown by normal incidence deposition. Furthermore, through the quantitative analysis of the RHEED patterns, it was found that the dispersion angle, @Delta@@theta@, of the texture evolved into a power law relationship with respect to time t before its saturation, @Delta@@theta@ ~ t@super p@, where p = - 0.49 ± 0.01. This is shown for the first time that the power law relationship exists not only in the process of morphology evolution but also texture evolution under oblique angle deposition. The analyses of SEM and TEM images reveal the column competition growth, column dispersion, and the single crystal structure of the individual nanorod. We correlate the evolution of column dispersion angle to the evolution of the texture dispersion angle. We also simulated the evolution of the column dispersion angle based on a modified needle model. The exponent of the power law relationship obtained from the simulation was consistent with experimental value and almost independent of the initial simulation conditions, which may indicate a universal scaling behavior. *F.T. is the recipient of the Harry Meiners Fellowship.

4:40pm **TF-WeA9 Microstructural Characterization of Single Crystal Ferromagnetic Shape Memory Films**, ***T.C. Shih***, *S. McKernan, S.K. Srivastava, J.Q. Xie, R.D. James, T.W. Shield, C.J. Palmstrom,* University of Minnesota

Microstructure and martensitic phase formation behavior are known to be important for magnetic-field-induced-strain in ferromagnetic shape memory alloys. Transmission electron microscopy (TEM) has been used to examine the microstructure and martensitic transformation behavior of non-stoichiometric Ni-Mn-Ga and Co-Ni-Ga post-growth-released single crystal films grown by molecular beam epitaxy (MBE) on GaAs (001). The twin and precursor tweed structures observed in the TEM images are of particular interests. The film compositions were determined using Rutherford backscattering spectrometry (RBS), particle-induced X-ray emission (PIXE), energy dispersive spectroscopy (EDS), and wavelength dispersive spectroscopy (WDS). For a thin film with nominal composition Co@sub 50@Ni@sub 25@Ga@sub 25@, convergent beam electron diffraction patterns indicated that the austenite exhibited primarily B2 ordering with additional weak L2@sub 1@ ordering at room temperature. Sharp satellite reflections appeared at 1/6 the spacing of the {220} reflections around the {220} spots along the directions at ~250 K, with the evidence of high-density striations or tweed contrast observed in the dark-field images. The tweed contrast became more pronounced on cooling, accompanied by increasing intensity of the four additional reflections. On further cooling and stabilizing at 100 K, no twin structure was observed. For thin films with nominal composition Ni@sub 50@Mn@sub 25@Ga@sub 25@, Ni@sub 50@Mn@sub 30@Ga@sub 20@, and Ni@sub 53@Mn@sub 25@Ga@sub 23@, the martensitic transformation temperatures showed linear dependence with increasing average valence electron concentration per atom (e/a). Each specimen transformed into different microstructures with the microtwins ranging from 10 nm to 80 nm. This presentation will emphasize the influence of composition and epitaxial growth conditions on the resulting microstructure of the FSMA films before and after being released from the substrates.

5:00pm **TF-WeA10 Vinyltrimethylsilane (VTMS) as a Probe of Chemical Reactivity and Surface Structure of a TiCN Diffusion Barrier Deposited on Silicon**, *L. Pirolli,* ***A.V. Teplyakov,*** University of Delaware

This study presents the first molecular level investigation of chemical reactivity of a surface of an amorphous diffusion barrier film deposited on a Si(100)-2x1 single crystal. Vinyltrimethylsilane (VTMS) is chosen as a probe molecule because of its role as a ligand in a common copper deposition precursor, hexafluoroacetylacetonato-copper-vinyltrimethylsilane. Surface chemistry of vinyltrimethylsilane (VTMS) on TiCN-covered Si(100)-2x1 has been investigated using multiple internal reflection Fourier-transform infrared spectroscopy (MIR-FTIR), Auger electron spectroscopy (AES), thermal desorption mass spectrometry, and computational analysis. On a film deposited at 600 K, VTMS adsorbs molecularly at cryogenic temperatures even at submonolayer coverages, the major pathway for its temperature-programmed evolution is desorption. Adsorption at room temperature leads to chemisorption via a double bond attachment. The desorption studies combined with the computational analysis suggest that the adsorption of VTMS occurs preferentially in two configurations: across the surface C-Ti bond and on a corner Ti, but not across the Ti-N bond.

[1] **TFD Student Award Winner**

Applied Surface Science
Room 206 - Session AS+TF-ThM
Thin Film Characterization
Moderator: P.M.A. Sherwood, Oklahoma State University

8:20am **AS+TF-ThM1 Characterization of Nanoscale Ceramic Gradient Coatings for Gas Analytical Microdevices**, ***M. Bruns,*** *V. Trouillet, H. Mueller, E. Nold,* Forschungszentrum Karlsruhe GmbH, Germany*; R.G. White,* Thermo Electron Corporation, England

The key element of the Karlsruhe Micro Nose is a thumbnail sized gas-sensitive microarray which at present consists of 38 sensor elements on an area of 4x8mm@super 2@. It is based on a noble metal-doped SnO@sub 2@ layer, the electrical conductivity of which is highly sensitive to the composition of the ambient atmosphere and is measured between adjacent parallel platinum strip electrodes. In order to enable pattern recognition techniques these initially identical sensors have to be gradually differentiated with respect to their gas response. For this purpose gas-permeable membranes with thickness variation of approximately 2 to 10 nm were deposited across microarray using ion beam assisted deposition. In this work we focus on mixed membranes combining the gas permeability of silica and the chromatographic discriminating capability of alumina. Different geometries were achieved by shaping the ion beam profile to gradually alter the ion current density across the microarray leading to laterally different deposition rates. Various Al/Si ratios within the membranes were obtained using different substrate temperatures during deposition. In the present paper a comprehensive characterization of differently shaped nanoscale membranes is reported. Auger electron spectroscopy is used for evaluation of the geometrical integrity of the uncoated electrode pattern and for the determination of thickness profiles, respectively. Parallel angle resolved X-ray photoelectron spectroscopy provides thickness information for the membranes together with information on chemical binding states in a non-destructive manner. Ellipsometry is presented as a powerful quantification method for the determination of the desired ultra thin membrane thickness profiles. Moreover, after calibration with surface analytical data, ellipsometry allows for rapid evaluation of Al/Si concentrations ratios within the membranes.

8:40am **AS+TF-ThM2 Characterization of Low k Dielectrics Using Auger Microprobe Analysis***,* ***C. Dziobkowski,*** IBM Corporation, E. Fishkill*; E.D. Adams,* IBM Corporation, Essex Jct.*; J.A. Coffin, R.E. Davis, P.L. Flaitz,* IBM Corporation, Hopewell Jct.*; E.G. Liniger,* IBM Research, Yorktown Heights*; S.E. Molis, D.D. Restaino,* IBM Corporation, Hopewell Jct.

As the dimensions of integrated circuits are reduced, the capacitance between metal lines has an ever increasing impact on device performance. It increases circuit delay, results in parasitic capacitance creating crosstalk, degrades the signal to noise ratio and increases power consumption. Reduction of capacitance by employing low k dielectric materials is thought to be a solution. These low k materials have to be characterized as to their composition, uniformity, void formation and oxygen permeability requirements. This paper gives a description of the methodology developed using Auger depth profile analysis to characterize these new materials. Also important is how these Auger microprobe results can be compared to data obtained from TEM, TOF-SIMS and Rutherford backscattering analyses. The synergism of these analytical techniques is necessary to obtain the understanding needed for the integration of these low k dielectric materials with copper metallurgy in successful device fabrication.

9:00am **AS+TF-ThM3 Semiconductor-Dielectric Interfaces: Composition and Structure***,* ***L.C. Feldman****, S. Dhar,* Vanderbilt University*; J.R. Williams,* Auburn University*; L. Porter,* Carnegie- Mellon University*; J. Bentley,* Oak Ridge National Laboratory*; K.-C. Chang, Y. Cao,* Carnegie-Mellon University **INVITED**

The semiconductor-dielectric interface is the key to a successful MOSFET technology and has played the essential role in the silicon revolution. Wide-band gap materials have presented a challenge to achieve the same degree of interface perfection as silicon, although considerable progress is underway. The SiC/SiO2 interface is of particular scientific interest in this development because of its close relationship to silicon, both in processing and structure. The oxidation process in SiC yields a heavily defected SiC/SiO2 interface giving rise to poor device characteristics. Systematic use of chemical modification and processing, combined with a careful analysis of interfacial structure, results in significant progress in reducing defects and increasing inversion layer carrier density and mobility. For example nitridation of this interface results in a remarkable improvement and is a driving force for understanding the nitrogen profile and concentration. The quantitative nitrogen profile is critical to this understanding and provides a significant depth profiling challenge. Using a variety of probes including medium energy ion scattering, secondary ion mass spectroscopy, nuclear profiling and electron energy loss spectroscopy we show that the nitrogen is confined to within ~1.5 nm of the buried interface, with concentrations that are crystal face dependent and vary from 0.5 to ~1.5 x 10@super 15@/cm@super 2@. From an analysis point of view the significant new finding is the comparison of techniques and the degree of quantitative agreement between the different probes. @FootnoteText@ Supported by DARPA, N00014-02-1-0628 and ONR,N00014-01-1-0616. Research at the O. R. N. L. was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

9:40am **AS+TF-ThM5 Comparison of Silicon Oxynitride Produced by PIII/D and Reactive Sputtering***,* ***N.D. Theodore****, M. Bagge-Hansen, B.C. Holloway, D.M. Manos,* College of William and Mary*; C. Hernandez, T. Siggins, H.F. Dylla,* Jefferson Lab

High-purity, hydrogen-free silicon oxynitride films were successfully created using two techniques, plasma immersion ion implantation/deposition (PIII/D) and reactive sputtering. Our previous work has shown that coating 6" polished 304 stainless steel electrodes with silicon oxynitride, created by PIII/D, dramatically reduces field emission from 27 µA of at 15 MV/m to 160 pA at 30 MV/m. We have recently developed a new procedure to deposit silicon oxynitride without ion implantation using a low temperature (<200°C) Rf reactive sputtering process. Both procedures use a 750 W inductively-coupled nitrogen plasma that sputters silicon dioxide from a quartz dielectric window. The purpose of this study was to determine and compare the composition and electrical properties of the silicon oxynitride coatings created using the reactive sputtering and PIII/D procedures. The homogeneity, stoichiometry, and density of deposited/implanted layers were determined using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and Rutherford backscattering spectrometry (RBS). AES depth profiles determined that both procedures created homogeneous films, and FTIR and XPS spectra confirmed the creation of silicon oxynitrides with approximately 10% nitrogen. Ultraviolet photoelectron spectra and capacitance-voltage measurements will also be presented and discussed.

10:00am **AS+TF-ThM6 Microbridge Testing of Plasma Enhanced Chemical Vapor Deposited Silicon Oxide Films on Silicon Wafers***,* ***Z. Cao,*** Boston University*; T.-Y. Zhang,* Hong Kong University of Science and Technology*; X. Zhang,* Boston University

Plasma-enhanced chemical vapor deposited (PECVD) silane-based oxides (SiOx) have been widely used in both microelectronics and MEMS (MicroElectroMechanical Systems) to form electrical and/or mechanical components. During fabrication of such microelectronic and MEMS devices, PECVD SiOx undergo many thermal cycles, which often causes unwanted changes in thermal-mechanical properties of the material, and consequent degradation of device performance and reliability. In this paper, a novel nanoindentation-based microbridge testing method for thin films is proposed to measure both the residual stresses and Young's modulus of PECVD SiOx thin films. In this method, freestanding microbridges are fabricated from the thin films using the micromachining techniques. The tests are performed at the center of the microbridges with an instrumented nanoindentation system and the load-deflection curves are recorded. Our theoretical model used a closed formula of deflection vs. load, considering both substrate deformation and residual stress in the thin film. To simulate real thermal processing in device fabrication, some microbridges underwent various rapid thermal annealing (RTA) at temperatures up to 800ÂºC. An interferometric microscope was also used to measure the curvature profiles of the bridges. Together with nanoindentation test results on the microbridges, we were able to decide the changes in residual stresses and Youngâ?Ts modulus of the PECVD SiOx thin films under different thermal annealing. Two factors, density change and plastic deformation, were identified as controlling mechanisms of stress changes in the films. A microstructure based mechanism elucidates "seams" as source of density change and "voids" as source of plastic deformation, accompanied by viscous flow. This mechanism was applied to explain our experimental results of thermal annealing of PECVD SiOx films.

10:20am **AS+TF-ThM7 Characterization of Ultra Shallow Arsenic Implants by ARXPS, LEXES, MEIS, and Dynamic SIMS**, ***G. Conti***, *Y. Uritsky, H. Graoui, M. Foad,* Applied Materials; *C.R. Brundle,* Brundle & Associates; *D. Kouzminov,* Materials Analytical Services; *C. Hitzman,* Full Wafer Analysis; *P. Mack, J. Wolstenholme,* Thermo Electron Inc., UK

Ultra-shallow As implants are a leading-edge technology. Low voltage results in implant layers of tens of A thickness after anneal. Reliable metrology for shallow implants is needed. We characterize the implant layer as a function of nominal dose (1E14 to 2E15 ions/cm2) at 2KV, using a variety of techniques. Angle Resolved-XPS gives precise measurement of SiO2 oxide thickness, monitors the chemical state of As, and gives a non-destructive rough depth profile. Low Energy X-Ray Emission Spectroscopy, LEXES, gives a non-destructive As dose measurement, which depends on calibration against a bulk standard, for accuracy. MEIS gives a non-destructive depth distribution of atoms not in Si substitutional sites, and a dose calibrated by reference to amorphised Si. Dynamic SIMS provides very precise dose and depth distribution measurement to very low As concentrations, but is destructive and has a problem with the initial part of the depth scale and any As dose within it. Taken together a complete picture of the implant layer is obtained. Prior to annealing the As has a broad distribution, centered at about 50A depth. The outer oxide layer increases from 13A at 1E14 ions/cm2 dose to 18A for 2E15 ions/cm2 dose. ARXPS showed that samples from one particular implanter had a component of As2O3 very near the surface, well removed from the elemental As implant. The annealing conditions (N2 with 10% O2) double the oxide thickness (22A at 1E14 ions/cm2 dose; 38A at 2E15 ions/cm2), and cause the As to pile up just on the Si side of the SiO2/Si interface, but with a strong diffusion tail to 150A depth (SIMS). XPS shows that any oxide component is eliminated by anneal. A comparison of the MEIS to the SIMS depth distributions shows that the diffusion tail is in substitutional sites, and therefore not observable in the MEIS.

10:40am **AS+TF-ThM8 Hot Electron Transport Across Manganese Silicide Layers on the Si(001) Surface**, ***A. Stollenwerk***, *M.R. Krause, V.P. LaBella,* University at Albany SUNY

The need for high efficiency spin injection for spintronic applications has led to the study of different ferromagnetic interfaces. Recent theoretical studies have shown that the MnSi interface orders ferromagnetically.@footnote 1@ We performed ballistic electron emission microscopy (BEEM) on the MnSi/Si(001) Schottky barrier to study the hot electron transport properties. BEEM allows the interface to be probed on the nanometer scale and also gives the option to perform spin dependent measurements. Samples for this study were fabricated by electron beam deposition of Mn onto n-type Si(001) with thicknesses ranging from 50 to 200 Å. These layers were annealed at various temperatures in ultra high vacuum (UHV). The front side contact was fixed ex situ before the sample was reinserted into UHV to perform BEEM. Film composition has been determined by secondary ion mass spectroscopy (SIMS). The Schottky heights have been determined by fitting the BEEM spectra to the Bell-Kaiser model. The effects of temperature, film thickness and composition on the BEEM current will be discussed. @FootnoteText@ @footnote 1@S.A. Wolf et al., Science 294, 1488 (2001).

11:00am **AS+TF-ThM9 Optimization and Deposition of CdS Thin Films As Applicable to TiO@sub2@/CdS Composite Catalysis**, ***K. Prabakar***, *T. Takahashi,* Toyama University, Japan; *T. Nakashima,* Kashiwa Chuo High School, Japan; *Y. Kubota,* Yokohama City University, Japan; *A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

Recently, the study of interparticle electron transfer between dissimilar semiconductors has received interesting investigations. Combining two semiconductor particles offers an opportunity to sensitize a semiconductor material having a large bandgap and energetically low-lying conduction band by another one having a small band gap and energetically high-lying conduction band. In our investigations, photosensitization of TiO@sub2@ by narrow band gap semiconductor such as CdS have been investigated and found to be effective for separation and transfer of photoexcited charge carriers. The TiO@sub2@ thin films were deposited by direct current reactive magnetron sputtering and CdS by chemical bath deposition. Thin films of CdS were deposited from a solution of analytical grade CdSO@sub4@ (1 M) and thiourea (1 M) in an alkaline solution of ammonia with a total volume of 80 ml. The temperature and time of the deposition were varied between 65 to 80 ° C and 30 to 60 minutes respectively. To vary the composition of the films, different concentrations of CdSO@sub4@ and thiourea were used. The optical band gap energy varied from 2.41 to 2.59 eV as the CdSO@sub4@ solution concentration increased from 0.4 to 2.8 ml while keeping the thiorea as 1.6 ml. The as deposited films were annealed at different temperatures to study the effect of structural (XRD) and surface properties (SEM and AFM) on the efficiency of the TiO@sub2@/CdS catalysis. The TiO@sub2@ films were found to be polycrystalline anatase structure with optical band gap energy of 3.1 eV. The degradation efficiency under visible light of methanol and methylene blue by TiO@sub2@/CdS films were investigated by FTIR and spectrophotometer respectively and the results are discussed in details. The visible light photocatalytic degradation efficiency TiO@sub2@/CdS is far higher than that of TiO@sub2@ film.

Thin Films
Room 306 - Session TF-ThM
Optical Thin Films
Moderator: C. Stoessel, Consultant

8:20am **TF-ThM1 Refractive Index Control of Sputtered Multicomponent Bismuthate Glass Films for Bi-EDWA**, ***J. Kageyama***, *Y. Kondo, M. Ono, N. Sugimoto,* Asahi Glass Co., Ltd., Japan

Multicomponent bismuthate glass films were deposited from a glass target by radio frequency planar magnetron sputtering for fabricating bismuthate erbium doped waveguide amplifier (Bi-EDWA).@footnote 1, 2@ It is essential to control the refractive index of the film, because it affects the beam propagation in optical waveguide structure. The appropriate refractive index difference between the core and the cladding of Bi-EDWA is about 0.03. Thus it is desired that the batch-to-batch reproducibility of refractive index is less than 0.001. The refractive index of the film is mostly stable during the beginning of target life, however it decreases as the total sputtering time increases. In this work, it was revealed that the main reason why the refractive index varies is not the change of cationic composition in the film, but the increase of oxygen concentration in the film as the deposition rate decreases. It was also found that the decrease of deposition rate is caused by the decrease of sputtering rate. Additionally it was considered that the decrease of sputtering rate is linked with the decrease of self bias voltage at the target as the target becomes thinner. We also examined the effect of new magnetic circuit having an improved magnetic alignment and a lower magnetic flux density to make the above-mentioned film properties stable. As a result, we succeeded in obtaining good reproducibilities of refractive index and deposition rate dramatically. It is expected that this method is widely applied in sputtering of insulating films and effective for suppressing the decrease of deposition rates and the variation of film properties. @FootnoteText@ @footnote 1@ Y. Kondo, M. Ono, J. Kageyama, M. Reyes, H. Hayashi, N. Sugimoto, Proc. OFC/NFOEC 2005, Anaheim, CA, USA, PDP2. @footnote 2@ Y. Kondo, M. Ono, J. Kageyama, H. Hayashi, M. Reyes, N. Sugimoto, Electron. Lett. 41, 317 (2005).

8:40am **TF-ThM2 Controlled Doping and Photoluminescence Properties of Er-doped Yttrium Oxide Thin Films**, ***T.T. Van*[1]**, University of California, Los Angeles; *J. Bargar,* Stanford Synchrotron Radiation Laboratory; *R. Ostroumov, K. Wang, J.P. Chang,* University of California, Los Angeles

Though silica has traditionally been used as the Er host in fiber amplifiers, it is an unsuitable host in small, compact amplifiers due to its low solubility for Er. One potential host is Y@sub 2@O@sub 3@. Its high refractive index allows for a compact geometry and large signal admittance angle, thus higher pumping efficiency. Due to the similarities in crystal structure and lattice constant between Y@sub 2@O@sub 3@ and Er@sub 2@O@sub 3@, a much higher Er concentration can be incorporated Y@sub 2@O@sub 3@, compared to that in silica. Er-doped Y@sub 2@O@sub 3@ thin films were synthesized by radical-enhanced atomic layer deposition (RE-ALD) at 350°C, using metal beta-diketonates as the metal precursors and O radicals as the oxidant. The deposition of Y@sub 2@O@sub 3@ was alternated with Er@sub 2@O@sub 3@ and the Er doping level was effectively controlled by varying the ratio of Y@sub 2@O@sub 3@:Er@sub 2@O@sub 3@ cycles. The films were polycrystalline with a preferential growth in the (111) plane. Room-temperature PL at 1.54 µm was observed in a 500-Å Er-doped (6.6 at.%) Y@sub 2@O@sub 3@ film, showing well-resolved Stark features indicating the proper incorporation of Er in Y@sub 2@O@sub 3@. The result is very promising, since the film is fairly thin and no annealing at high temperature is needed to activate the Er ions. Extended X-ray absorption fine structure (EXAFS) analysis showed an identical Er local environment for samples with 6-14 at.% Er, suggesting the PL quenching at high Er concentration (>12 at.%) is likely dominated by ion-

[1] **TFD Student Award Winner**

ion interaction and not by clustering. The effective absorption cross section for Er in Y_2O_3 was estimated to be on the order of 10^{-18} cm^2, about three orders of magnitude larger than that in the silica host. These results validate Y_2O_3 as a promising Er host and demonstrate that RE-ALD is a viable technique for synthesizing thin films with well-controlled dopant incorporation.

9:00am **TF-ThM3 Alternating Current Thin Film Electroluminescence (ACTFEL) from Zinc Sulfide Doped with Rare Earth Fluorides*, D.M. DeVito,* *A.A. Argun, M.R. Davidson, P.H. Holloway,* University of Florida

Thin film electroluminescent (EL) devices are an excellent source for efficient infrared emission. A wide variety of applications exist for infrared emitters, including therapeutic medical treatment, chemical analysis, infrared displays and telecommunications. Rare earth elements, such as erbium, thulium and holmium are ideal choices for dopants in phosphors because they possess a number of sharp transition in the infrared region from 850-2800nm. These rare earth dopants also emit in the visible region (400-700 nm) and have been used in a variety of visible display technologies. Zinc sulfide is a suitable semiconductor host material because it is chemically stable, possesses a bandgap of 3.6 eV at 300 K and is therefore transparent to visible and NIR photons, and provides a lattice in which electrons can be excited to ballistic energies in order to excite emission from rare earth dopants. Thin films, approximately 0.8 microns thick, of rare earth doped ZnS were RF magnetron sputter deposited at 120 W from dual targets of undoped ZnS and rare earth fluoride doped ZnS. Deposition temperature, duty cycle, sputter gas pressure and post-deposition annealing temperature were varied in a design-of-experiment to optimize the ratio of near-infrared to visible emission. Suppression of visible emission can result in energy transfer into the infrared transitions and higher NIR/visible intensity ratios. Post-deposition annealing is a key parameter for increasing this ratio, and temperatures between 350°C and 525°C for 1 hour in N_2 show good results. Maximum EL radiance for ZnS:ErF_3 at 1550 nm was increased from ~1 µW/cm^2 before annealing to 28 µW/cm^2 post-anneal. The optimum concentrations of both rare-earth ion and fluorine were determined by EDS and SIMS analysis.

9:20am **TF-ThM4 Custom-design of Optical Thin Films of Silicon Oxide by Direct Write Deposition*, H.D. Wanzenboeck,*** *M. Fischer, E. Bertagnolli,* Vienna University of Technology, Austria

The fabrication of optical transparent thin films on specific areas has gained increased interest due to optical interconnect concepts. Robust, inorganic materials such as silicon oxide provide optical interconnects with a high bandwith and a fast, power-saving data transmission. Moreover, the fabrication of transparent thin flims is also desirable for the modification of optical photomasks. This work describes a rapid fabrication approach of thin silicon oxide films on confined areas by direct-write deposition. This maskless process utilizes the localized chemical vapor deposition on specific areas utilizing a focused electron beam. The deposition from siloxane vapor in presence of oxygen is initiated by the energy of the electron beam with a 5 nm diameter. By scanning the beam, thin films with arbitrary geometry and 3-dimensional structures were deposited. The process was optimized towards a high deposition rate and high material purity. The influence of process parameters on the deposition efficiency is discussed. A characterization of the chemical composition and of the surface roughness was performed with AES and AFM respectively. The optical properties were investigated by infrared and UV/Vis spectroscopy. The correlation to processing conditions and the growth mechanism is discussed. The electrical features of silicon oxide were tested with a metal-insulator-metal capacitor setup. This work illustrates the flexibility of this maskless method and the potential to control material properties via the process parameters. The fabrication of exemplary structures such as 3-dimensional silicon oxide rods, transparent films in trenches and networks of silicon oxide wires illustrate the application potential of this versatile direct-write method.

9:40am **TF-ThM5 Vacuum-Deposited Form-Birefringent Materials for Use as Retarders and Polarizers*, I.J. Hodgkinson,*** University of Otago, New Zealand **INVITED**

Vacuum-deposited form-birefringent films are of special interest today due to their potential use as trim retarders for front and rear projection TV systems. The presentation reviews basic computational methods, deposition geometries, and experimental techniques for characterizing nanostructures, optical performance and physical properties. As well several related developments are discussed, including multilayered birefringent coatings, birefringent arrays and chiral coatings deposited as twisted stacks of birefringent layers.

10:20am **TF-ThM7 Birefringent Films for Contrast Enhancement of LCoS Projection Systems*, K.D. Hendrix,*** *M. Duelli, D.M. Shemo, K.L. Tan,* JDS Uniphase **INVITED**

High performance projection displays based on LCoS panel technology have the potential to deliver very high contrast and performance at an attractive price. These systems use polarization-based light engines that utilize wire grid polarizers (WGP) and vertical-aligned nematic (VAN) LCoS panels. To achieve high contrast, the linear polarization state created by the WGP must be maintained in the dark state to prevent light leakage to the screen. However, the LCoS panel has a residual retardance, and without compensation, this leakage degrades the system contrast. We describe the design and contrast measurement results of a birefringent contrast enhancing component that compensates this residual retardance and improves the overall system contrast to 4500:1. The component is comprised of birefringent films with individually controllable a-plate and c-plate compensation, accurate retardance targeting and excellent uniformity for both retardance magnitude and orientation. The component also has good environmental durability and low defects.

11:00am **TF-ThM9 New Imaging Ellipsometric Techniques for Thin Film Dielectric Tensor Measurement*, R.A. Chipman,*** University of Arizona **INVITED**

NO ABSTRACT SUBMITTED.

11:40am **TF-ThM11 Thin Film Optical Constants in the EUV using Simultaneous Reflection and Transmission Measurements***, D.D. Allred,* ***G.A. Acosta****, R.S. Turley, J.E. Johnson,* Brigham Young University*; K.R. Adamson,* Harvard University*; N. Farnsworth,* Brigham Young University

We discuss the use of variable-angle transmission/reflection measurements for determination of optical constants of thin films from 50 to 600 eV. Such techniques have been widely used in the visible portion of the electromagnetic spectrum, but are relatively less well known in the EUV and beyond. For this range, depositing a thin film on a transparent substrate is impossible since partially transparent films must be less than ~50 nm and transparent substrates are unknown. Instead we deposited films directly on the surface of a diode detector. We expanded the technique by measuring simultaneously, both reflection from, and transmission at, the same position on the diode to minimize errors stemming from film nonuniformity. Two materials so studied at CXRO's beamline 6.3.2 at the Advanced Light Source at the Berkeley National Laboratory were reactively sputtered thorium oxide and scandium oxide. We will report the complex index of refraction obtained by fitting this data for a number of energies in this range.

Plasma Science and Technology
Room 302 - Session PS+TF-ThA

Emerging Plasma Applications

Moderator: H. Barankova, Uppsala University, Sweden

2:00pm **PS+TF-ThA1 Emerging Plasma Deposition Applications***, **D.P. Monaghan**,* Gencoa, UK **INVITED**

Vacuum plasma deposition has been the mainstay of the thin film industry since its inception. In particular magnetron sputter based processes have come to the forefront due to the inherent stability and scalability of the technique. However, the method has to constantly re-invent itself in order to provide better solution for the ever-changing world of micro-electronics and consumer products. New generations of products are also being created that rely partly or completely on new sputter based processes. This in turn can require radical changes to the usual production methods. The presentation will highlight the state-of-the art in sputter technology and in particular a number of areas that will drive further market expansion and technical advancement in the field. Some examples will include thin film batteries where virtually every feature relies upon sputtered layers of a low or high tech. nature. Due to the miniature and highly efficient nature of the product, it opens up the possibility of providing "power" to many new product classes and new devices. Thin film solar cells that have the ability to create efficient conversion of energy via a low cost and lightweight structure may lead to a reduction of societies dependence upon fossil fuels. The introduction of vertical magnetic recording comes ever closer if longitudinal recording is limited to <200 Gbit/in2. Vertical recording can potentially achieve terabyte recording density, but places much higher demands on the process equipment and magnetron source technology. Another high growth area is display technology. The emergence of high definition large area LCD displays puts a corresponding demand upon the digital video disk storage capacity. New disk formats such have Blu-ray have been shown to offer up to 3x the storage capacity. In addition the possibility of a high and low video formats on a single disk means the creation of two separate recording media in a single production process.

2:40pm **PS+TF-ThA3 Investigating the Plasma-Propellant Interaction through Experimental Modeling***, **R. Valliere**, R. Blumenthal,* Auburn University

There has been a significant interest in the use of plasmas to ignite propellants in large bore artillery. A short, reproducible ignition delay and a reduced temperature dependence are the most important advantages of plasma ignition over conventional ignition. Using the experimental modeling method, pioneered by Winters and Coburn,@footnote 1@ the erosion rates of sprayed-on films of RDX and HMX have been investigated in inert and reactive plasmas, as a function of sample bias in order to isolate the ion and electron bombardment and chemical effects on the erosion rate. No significant erosion rate was observed in argon plasmas with zero or positive bias, indicating that erosion by electron bombardment alone is not significant. Under ion bombardment conditions, large negative bias, only a slow erosion rate (presumably due to sputtering) was observed. Erosion in hydrogen plasmas is quite different. The minimum erosion rate, observed at positive and zero sample biases, was ~100x the maximum rate observed in negative-biased argon plasmas. Under negative bias the erosion rate increased as a much as 20-fold, depending on a combination of ion current and sample bias. All observed erosion rates obey pseudo-first order kinetics. The fact that the erosion rates in the hydrogen plasmas are all much greater than the rates of the argon plasmas, even at large negative bias, indicates a strong chemical component to the erosion process. The bias and current dependence of the erosion rate in hydrogen plasmas indicate a synergistic effect between ions and reactive neutrals. The kinetics of erosion for the individual species and the synergistic effects between them will be presented. @FootnoteText@ @footnote 1@ H.F. Winters, and J.W. Coburn, JVSTB @bold 3(5)@, 1376 (1985).

3:00pm **PS+TF-ThA4 PECVD of SiO@sub 2@ Thin Film from Electron-Beam Generated Plasmas***, **D. Leonhardt**, S.G. Walton,* US Naval Research Laboratory

The deposition of thin films of SiO@sub 2@ is an integral part of flexible displays/electronics, medical implant bio-functionalization, as well as a robust barrier layer ideal for space applications. In all of these applications, the SiO@sub 2@ layer 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 used electron beam-generated plasmas to produce a variety of SiO@sub x@ films, with the focus on PECVD processes for temperature sensitive substrates that are scalable to large areas. Mixtures of TEOS or HMDSO with Ar/O@sub 2@ based plasmas were used to grow films in modulated electron beam generated plasmas. The inherent low electron temperature of these plasmas results in low plasma fields and potentials, which in turn provide low energy (< 3 eV) ions to the substrate. The resultant film electrical, optical and chemical properties with respect to gas mixtures, substrate temperature and ion energy will be presented. The low ion energies were critical in producing films with lower defect densities than typical SiO@sub 2@ deposition processes. Using the ion energy as an additional process control ‘knob’ the film composition ranged from stoichiometric SiO@sub 2@ to heavily hydrolyzed. Fluxes to the substrate determined by mass spectrometry measurements will be correlated to these process variables and final film composition. Along with a highly tunable PECVD process, these plasmas offer tremendous scaling and uniformity capabilities that will also be discussed.

3:20pm **PS+TF-ThA5 Nanoparticles and Nanocoatings from Plasmas: Old Problems with a New Twist***, **K.P. Giapis**,* California Institute of Technology **INVITED**

The formation of particles in processing plasmas has generally been related to contamination and lower yields and is considered undesirable. However, nanometer-size particles can have unusual properties, very different from those of bulk materials, which makes them attractive for nanotechnology applications. We have explored the formation of Si nanoparticles in continuous-flow atmospheric-pressure dc microdischarges confined in capillary tubes. The intensity and size of these discharges permits the rapid decomposition of silane, leading to nucleation and growth of 1-3 nm Si particles, whose growth is abruptly terminated as they exit the microreactor. Narrow size distributions are obtained as inferred from classification and imaging. Particles of both charge polarities are detected with similar size distribution but 2X more positively charged particles. As-grown Si particles luminesce in the blue (420nm) with a quantum efficiency of 30% and may find applications in imaging and Si-based optoelectronics. The microdischarge synthesis route is generic to any gas-phase precursor and has been also used to grow Ge and Fe nanoparticles of 1-3 nm in size in benchtop setups. Nanowires and nanotubes are promising as nanoprobes, provided they can be coated with insulating materials followed up by tip end exposure and functionalization. We have used inductively-coupled plasmas to deposit conformal fluorocarbon coatings of a few nm thickness on carbon nanotubes. The coatings provide good insulation while they improve the rigidity of the nanotubes for surface imaging. We will present results from probe immersion experiments in Hg and water. Plasmas provide a versatile way to deposit a wide variety of extremely thin coatings to enable passivation, isolation, or functionalization at the nanoscale.

4:00pm **PS+TF-ThA7 Effect of Substrate Material on Properties of TiN Films Deposited in the Hybrid Plasma Reactor***, **L. Bardos**, H. Barankova, L.-E. Gustavsson,* Uppsala University, Sweden

Parameters of TiN films deposited in the hybrid hollow cathode and microwave ECR plasma reactor can be strongly affected by the substrate material. Differences have been found between films grown on Si substrates and steel substrates, as well as between steel substrates from martensite and austenite steels. Temperature measurements by simple probes made from different materials with surfaces covered by wafers from Si or from steel confirmed substantial differences depending on individual materials. These differences can be explained by material-dependent absorptions of the microwave power as well as by enhanced particle bombardment of ferromagnetic substrates connected with deformation of the magnetic field in the hybrid plasma reactor. The effect of surface bombardment has been confirmed by voltage current measurements using electrically biased probes. The results correspond well with properties of the obtained TiN films. Observed effects could be of more general importance, e.g. for microwave ECR plasmas, magnetron sputtering as well as for most magnetized plasma systems.

4:20pm **PS+TF-ThA8 Synthesis of Aligned Carbon Nanotubes by RF-Plasma-Assisted DC Plasma Chemical Vapor Deposition***, **Y. Hayashi**, T. Fukumura,* Kyoto Institute of Technology, Japan*; R. Utsunomiya,* Nissin Electric Co. Ltd., Japan

Aligned carbon nanotubes (CNTs) grown on a substrate are expected to be applied to the electron emitters of a field emission display. Plasma-enhanced chemical vapor deposition (plasma CVD) enables highly aligned growth of multi-walled CNTs by drawing them toward plasma in the sheath

electric field.@footnote 1@ However the problem of aligned CNT growth by plasma CVD is large-area growth. We have developed a new method of large-area growth of CNTs under stable DC plasma sustainment without arcing by the assistance of RF plasma. Plates of RF electrode, a grounded electrode, and DC cathode were placed parallel in this order in a vacuum chamber. The grounded electrode was gridded so as to pass a part of the RF generated plasma into the space of DC discharge. Iron substrates were placed on the cathode electrode. 13.56 MHz RF power of 500 W was induced to the RF electrode and negative bias of 325 V was induced to the cathode electrode. 20 % methane diluted in hydrogen was introduced into the chamber with the operating pressure of 1000 Pa during the growth of CNTs. Well-aligned carbon fibers were observed by scanning electron microscopy and about 50 concentric layers of graphite with hollows were observed by transmission electron microscopy. These results confirm that CNTs can be synthesized by this method. DC discharge current was 0.7 A at the discharge voltage of 325 V under the assistance of 500 W RF-plasma, while it was 0.57 A without RF-plasma. The decrease of discharge impedance caused the stable sustainment of DC glow discharge without arcing. It is concluded that the large-area growth of well-aligned CNTs under the stable sustainment of DC glow discharge can be carried out by RF-Plasma-Assisted DC Plasma CVD. @FootnoteText@ @footnote 1@Y. Hayashi, T. Negishi and S. Nishino, J. Vac. Sci. Technol. A19, 1796(2001).

4:40pm **PS+TF-ThA9 In Situ Oxidation and Plasma Studies for Magnetic Tunnel Junctions: The Mechanism of Plasma Oxidation of Ultra-Thin Aluminum Films Unraveled**, ***M.C.M. Van De Sanden,*** Eindhoven University of Technology, The Netherlands*; K. Knechten,* Oce Technology, The Netherlands*; B. Koopmans, H.J.M. Swagten, W.J.M. de Jonge,* Eindhoven University of Technology, The Netherlands

Plasma oxidation of thin aluminum films is a commonly used technique to form thin aluminum oxide barriers for application in magnetic tunnel junctions (typically 1 nm). In this technique a glow discharge in oxygen (P = 5-12 W, p = 5-40 Pa) is used to oxidize ultra thin sputtered aluminum films. In comparison with thermal oxidation the process is faster and provides high values of tunneling magnetoresistance (TMR) but at the cost of higher resistance-area products (RxA). However, whereas thermal oxidation of thin aluminum films is well understood in terms of the original model of Cabrera, where the oxidation rate is limited by field-assisted thermal 'hops' of aluminum ions into the oxide, the detailed mechanism of plasma oxidation of thin aluminum films is still unknown. To unravel the mechanism in situ measurements of the oxidation rate and plasma parameters such as the ion and oxygen density are performed. The oxidation rate is determined from single wavelength ellipsometry. From these measurements we have concluded that not one single particle in the plasma is responsible for the increase in oxidation rate observed. A clear correlation of the oxidation rate with the ion flux towards the sample is observed. In addition the oxidation rate is also correlated with the atomic oxygen density in the gas. These results can be explained within a modified Cabrera model of oxidation in which the oxidation temperature is locally enhanced due to the thermal spike of an impinging ion. Additionally, due to the presence of atomic oxygen in the plasma, the field over the oxide during oxidation is enhanced by the increased adsorption of atomic oxygen on the oxide surface. Including both effects in an adjusted equation for the oxidation rate provides a good agreement between model and experiments. The model provides new insights into plasma based oxidation of ultra thin films and offers oppertunities to further control the quality of the tunnel barrier.

5:00pm **PS+TF-ThA10 High Density Plasma Processing of Si Nanocrystal Embedded SiO@sub x@ Thin Films**, ***P.C. Joshi,*** SHARP Labs of America, Inc., US*; T.K. Li, W. Gao, Y. Ono, A.T. Voutsas, J.W. Hartzell, S.T. Hsu,* SHARP Labs of America, Inc.

The optical properties of Si nanocrystals are of interest for efficient and low cost integrated optoelectronic applications. The fabrication of novel optoelectronic devices, exploiting the unique optical properties of Si nanocrystals, requires thin films with high PL/EL quantum efficiency. One approach that is being actively pursued for optoelectronic devices is the fabrication of Si nanocrystal embedded SiO@sub x@ thin films. The development of stable and reliable optical devices requires thin films with high concentration and uniform distribution of Si nanocrystals with controlled particle size. In this paper, we report on the high-density plasma processing of Si nanocrystal embedded SiO@sub x@ thin films. The high-density plasma technique is characterized by low plasma potential, high plasma density, and independent control of plasma energy and density; which provide unique process possibilities and control. The high plasma concentration and low plasma potential of the HDP process are attractive for the generation of Si nanocrystals while minimizing the plasma induced bulk and interfacial damage. We have been successful in controlling the optical properties SiO@sub x@ thin films and the wavelength of the emitted PL signal over a wide range exploiting the unique characteristics of the high-density PECVD technique. The present paper describes a correlation between the optical properties and the PL characteristics of the SiO@sub x@ thin films deposited in the temperature range of 25-300 °C. The high-density plasma deposited SiO@sub x@ films have shown PL signal even in the as-deposited state while subsequent annealing (900-1100 °C) has resulted in significant enhancement of the PL intensity. The present results demonstrate the potential of the high-density PECVD technique for the low temperature processing of the Si nanocrystal embedded SiO@sub x@ thin films with controlled physical and optical characteristics for novel optoelectronic applications.

Thin Films
Room 306 - Session TF+EM-ThA
Transparent Conducting Oxides

Moderator: S. Gupta, The University of Alabama

2:00pm **TF+EM-ThA1 Transparent Conducting Oxides**, ***J.C.C. Fan,*** Kopin Corporation **INVITED**

Transparent Conducting Oxides (TCO) have enormous practical applications in energy-conserving heat mirrors, in solar-energy collectors, solar photovolactic and in electronic devices such as liquid crystal displays and light-emitting diodes. These oxides which are transparent in the visible spectrum are yet electrically conducting have been around for many decades. The most popular ones are In2O3-doped with Sn, and SnO2-doped with Sb. These two classes of TCOs have been extensively researched for many years and their results and applications will be reviewed. In addition, there are newer TCOs in the fields, such as MoO3, ZnO, and others. Their status and potential will also be discussed.

3:00pm **TF+EM-ThA4 Study on Initial Growth Process of Transparent Conductive Oxide Films Deposited by dc Magnetron Sputtering**, ***Y. Sato,*** *M. Taketomo, A. Miyamura, Y. Shigesato,* Aoyama Gakuin University, Japan

It has been noticed that surface defects such as spike or pinhole of transparent conductive oxide (TCO) films should cause the degradation on the performance of organic organic light emitting diode (OLED) displays as appearances of dark-spots. In order to improve their performances, the film surface morphology has been required to be extremely flat. Such surface morphology should be highly related to the initial growth processes of the thin film electrodes. In this study, we investigated the early stages of film growth of representative TCO films such as ITO (Tin doped Indium oxide), IZO (Indium Zinc oxide) and GZO (Gallium doped Zinc oxide) deposited by sputtering. These films with thickness of 5-200 nm were deposited on unheated non-alkali glass substrates by dc magnetron sputtering under a various total gas pressures of Ar/O@sub 2@ mixture gases. The surface morphology of the films was analyzed quantitatively by atomic force microscope (AFM). The average roughness (Ra) of ITO and GZO films with the nominal thickness of 5 nm, deposited under 1.0 Pa, reached maximum of 0.4 and 0.8 nm, respectively. Ra of the both films decreased and remained constant around 0.2 and 0.4 nm, respectively, with the farther increase in thickness larger than 25 nm. These trends implied that three dimensional (Volmer-Weber) growth occurs for the polycrystalline ITO or GZO films, i.e. after an initial nucleation, an island structure grew and coalesced with each other with increasing film thickness. This expectation is consistent with the electrical properties of these films. On the other hand, Ra for the amorphous IZO film remained constant with the increasing nominal thickness from 5 to 200 nm. It must be considered that a nucleation density of IZO film should be much higher than those of ITO or GZO films. This work was partially supported by a Grant-in-Aid for 21st COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

3:20pm **TF+EM-ThA5 Transparent Conducting Oxide Deposition using Closed Field Reactive Magnetron Sputtering**, ***J.M. Walls,*** *D.R. Gibson, I. Brinkley, E.M. Waddell,* Applied Multilayers Ltd, UK

Magnetron Sputtering has many advantages for the deposition of optical coating materials. The sputtering process is "cold", making it suitable for use on the widest range of substrates including damage sensitive polymers. This paper will describe a "Closed Field" reactive sputtering process that allows high quality, transparent conducting oxide (TCO) thin films to be deposited at high rates. In contrast to previous reactive dc sputtering

strategies the Closed Field process does not require a separate energetic ion or plasma source. The Closed Field automatically creates a magnetic confinement that extends electron mean free paths and leads to high ion current densities (>1mA.cm@super -2@). The combination of high current densities with ion energies in the range 15eV to 30eV creates optimum thin film growth conditions. As a result the films are dense, spectrally stable and exceptionally smooth (rms roughness

3:40pm **TF+EM-ThA6 Effect of Dendrimer Underlayers on Sputtered Indium-Tin Oxide Thin Film Microstructure, Morphology, Optical and Electrical Properties***, **R. Thunuguntla**, S. Gupta, S. Street,* The University of Alabama*; D. Loy,* The Army/ASUFlexible Display Center

Minimization of surface roughness is extremely important for sputtered indium-tin oxide (ITO) films used for organic light-emitting diode (OLED) applications. One of the techniques used to achieve smooth ITO films is the optimization of process parameters together with injection of cesium vapor into the plasma -- the recently-introduced negative sputter ion beam or NSIB process.@footnote 1@ We have investigated an alternative simpler approach -- the application of dendrimer monolayers by dip- or spin-coating techniques prior to ITO sputter deposition at ambient temperatures. The ITO films have been characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM), and the film microstructure and morphology have been correlated with the optical and electronic properties such as transmission, resistivity, mobility and carrier concentration. The presence of the dendrimer underlayer appears to mediate the film roughness by grain size reduction and improved adhesion. The greatest effect is seen in films sputtered at low powers. This is expected, since a high level of ion bombardment is expected to damage or destroy the dendrimer underlayer. The observed improvement is most encouraging for flexible display applications, where good film properties and low surface roughness are required at low deposition temperatures. @FootnoteText@ @footnote 1@ M. H. Sohn et al., J. Vac. Sci. Technol. A21(4), 1347 (2003).

4:00pm **TF+EM-ThA7 Ferromagnetic Behavior in Indium Oxide Based Transparent Semiconductors***, **J. Moodera**,* Massachusetts Institute of Technology **INVITED**

Ferromagnetic semiconductors are expected to provide smooth transition for spin injection and transport needed for spin based technology leading to multifunctional devices of the future. Although the field of dilute magnetic semiconductors has been explored for a long time, in recent years there is increased activity due to the significant increase in the ferromagnetic ordering temperature (T@sub c@) of Ga@sub 1-x@Mn@sub x@As system and in various doped oxide systems, despite the existing skepticism in the latter area. We have observed ferromagnetism well above room temperature in Mn doped indium-tin oxide (ITO), Cr doped indium oxide (IO) as well as Mn doped zinc oxide films by reactive evaporation as well as sputtering. Films grown on sapphire (0001) and on silicon show excellent magnetic behavior with a moment ranging from 1 to 5µ@sub B@ for low concentrations of the dopant. Mn doped ITO and Cr doped IO are highly transparent as well as conducting. The electrical conduction is n-type with a carrier concentration in the range of 10@super 18@ to 10@super 20@ cm@super -3@. The charge carriers are seen to be spin polarized shown by the presence of anomalous Hall effect, revealing the magnetic interaction between itinerant electrons and localized Mn or Cr spins. What is interesting in these compounds is that the charge carriers can be independently varied independent of the dopant by the oxygen or the tin concentration in this transparent semiconductor for its easy integration into magneto-optoelectronic devices. In this talk the status of the field will be reviewed and compared with our work. Work carried out in collaboration with John Philip and Nikoleta Theodoropoulou. Supported by the CMI funds at MIT and NSF funds.

Thin Films
Room 306 - Session TF-FrM
Thin Films on Flexible and Polymer Substrates

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

8:20am **TF-FrM1 Thin Film Electronics on Flexible Polymer and Steel Substrates***, **S. Wagner**, I.-C. Cheng, S.P. Lacour, H. Gleskova, J.C. Sturm,* Princeton University **INVITED**

The flat panel display industry, growing rapidly, is developing flexible displays for its next technology generation. Flexible displays are attractive for light weight and resistance to fracture. They can be bent, conformally shaped, and possibly even stretched elastically. While the optoelectronic functions of flexible displays are similar to those of rigid displays, many of their materials, fabrication processes, and mechanics are new. We will concentrate on transferring the processes for display fabrication from glass plates to flexible substrates, and on the mechanics of flexible substrates. A manufacturer can choose from several display technologies, but only silicon is available for the transistors of the active-matrix transistor backplane. Therefore, the design of a flexible backplane begins with the selection of a foil substrate that is compatible with the silicon thin-film transistor process. The substrate may be an organic polymer or steel. It may need a planarization layer, and must have a layer that provides adhesion, chemical passivation, and electrical insulation. Converting from the chemistry of the substrate foil to the chemistry of a silicon nitride or silicon dioxide passivation layer enables the adoption of many processes developed for glass substrates. The mechanics of flexible substrates plays a role during processing, where it affects device film integrity and mask overlay alignment, and during post-process shaping. Shaping by bending is straightforward and is done in the elastic regime; the device films remain intact. Shaping to a spherical surface, or elastic stretching over an arbitrary surface, produce mechanical strain so large that devices break. A new physical architecture based on rigid device islands has been developed to prevent fracture. Flexible electronics offers a unique combination of materials, processes, devices, and mechanics.

9:00am **TF-FrM3 A Compliant System of Polyimide Microwires for Cryogenic Detector Applications***, **C.A. Allen**, D. Franz, S.H. Moseley,* NASA Goddard Space Flight Center

We have developed a highly compliant, low thermal conductance system of electrical interconnects for cryogenic detector applications. The arrays of microwires are metallic thin film electrical leads supported by a layer of polyimide, capable of spanning the thermally isolated gap between the detector array and the cryogenic heat sink in cryogenic detector assemblies. The low thermal conductance of the microwires enables cryogenic detector thermal isolation without the need for conventional hard wiring, such as soldered manganin or stainless steel. Designed for compactness, an array of 30 microwires fits on a silicon chip less than one half of one square centimeter in total surface area. The free standing length of our microwires is measured in millimeters, as contrasted by units of microns for conventional air-bridge structures. Microwire arrays are terminated on each end by a solid silicon chip containing wire-bonding pads. The two ends of the chip are temporarily supported by a silicon frame, which is removed by laser dicing after the chip has been applied to the detector's thermal isolation platform. We describe techniques for fabrication of arrays of polyimide microwires with several different types of conductive traces, both superconducting and normal-metal. We will discuss their mechanical, electrical, and thermal properties.

9:20am **TF-FrM4 Hysteresis Behaviour during Reactive Sputtering using a Rotatable Magnetron***, **D. Depla**, J. Haemers, R. De Gryse,* Ghent University, Belgium

Reactive magnetron sputtering is a widely used technique to deposit thin compound films on different types of substrates. On laboratory scale the use of a planar magnetron is common practice. However, on an industrial scale one prefers a rotatable magnetron as the target is consumed more efficiently. Unfortunately, detailed experimental results are scarce. Some authors have reported that the well known hysteresis behavior is influenced by the target rotation speed. To study this interesting phenomenon a small rotatable magnetron was developed with a cathode length of only 20 cm making a study on laboratory scale possible. In this paper we present the first results obtained with this device. As we have investigated reactive sputtering of aluminum oxide before using a planar cylindrical magnetron@footnote1,2,3@ this reactive gas/target combination was also used in this study. The discharge voltage was measured as function of the oxygen flow. First, the oxygen flow was increased stepwise until the discharge voltage decreases abruptly, indicating target poisoning. Then the oxygen flow was decreased stepwise. In this way, several hysteresis curves were measured. Two major conclusions can be drawn from these experiments. First, the critical flow to fully poison the target, i.e. when the discharge voltage decreases abruptly, shifts towards lower values with increasing rotation speed. Secondly, we notice that the critical flow to de-poison the target, i.e. when the discharge voltage abruptly increases, also shifts towards lower values with increasing rotation speed but the influence of the rotation speed is much stronger. As such, the hysteresis widens with increasing rotation speed. @FootnoteText@ @footnote 1@D. Depla, R. De Gryse, Plasma Sources Sci. Technol. 10 (2001) 547-555@footnote 2@D. Depla, R. De Gryse, J. Vac. Sci. Technol. A 20 (2002) 521-525@footnote 3@D. Depla, R. De Gryse, Surf. Coat. Technol. 138 (2004) 190-195.

9:40am **TF-FrM5 Bend Testing of OLED Devices on Polymer Substrates***, **J. Lewis**, S. Grego, E. Vick, D. Temple,* RTI International **INVITED**

The flexibility of organic light emitting diode (OLED) displays on flexible substrates is limited by the use of brittle inorganic films for components such as permeation barriers, transparent conductors, and TFTs. The development of a "rollable" display demands significant advances in the mechanical robustness of these brittle films. We will discuss advances in metrology techniques for the mechanical evalution of thin film components, including bend test and failure analysis methods. The fabrication of highly flexible displays requires not only highly flexible component films but also a well-designed display architecture, as layer-layer interactions can lead to mechanical effects not observed when bending components. We will report on the mechanical testing of OLED devices and demonstrate the effects of bending on the current-voltage characteristics, as well as inter-layer propagation of defects. We will discuss the potential impact of the mechanical failure of thin film components on overall device performance and robustness. This work was supported by the Army Research Laboratory (Contract No. DAAD17-01-C-0085).

10:20am **TF-FrM7 Magnetic Thin Film Media on Flexible Substrates by Vacuum Roll to Roll Magnetron Sputtering***, **J. Skorjanec**,* Imation Corporation, US*; C. Merton, M. Hintz,* Imation Corporation

Thin film magnetic media similar to thin film disk has been prepared on polymer substrates by magnetron sputtering in a vacuum roll to roll process. Initial samples to determine film composition, magnetics, and layer thicknesses were prepared in a coupon coater and then transferrred to the roll to roll coater. The roll to roll coater equipment will be described. Some effects of substrate type and deposition parameters on magnetic properties will be discussed. Single pass , multilayer films of long lengths(>300 ft) on polymer substrates were made with final magnetic properties equivalent to the coupon samples with Hc~3400 Oe and Mrt~1memu.cm2.

10:40am **TF-FrM8 Enhanced Properties of IZO Films Deposited on Polymeric Substrate Using Ion-beam Assisted Sputtering for Organic Light-emitting Diode***, **H.C. Pan**, C.Y. Su,* National Applied Research Laboratories, Taiwan, R.O.C.*; C.N. Hsiao,* National Applied Research Laboratories, Taiwan, R.O.C., Taiwan*; Y.-S. Chiu, J.-H. Jou,* National Tsing Hua University, Taiwan, R.O.C.

Zn-doped In@sub 2@O@sub 3@ (IZO) thin films with 5 and 10 wt.% Zn content were prepared on polymeric polyethylene terephthalate (PET) substrate using ion-beam assisted deposition (IBAD) at room temperature. A 15 nm-thick SiO@sub 2@ films were therefore deposited prior to IZO films on PET substrate act as passivation layer to prevent the movement of impurity from underneath layer. The deposited IZO films show amorphous structures with highly electrical conductivity, optical transmittance and surface smoothness on the PET substrate. The 10 wt.% IZO films deposited in a pure Ar atmosphere without IBAD show low resistivity of about 8x10@super -4@ @ohm@-cm, comparable to that of 5 wt.% IZO films (2x10@super -3@ @ohm@-cm). It is found that increase of IZO film thickness leads a high electrical conductivity and decrease of energy band gap regardless of the Zn content of IZO films. The IZO surface morphology increased smoothness with increasing the ion-beam voltage, while the 5 and 10 wt.% IZO film showed a surface roughness variation ranging from 1.7 nm to 1.5 nm and 2.1 nm to 1.5 nm, respectively. Both trends are consistent with more energetic growth condition that enhances the surface diffusion. The energetic contribution of ions with applied 90 V improves the crystallinity of 5 wt.% IZO thin films as shown by a (222)-diffraction peak in the XRD examination. The 5 wt.% IZO films exhibiting higher conducting

distribution uniformity with IBAD was characterized using conducting atomic force microscopy (CFAM). The Al/Alq@sub 3@/IZO/SiO@sub 2@/PET stacks were evaluated for flexible organic light-emitting diode (OLED). OLED were fabricated with both 5 and 10 wt.% IZO film electrodes, and the OLED devices with 5 wt.% IZO electrode showed improved electrical performance due to its crystalline than that of 10 wt.% IZO films.

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