Surface Engineering
Room 132 - Session SE-MoM
Nanocomposites, Multilayers, & Nanostructured Materials

Moderator: G.J. Exarhos, Pacific Northwest National Laboratory

9:40am **SE-MoM1 Magnetron Sputtered W/C Films with C@sub 60@ as Carbon Source*, J.-P. Palmquist,*** Uppsala University, Sweden*; M. Oden, Zs. Czigany, J. Neidhart, L. Hultman,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Sweden

Thin films in the W-C system have been prepared by magnetron sputtering of W with co-evaporated C@sub 60@ as carbon source. We have previously demonstrated epitaxial growth of several binary and ternary metal carbides as well as superlattice structures and gradient films at very low deposition temperatures (100-500 oC). In this study, we present the first results of epitaxial deposition of several phases in the W-C system. In addition, nanocrystalline tungsten carbide films can be deposited. At low C@sub 60@/W ratios, epitaxial growth of @alpha@-W with a solid solution of carbon was obtained on MgO(001) and Al@sub 2@O@sub 3@(0001) at 400 oC. The carbon content in these films (10-20 at%) was at least an order of magnitude higher than maximum equilibrium solubility and gives rise to an extreme hardening effect. Nanoindentation measurements showed that the hardness of these films increased with the carbon content and values as high as 35 GPa were observed. At high C@sub 60@ /W ratios, films of the cubic @beta@-WC@sub 1-x@ (x = 0-0.6) phase was deposited. This phase is not thermodynamically stable at T< 2500 oC but is frequently observed in thin film deposition. The microstructure of the @beta@-WC@sub 1-x@ films was dependent on the deposition conditions. At high deposition rates, nanocrystalline films with a grain size <30 Å were obtained in the temperature range 100-800 oC. The hardness of these films varied from 14 to 24 GPa. Also, for the first time, we have demonstrated epitaxial growth of single-crystalline @beta@-WC@sub 1-x@ films on MgO(001) at very low deposition rates, ~5 Å/min. Finally, at intermediate C@sub 60@/W ratios, epitaxial films of hexagonal W@sub 2@C was deposited on MgO(111), while polycrystalline phase mixtures was obtained on other substrates.

10:20am **SE-MoM3 Synthesis and Characterization of Thermally Stable TiB@sub 2@/TiC Nanolayered Superlattice Coatings for Dry Machining Applications*, K.W. Lee,*** Northwestern University, US*; Y.H. Chen, Y.-W. Chung, K. Ehmann, L.M. Keer,* Northwestern University

It was demonstrated from previous studies that nanolayered superlattice coatings with the correct choice of components and layer thicknesses have enhanced hardness, due to interfaces providing barriers against dislocation motion and multiplication. We expect superlattice coatings made of two immiscible components to be stable against interdiffusion. Therefore, the layer structure and reasonable hardness for such superlattice coatings should be preserved at high temperatures. These thermally stable coatings are desirable for protection of cutting tools in dry machining applications, which may operate at temperatures in the 800 â€“ 1000 C regime or higher. For this reason, TiB@sub 2@ and TiC were chosen for this investigation. Nanolayered coatings made of these two immiscible components were synthesized by dc dual-cathode magnetron sputtering. Substrate rotation was used to enhance uniformity of the coating. Substrates included silicon, M2 steel and WC cutting inserts. Superlattice coatings with TiB@sub 2@ (001) and TiC (111) preferred orientations on Si (001) were synthesized. Transmission electron microscopy studies showed that the layer structure of the coating was preserved after annealing in vacuum at 1000 C for one hour. Room-temperature hardness of these coatings approaches 50 GPa, far exceeding the rule-of-mixture value. Coatings synthesized using the substrate rotation system have improved surface smoothness and reduced internal stress. Wear and durability tests on coated M2 steel and WC cutting inserts demonstrated the improved tribological performance of these coatings under unlubricated conditions compared with other standard coatings such as TiN.

10:40am **SE-MoM4 Chemical Vapor Deposition and Characterization of TiO@sub 2@ Nanoparticles*, W. Li,*** *S.I. Shah, C.P. Huang,* University of Delaware*; O.J. Jung,* Chosun University, South Korea

Chemical vapor deposition (CVD) was used to deposit TiO@sub 2@ nanoparticles with and without metal ion dopants. X-ray photoelectron spectroscopy (XPS) and X-ray energy dispersive spectroscopy (EDS) experiments confirmed the TiO@sub 2@ chemical composition. X-ray diffraction (XRD) patterns showed the polycrystalline anatase structure of TiO@sub 2@. Transmission electron microscopy (TEM) revealed that these particles are nanosized with an average diameter of approximately 20-30 nm. The nanosized particles can provide a large surface to volume ratio and large number of free surface charge carries which are crucial for the enhancement of photocatalytic activity. In order to improve the photocatalysis efficiency, Pd@super 2+@, Pt@super 2+@, Nd@super 3+@ and Fe@super 3+@ transition metal ion were also incorporated as dopants. The effects of dopants on photocatalytic kinetics were investigated by studying the degradation of 2-chlorophenol (2CP) with an ultraviolet light source. The results showed that doped TiO@sub 2@ nanoparticles have higher photocatalytic efficiency than those without dopants with Nd3+ showing the highest efficiency. Time of 90% destruction of 2CP was reduced by one half with Nd3+ doping when compared with undoped TiO@sub 2@.

11:00am **SE-MoM5 Nanocomposite Tribological Coatings with "Chameleon" Surface Adaptation*, A.A. Voevodin,*** *J.S. Zabinski,* Air Force Research Laboratory **INVITED**

Composite coatings where hard nanocrystalline grains are embedded in an amorphous matrix provide considerable improvement in hardness, toughness, wear resistance, and friction reduction. A review of their design concepts is provided with a focus on: (1) improvement in toughness characteristics; and (2) adaptive tribological behavior. Embedding small 5-20 nm hard nanocrystalline grains in an amorphous matrix helps to arrest crack development and introduces ductility through grain boundary sliding. Matrix materials may be selected to provide adaptation of the surface chemistry and/or microstructure to variations in environment and loading conditions to mantain tribological properties. Such materials have been coined chameleon coatings. A combination of nanocrystalline TiC and WC embedded into an amorphous diamond-like carbon (DLC) matrix enabled the coatings to adjust their mechanical response from hard to ductile and significantly reduced the danger of brittle failure. A similar concept was used to improve toughness of composite coatings made of nanocrystalline yttria-stabilized zirconia (YSZ) embedded in an amorphous YSZ/Au matrix. In another example, a combination of nanocrystalline WC and WS2 in an amorphous DLC matrix exhibited surface chemical and microstructural self-adjustment in sliding contact when test environment was cycled from humid to dry. This coating could repeatedly adjust its surface from hexagonal WS2 for sliding in dry nitrogen or vacuum environments to graphitic carbon for sliding in humid air, maintaining a low friction coefficient in both environments. The YSZ/Au nanocomposite developed a gold rich surface layer during heating at 500 °C in air, which considerably improved YSZ tribology in temperature cycling. This coating was further doped with MoS2 and carbon to obtain an environmental adaptation similar to that in the WC/DLC/WS2 system. Chameleon coating designs and applications for advanced tribological coatings are discussed.

11:40am **SE-MoM7 Nanometer-size Monolayer and Multilayer Molecule Corrals on HOPG: A TOF-SIMS, XPS and STM Study*, Y.J. Zhu,*** *T.A. Hansen, S. Ammermann, J.D. McBride, T.P. Beebe, Jr.,* University of Utah

The surface chemistry of highly oriented pyrolytic graphite (HOPG) bombarded with energetic Cs@super +@ ions was studied using the combined surface analysis techniques of TOF-SIMS, (time-of-flight secondary ion mass spectrometry), XPS (x-ray photoelectron spectroscopy) and STM (scanning tunneling microscopy). Controlled surface modification and defect production were achieved by bombardment of HOPG with Cs@super +@ ions at various energies and at various dose densities. XPS shows cesium implanted into HOPG exists in an oxidized state. The Cs@super +@ bombardment of HOPG enhances oxygen adsorption due to both the dissociative adsorption of oxygen at defect sites produced by Cs@super +@ ions, and by the formation of cesium oxide. The surface coverage of cesium on HOPG increases linearly with increasing Cs@super +@ dose density at low bombardment energies, and decreases rapidly with increasing Cs@super +@ bombardment energy due to cesium implantation below the surface. The thermal stability of cesium in HOPG has a complex behavior at elevated temperatures. Defects created by Cs@super +@ ion bombardment in HOPG were subsequently oxidized at 650 @super o@C in air to controllably produce nanometer-size monolayer and multilayer molecule corrals (etch pits). Multilayer pits can be produced using higher energy Cs@super +@ ion bombardment, and monolayer pits can be produced using lower energy Cs@super +@ ion bombardment. The pit density, pit yield, pit diameter and pit depth can be controlled by varying experimental conditions, and they were studied systematically by STM. The measured depth-resolved growth rates for multilayer pits are in good agreement with the model of the growth rate acceleration by adjacent layers. The results obtained lead to a better understanding of the kinetics and mechanism of the graphite oxidation reaction, and more importantly to the accurate production and control of nanometer-size monolayer and multilayer molecule corrals on HOPG.

Thin Films
Room 123 - Session TF+MM-MoM
Thin Film Sensors

Moderator: D.L. Pappas, Duracell

10:20am **TF+MM-MoM3 MEMS Device Platforms as Research Tools for Developing Improved Sensing Films*, C.J. Taylor*,** *S. Semancik, R.E. Cavicchi,* National Institute of Standards and Technology

Gas sensing characteristics of metal oxide films are dependent on the preparation method used in their fabrication. To optimize sensing film performance, one must understand how processing parameters influence composition and microstructure, and then correlate these changes with changes in the selectivity, sensitivity and stability of a sensor. We have been using arrays of microhotplates, MEMS devices fabricated with individually addressable heaters and sensing contacts, for both combinatorial studies and gas sensing. The short thermal time constant of the microhotplates makes them excellent microsubstrates for materials research where rapid heating and cooling during deposition are desired (heating rates of 10@super 5@ - 10@super 6@ °C /s are possible). Experiments have been performed using 4- and 16-element arrays as microsubstrates for CVD processing of titanium oxide and tin oxide using the single source precursors titanium(IV) nitrate, titanium(IV) isopropoxide and tin(IV) nitrate. Sensing films have been deposited both isothermally in the temperature range 100 to 450 °C, and using variable temperature deposition. Variable temperature deposition was achieved by applying triangle or square waves of varying frequency and amplitude to the heater. Film microstructure was examined by FESEM and its composition measured by EDS. We report on correlations between processing method, film microstructure and temperature dependent sensing performance for toluene, methanol, isopropanol, carbon monoxide, acetone, and other compounds.

10:40am **TF+MM-MoM4 Correlation Between Gas Response of MIS Field-Effect Sensors and the Bond Strength Between the Metal and the Insulator Layer of the Device*, A.E. Åbom*,** *L. Hultman, M. Eriksson,* Linköping University, Sweden

Chemical gas sensors based on the field-effect are used in so called electronic noses as a powerful tool for various applications. The response mechanism is, however, not fully understood. In this work we monitor the material properties in order to understand the sensor properties. The sensors used in this work are Metal Insulator Semiconductor field-effect capacitors. The metal, Pt in this case, is grown by dc magnetron sputtering with varying growth parameters, with the Ar pressure ranging between 3 and 60 mTorr. The response to H@sub 2@ can be described by three steps,@footnote 1@ dissociation of H@sub 2@ molecules on the Pt surface, transport of H atoms through the Pt film and adsorption of H (at the metal-oxide interface) as polarized species (either as dipoles or as charged species). The polarized H affects the electric field as a shift in the applied voltage. This voltage shift increases with increasing hydrogen concentration in the ambient and reaches a saturation value depending on the amount of adsorption sites at the interface and on the magnitude of the polarization. We have found that the largest obtained voltage shift varies with the deposition process. The lower the saturation response is, the stronger the film is adhering to the substrate, as measured with e.g. scratch adhesion tests in a Hysitron TriboScope. From in-situ XPS studies it is found that no chemical reactions occur between Pt and SiO@sub 2@. We will discuss how the varying bond strength between the two materials is caused either by mechanical interlocking or electrostatic forces. We will further elaborate on whether the amount of adsorbed H at the interface changes between the different samples due to a varying electron density@footnote 2@ at the interface, or if the separation between the charges in the dipole layer is varying. @FootnoteText@ @footnote 1@ Lundström K.I., Shivaraman, M.S., Svensson, C.M., J. of Appl. Phys. 46(9) 1975 @footnote 2@ Norskov, J.K. Phys. Rev. B 26 (6) 1982.

11:00am **TF+MM-MoM5 On the Ammonia Response Mechanism of Field-effect Gas Sensors with Thin Pt Gates*, M. Lofdahl*,** *M. Eriksson, I. Lundstrom,* Linköping University, Sweden

The ammonia sensitivity of Pt gate field-effect chemical sensors shows a strong dependence on the morphology of the thin metal gate. Several investigations have shown that thin Pt gates are necessary to achieve high ammonia sensitivity and that thick gates show a low or even no sensitivity to ammonia.@footnote 1,2,3@ Thin thickness means in this context that the Pt gate metal has to be made so thin that the underlying oxide is partly exposed. However, there exist an optimum, and if the thickness of the metal is made too thin the sensitivity decreases again. In this contribution the morphology of the thin Pt gate has been carefully investigated and characterised by SEM and complementary TEM studies and morphological parameters have been extracted for different processing conditions of the metal film deposition. By correlating the morphological parameters to measurements of the ammonia sensitivity in inert and oxygen-containing ambient the response mechanism is attributed to the existence of Pt-SiO2 boundaries in the metal. Further experimental investigations show that the Pt-SiO2 interfaces acts as catalytic sites for the dissociation of ammonia molecules and diffusion of detectable species from these sites determine the response. The diffusion length of the detectable species from the dissociation sites is strongly dependent on the existence of oxygen in the ambient. In an inert ambient the diffusion length can be several mm, whereas in 20 % of oxygen it is only in the order of mm. The most likely candidate for the detectable species is atomic hydrogen. @FootnoteText@ @footnote 1@ A. Spetz, M. Armgath, and I. Lundström, Journal of Applied Physics 63, 1274-1283 (1988). @footnote 2@ J. F. Ross, I. Robins, and B. C. Webb, Sensors and Actuators 11, 73 (1987). @footnote 3@ M. Löfdahl, C. Utaiwasin, A. Carlsson, I. Lundström, and M. Eriksson, Submitted to Sensors and Actuators B (2001).

11:20am **TF+MM-MoM6 Charge Transport Mechanisms in Epitaxial Tungsten Oxide Films Used for Chemiresistive Sensors*, S.C. Moulzolf*,** *R.J. Lad,* University of Maine

Chemiresistive gas sensors fabricated from ultra-thin WO@sub 3@ films containing surface catalysts can be made highly sensitive towards a variety of target gases via manipulation of oxide surface chemistry. However, other important sensor characteristics including baseline stability, response time, and reproducibility are strongly dependent on the specific film microstructure and charge transport within the film. Using in situ Hall effect measurements coupled with structural analysis and gas testing experiments, we have determined a correlation between film deposition parameters, microstructure, and electrical response. WO@sub 3@ films were grown by rf magnetron sputtering on sapphire substrates to produce either epitaxial tetragonal or epitaxial monoclinic phases as deduced by RHEED and XRD. Exact film stoichiometries were controlled via post-deposition annealing treatments in vacuum and/or synthetic air environments. Four-point van der Pauw conductivity and Hall effect measurements as a function of temperature indicate that charge mobility is very small (<2cm@super2@V@super -1@s@super -1@) and that polaron hopping is the dominant conduction mechanism. The conductivity of the monoclinic phase is an order of magnitude larger than the tetragonal phase and exhibits temperature dependence similar to measurements from single crystal WO@sub 3@. The mobility of the tetragonal phase increases with temperature consistent with scattering from the increased number of grain boundaries and smaller grain size as observed by STM and XRD. Extended annealing in vacuum to reduce the oxide stoichiometry causes higher conductivity and temperature dependent mobility behavior that may be attributed to crystallographic shear plane defects in the WO@sub 3-x@ lattice. Upon gas exposure to H@sub 2@S or methanol, the tetragonal phase shows higher sensitivity compared to the monoclinic phase but a slower response which correlates with the lower Hall mobility.

Thin Films

Room 123 - Session TF+NS+SE+VST-MoA

Nanophase & Multilayered Thin Films

Moderator: E. Majkova, Institute of Physics SAS

2:40pm **TF+NS+SE+VST-MoA3 Precision Multilayered Thin Films for Manufacturing of the Next Generation of Computer Chips***, E Spiller,* Lawrence Livermore National Laboratory **INVITED**

Lithographic cameras for the fabrication of circuits below 70 nm line width can not use lenses because no transparent material exists for the required short wavelengths in the ultraviolet. Extreme Ultraviolet (EUV) lithography with wavelengths around 13 nm using multilayer coated mirrors is a main contender for chips with line widths between 30 and 70 nm. Meeting the one Angstrom tolerances on the figure and smoothness of the optical surfaces before and after the multilayer deposition and controlling the profile of the multilayer period to better than 0.1 Angstrom has been a major challenge. The talk will give an update on the status of EUV lithography with emphasis on the fabrication, characterization and understanding of the required film deposition processes.

3:20pm **TF+NS+SE+VST-MoA5 Ion Beam Growth and Properties of SiN/TiN Multilayer Thin Films for Phase-shift Masks in Optical Lithography***, **P.F. Carcia**, M.H. Reilly,* DuPont Central Research and Development*; L.J. Pilione, R.F. Messier,* Pennsylvania State University*; L. Dieu,* DuPont Photomask*; R.S. McLean,* DuPont Central Research and Development

Today's high speed microprocessors and dense memory chips are the result of modern optical lithography that allows printing smaller and smaller circuit features on a Si wafer. In 2002, optical lithographic tools with imaging radiation of 193 nm will produce leading edge devices with sub 100 nm critical dimensions. The continued success of optical lithography, which has delayed the introduction of next generation technologies with X-rays, ions, or electrons, can be attributed to the innovative application of optical resolution enhancement techniques that improve feature resolution and increase process latitude. One of these, the attenuating phase-shift mask (attPSM) improves image contrast with destructive optical interference by transmitting (6-17%) and simultaneously phase-shifting 180 degrees imaging radiation through the mask. In this paper we describe a systematic approach for designing wavelength tunable (248nm to 157 nm) attPSMs with SiN/TiN multilayers. We grew these multilayers by dual ion beam deposition (IBD) because it is potentially a cleaner process than magnetron sputtering. Compared to SiN/TiN multilayers grown by magnetron sputtering, IBD produced films with smaller surface roughness (AFM), less chemical contamination (XPS), and flatter interfaces (XRD, TEM). However, IBD films had higher stress, which can cause distortion of the mask and consequent image placement errors. We have therefore investigated strategies, which will also be discussed, to reduce stress in ion beam sputtered SiN/TiN multilayers.

3:40pm **TF+NS+SE+VST-MoA6 Gold Nanoparticle Films via Inert Gas Deposition: Biased Percolation and Current Induced Organization During and after Deposition***, **L.B. Kish**, P. Chaoguang, J. Ederth,* Uppsala University, Sweden*; W.H. Marlow,* Texas A&M University*; C.G. Granqvist,* Uppsala University, Sweden **INVITED**

Gold nanoparticle films made by inert gas deposition have been attracting attention due to their super hardness and thermal stability, which make the films promising objects for future microelectronics applications. The exact origin of the superior proper ties is unknown and to learn the conditions for optimal properties, strong efforts have been made. The published investigations have been made after the films were deposited. This talk reports a different way of study: measuring the electrical conductivit y during deposition. During the measurement, various electrical fields have been applied in order to test the possible influence of the measuring current on the film formation. The time dependence of the conductivity showed various rich patterns including local maximums/minimums. The exact interpretation of the whole process is yet to be make, however, it is possible to make a phenomenological picture of the origin of the observed current-induced-organization phenomena, which include elements of: - Biased percolation: conductor-insulator transition; - Biased percolation: bad conductor - good conductor transition; - Annealing; - Sintering; - Electromigration. A possible technological application of the observed phenomena is the fabrication of nanoparticle films with controlled disorder, such as, fine tuning of chemical sensors.

4:20pm **TF+NS+SE+VST-MoA8 Deposition of Metallic Nanoclusters by Galvanic Displacement***, **L. Magagnin**,* Politecnico di Milano, Italy*; C. Carraro, R. Maboudian,* University of California at Berkeley

Wet processes for the deposition of metallic films on silicon from fluoride containing solution are currently under investigation,@footnote 1,2@ for applications in microelectronics and in micromechanical systems technology. This work presents a novel method for depositing nanostructured films of noble and platinum-group metals by galvanic displacement from water-in-oil microemulsions. One possible application of this process is coating of the interior walls of microchemical reactors@footnote 3@ for enhanced catalytic activity. The water-in-oil system investigated comprises an organic phase (n-heptane), a surfactant (AOT), and an aqueous solution of hydrofluoric acid and metallic ions. Metallic nanoclusters are deposited by galvanic displacement at the silicon substrate in contact with the fluoride containing water droplets. Nanoclusters with controlled size and distribution are obtained on silicon by regulating the micellar radius and deposition time. Scanning probe microscopy is employed to characterize the deposited films. Microscopic observations are correlated with X-ray diffraction and SEM/EDS analyses to investigate the nucleation and growth of the nanoclusters. @FootnoteText@ @footnote 1@M.K. Lee, J.J. Wang, H.D. Wang, J. Electrochem. Soc. 144, 5 (1997): p. 1777. @footnote 2@L. Magagnin, R. Maboudian, C. Carraro, Electrochemical and Solid-State Letters 4, 1 (2001): p. C5. @footnote 3@K.F. Jensen, "The impact of MEMS on the chemical and pharmaceutical industries", Solid-State Sensor and Actuator Workshop, Hilton Head Island, South Caroline, June 4-8 (2000): p. 105.

4:40pm **TF+NS+SE+VST-MoA9 Cross-Linked Nano-Onions of Carbon Nitride in Thin Solid Films***, **L. Hultman**, S. Stafstrom, Zs. Czigany, J. Neidhardt,* Linköping University, Sweden*; N. Hellgren,* University of Illinois at Urbana-Champaign*; I.F. Brunell,* Linköping University, Sweden*; K. Suenaga,* Meijo University, Japan*; C. Colliex,* Universite Paris-Sud, France

We report on cross-linked carbon nitride nano-onions forming thin solid films by reactive unbalanced magnetron sputtering of graphite in an argon-nitrogen discharge. The onion shells, which contain up to 20 at% N, nucleate and grow atom-by-atom on substrates at temperatures as low as 200 °C. Nanoindentation studies reveals a highly resilient material that is relevant for wear-protective applications. Total energy calculations show the relative stability of C@sub 60-2n@N@sub 2n@ aza-fullerenes and suggests the existence of a novel C@sub 48@N@sub 12@ molecule with the unusual S@sub 6@ point group.

Dielectrics
Room 134/135 - Session DI2-MoP
Low K Dielectrics Poster Session

DI2-MoP1 Deposition of Si-C-O-H Alloy Dielectric Films as a Low Dielectric Permittivity Insulators*, **B.K. Hwang**,* Dow Corning Corporation*; M.J. Loboda,* Wacker Siltronic Corporation*; W.D. Gray, G.A. Cerny, R.F. Schneider, J.A. Seifferly, D.W. Roehl,* Dow Corning Corporation

As the feature size in ultra large scale integrated circuit (ULSI) decreases, the minimization of interconnect resistance - capacitance (RC) coupling through the use of copper interconnect metalization and low dielectric permittivity (low-k) has become an intensive interest to the semiconductor industry. Among many low-k candidate materials, carbon-doped silicon oxides, i.e., Si-C-O-H alloy dielectric films have been investigated. These films can be deposited by plasma enhanced chemical vapor deposition (PECVD) of organosilicon gas, (CH3)xSiH4-x, and oxidant mixtures. In this study, we will present the structure, composition, and electrical characteristics of PECVD Si-C-O-H films with different process parameters. The precursor gas mixture used in this study is the trimethylsilane (Dow Corning Z3MS(TM), Semiconductor Grade), oxygen (O2), and helium (He). Samples of Si-C-O-H films were deposited on silicon wafers using a 200mm PECVD reactor. Rutherford backscattering spectrometry and hydrogen forward scattering spectrometry (RBS/HFS), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were evaluated to understand the composition and structure of films. The electrical properties such as a dielectric constant, leakage current density, and dielectric breakdown voltage were tested with a metal-insulator-silicon (MIS) structure. The typical film properties of this study are as follows: (1) FTIR spectra indicate that the hydrogen and carbon are incorporated in the form of Si-(CH2)n-Si, Si-H, Si-CH3, and Si-C into a SiO2 backbone. (2) Composition of Si-C-O-H film : Si / O / C / H = 0.2 / 0.36 / 0.12 / 0.32 (based on RBS/HFS). (3) Bulk film density : 0.97 (g/cm3). (3) Dielectric constant (k) at 1MHz : 2.7 ~ 3.2 and k value has a strong relationship with Si-OH content. (5) Leakage current density : 3x10-10 (A/ cm2) at 0.5 (MV/cm) (6) Dielectric breakdown field : > 4 (MV/cm).

DI2-MoP2 Characterization of Plasma-CVD Grown Low-k Porous Silica Films using Positron-annihilation Lifetime Spectroscopy*, **T. Ohdaira**, R. Suzuki,* National Institute of Advanced Industrial Technology (AIST), Japan*; Y. Shioya,* Semiconductor Process Laboratory Co., Ltd., Japan*; T. Ishimaru,* Canon Sales Co. Inc., Japan

Positron-annihilation lifetime spectroscopy was used to determine the pore size distributions in low-k porous silica films deposited by plasma-enhanced chemical vapor deposition (PE-CVD) with source gases of hexamethyldisiloxane (HMDSO) and nitrous oxide (N@sub 2@O). In PE-CVD, the porosity of the film can be controlled by the deposition conditions, e.g. the pressures and flow rates of the source gases. In the present study, several kinds of porous films with k values ranging from 2.6 to 3.2 were prepared. The positron-annihilation lifetimes at selected depths in the porous films (500 nm thick) were measured by using a mono-energetic pulsed positron beam (0.5 keV - 20 keV). The obtained results show that the pores with average volumes of 0.3 - 1.1 nm@super 3@ are introduced in the films, and that the pore size strongly depends on the deposition conditions. The correlation between the pore size and the dielectric constant will be discussed.

DI2-MoP3 Plasma-Reacting Behaviour of Spin-on Hybrid Organic Siloxane Polymer (HOSP) Low-Dielectric-Constant Thin Films*, **S.-T. Chen**, G.-S. Chen,* Feng Chia University, Taiwan*; T.-C. Chang,* National Sun Yat-Sen University, Taiwan*; C.-P. Liu,* National Cheng Kung University, Taiwan

This work employs Fourier transform infrared spectroscopy and Raman spectroscopy, along with atomic force and transmission electron microscopies to examine microstructure and bonding stabilities of spin-on hybrid organic siloxane polymer (HOSP) low-dielectric-constant (k) thin films after they are exposed to oxygen ashing and (or) various passivating plasma treatments. The spectroscopic and microscopic analyses reveal that, upon exposure to the oxygen plasma, the Si-CH@sub 3@ and Si-C bonds inherent in the thin HOSP (k = 2.5) film are disrupted substantially and, subsequently replaced by highly polarized Si-O, Si-H and (or) Si-OH bonds. These replacements thus degrade the HOSP dielectric film by increasing the magnitude of k significantly. Preliminary results indicate that the HOSP film can be strengthened by passivating it in an adequate plasma. Doing so allows the HOSP to be treated by oxygen-plasma ashing while still maintaining a fairly stable bonding and dielectric properties. Finally, the capability of several ultra-thin (<= 5 nm) capping layers in retarding copper diffusion into the HOSP dielectric layer will be evaluated by measuring C-V and I-V curves of Si/HOSP/capping layers/Cu capacitor samples under conditions of biased thermal stress of 2-4 MV/cm and 150-250 °C.

DI2-MoP4 Process Characterization of Low Dielectric Constant Silicon Containing Fluorocarbon Films by Plasma Enhanced Chemical Vapor Deposition*, **Y.Y. Jin**,* Louisiana State University*; H. Kim,* Kyungpook National University, S. Korea*; G.S. Lee,* Louisiana State University

The development of low dielectric constant (low-k) materials has become one of the most important key challenges for interlayer dielectrics (ILD) of the high performance ultra-large-scale-integration (ULSI) devices. As the decreased design rule and increased complexity of ULSI circuits have essentially increased the crosstalk and RC time delay caused by parasitic capacitance, a great deal of effort has been spent in reducing the dielectric constant of the interlayer as well as reducing the resistance of the wiring metals. Silicon containing fluorocarbon (SiCF) thin films for use as low dielectric ILD have been investigated. The SiCF films were deposited with plasma enhanced chemical vapor deposition (PECVD) using 5% disilane in helium (5%Si2H6/He) and carbon tetrafluoride (CF4) as the precursors. The properties of SiCF films effected by the total flow, the flow rate ratio of CF4/Si2H6 and annealing were investigated to obtain optimal deposition. This work presents the results of a process characterization of PECVD which are the deposition rate, the refractive index and the roughness as functions of the total flow and the flow ratio, and the shrinkage rate and the dielectric constant before/after annealing.

DI2-MoP5 Etching Characteristics of Polyimide Film as Interlayer Dielectric Using Inductively Coupled Plasma*, **P.S. Kang**, C.I. Kim,* Chung-Ang University, Korea*; S.G. Kim,* ETRI, Korea*; H.S. Choi,* Juseong College, Korea*; C.I. Lee,* Ansan College of Technology, Korea*; E.G. Chang,* Chung-Ang University, Korea

In ultra-large-scale integrated circuits, where critical dimensions continue to shrink into the deep submicrometer range, RC constant becomes an increasingly dominant factor in governing both the velocities of operation and the corresponding power consumption. One method to reduce RC constant is the reduction of the dielectric constant of the intermetal material. Therefore, many low-k materials such as amorphous carbon, Teflon, SiOF, Polyimide have been studied by the various research institutes. Among them polyimide (PI) films are widely due to low dielectric constant ,low water absorption, high gap-fill and planarization capability. In this study, etching characteristics of polyimide film with O@sub 2@/CF@sub 4@ gas mixing was studied using inductively coupled plasma (ICP). The etch rate and selectivity were evaluated to rf power, dc-bias voltage, chamber pressure, and substrate temperature. High etch rate (over 10000Å/min) and vertical profile was acquired in CF@sub 4@/(CF@sub 4@+O@sub 2@) of 0.2. The selectivities of polyimide to PR and SiO@sub 2@ was 1.1, 34, respectively. The profiles of polyimide film etched in CF@sub 4@/O@sub 2@ were measured by a scanning electron microscope (SEM) with using an aluminum hard mask pattern. The chemical states on the PI film surface were measured by x-ray photoelectron spectroscopy (XPS). Ion current density and plasma density of O radical and fluorine in O@sub 2@/CF@sub 4@ were investigated by Langmuir probe and optical emission spectrometer (OES). After the etching process, leakage current and dielectric constant were characterized by semiconductor parameter analyzer (HP4145B) and impedance analyzer (HP 4192 at 1MHz) using Al/PI/Al capacitor.

DI2-MoP6 An Opportunity to Study the Outgassing Behavior of a Novel Organic Low K Material*, **J.F. Bernard**, S. Pangrle, C. Gabriel,* Advanced Micro Devices

Lowering interlayer dielectric(ILD) capacitance is key to enjoying the benefits of further advances in IC design and Cu interconnect technology. Conventional SiO2 is now being replaced as an ILD by an array of new materials. In some cases porosity is used to lower k, in others the films are actually novel organic materials. These new low k dielectrics can behave very differently from the SiO2 used in conventional IC fabrication to date. Outgassing is one metric that is a direct measure of film stability, curing, and contamination. Organic films especially can exhibit significant changes in outgassing vs. etch, cleaning and thermal budget. This complex outgassing of organics due to or during processing is a definite departure from SiO2, even for organo-precursor based glasses such as TEOS. We at AMD have had the opportunity to extensively study the outgassing behavior of DOW Chemical's organic low k, SiLK, with both Dynamic and Isothermal Evolved Gas Analyses(EGA). Two distinct regimes of outgassing were observed. At lower temperature atmospheric contaminants are dominant. Benzene related film outgassing was observed above 450°C. XPS analyses confirmed the presence of aromatic binding. The stability of SiLK with respect to various processing steps was investigated with interesting results. These investigations led us to also take a look at our wafer storage materials. The affinity for the absorption of organics was demonstrated and minimized. The effects of processing on a porous derivative were examoned with an etch and clean matrix. Overall evolved gas analyses are proving to be a key data point in understanding and, ultimately, utilizing low k films in advanced IC fabrication.

DI2-MoP8 The Effect of Hydrogen Plasma Treatment on Low-k Hybird-Organic-Siloxane-Polymer (HOSP) Against Damage During Photoresist Removal*, T.C. Chang,* National Sun Yat-Sen University, Taiwan, R.O.C.*; Y.S. Mor,* National Chiao Tung University,Taiwan, R.O.C., Taiwan, R.O.C.*; **P.T. Liu**,* National Nano Device Laboratory, Taiwan, R.O.C*; T.M. Tsai, C.W. Chen,* National Chiao Tung University, Taiwan, R.O.C.*; W.C. Gau,* National Tsing Hua University, Taiwan, R.O.C.*; S.M. Sze,* National Chiao Tung University, Taiwan, R.O.C.

While critical dimensions continue to shrink into the deep submicron range for the need of ULSI circuit, the RC constant that governs both the parasitic delay time (i.e. the speed of operation) and corresponding power dissipation, becomes a dominant factor in improving the chip performance. An organic SOG, the Hybird-Organic-Siloxane-Polymer (HOSP) has high evaluation in ULSI applications because of the low dielectric constant about 2.5. It is also one suitable material of Methyl-Hybrido-Silsesquioxane (MHSQ) films, and simultaneously has good gap filling, low stress and comparable enough strength etc. Face with the same issues of organic low k materials, however, the quality of HOSP film is degraded after photoresist removing. This instability is one of the major problems in using HOSP as a low-k material. In this study, the HOSP film has been investigated for the intermetal dielectric application. In addition, H@sub 2@ plasma pre-treatment was applied to HOSP films. This treatment prevents HOSP films from O@sub 2@ plasma and chemical wet stripper damage during photoresist stripping processes. In the H@sub 2@ plasma treatment, hydrogen radicals can passivate the HOSP surface, preventing the formation of Si-OH bonds so that moisture uptake can be avoided. In addition, dielectric degradation due to photoresist stripping process can thereby solve by H@sub 2@ plasma treatment. These experimental results indicate that H@sub 2@ plasma treatment is a promising technique for integrating the HOSP as intermetal dielectric application.

Thin Films
Room 134/135 - Session TF-MoP
Multilayers and Thin Film Characterization Poster Session

TF-MoP1 The Interfacial Reaction in the W/WN@sub x@/poly Si@sub 1-x@Ge@sub x@ with Ge Contents and Annealing Process*, **S.-K. Kang**, J.J. Kim, D.-H. Ko,* Yonsei University, Korea*; H.B. Kang,* Sungkyunkwan University, Korea*; T.H. Ahn, I.S. Yeo,* Hynix Semiconductor Inc., Korea*; T.W. Lee, Y.H. Lee,* Ju-Sung Eng., Korea

As CMOS device dimensions are continuously scaled down to achieve high performance, new gate structures with low resistivity materials are required to enhance the electrical properties. In order to reduce the resistivity of gate electrode materials, metal silicide/poly Si structures have been employed. However, with metal silicide/poly Si structures, it is difficult to obtain low gate resistance in a narrow gate line. As a low resistivity gate electrode, metal/barrier/poly Si or poly Si@sub 1-X@Ge@sub X@ gate stack is one of the candidates for the gate structures in the high performance CMOS-FET. In addition, poly Si@sub 1-X@Ge@sub X@ films have been suggested as a promising alternative to the poly-Si gate electrode for CMOS technology due to the low resistivity, variable workfunction, and compatibility with Si processes. In order to investigate the interfacial reactions in the W/WNx/Poly Si1-xGex structure, poly poly Si@sub 1-X@Ge@sub X@ films with 0%, 20%, and 60% Ge content were deposited using LPCVD (EUREKA 2000, Ju-Sung Co. Ltd.) on the 8in silicon wafers. Following the deposition process of poly Si@sub 1-X@Ge@sub X@, WNx and W films were deposited using sputtering method. To study the interfacial reactions in the W/WNx/Poly Si@sub 1-X@Ge@sub X@ with Ge contents in poly Si@sub 1-X@Ge@sub X@ and annealing process, the films were annealed at temperatures between 600°C and 900°C in N@sub 2@ ambient. The interfacial reactions in the W/WNx/poly Si@sub 1-X@Ge@sub X@ films were observed by AES, XPS, HR-TEM, and EDX. After annealing treatment, N composition decreased in WNx and the interfacial layer was formed between WNx and poly Si capping layer. The interfacial layer was expected to be composed of W, Si, Ge, and N by the analysis of XPS and EDX. In addition, the formation of interfacial layer with the increase of Ge contents in poly Si@sub 1-X@Ge@sub X@ will be discussed.

TF-MoP2 The Role of Interfaces in Fe/W and Co/W Multilayers*, **E. Majkova**, A. Anopchenko, Y. Chushkin, M. Jergel, S. Luby, R. Senderak,* Institute of Physics SAS, Slovak Republic

With GMR multilayers (MLs) the attention has been mostly paid to the combinations of transition metals with Ag, Au and Cu. Due to the immiscibility of constituents the multilayer interfaces are chemically sharp, formation of magnetically dead layers at the interfaces is suppressed and electron transport does not suffer from additional scattering phenomena. For applications, the use of refractory metals (W, Mo) as non- magnetic spacer provides an interesting alternative. In this paper the interfaces in e-beam deposited Fe/W and Co/W multilayers (MLs) with 5 and 10 periods and magnetic layers 1 or 2nm thick are studied. For analyses the X-ray diffraction (XRD), X-ray reflectivity (XRR) and diffuse scattering at grazing incidence (GIXDS) completed by simulations of the spectra were used. All MLs showed regular periodic structure with layer thicknesses close to the nominal values. The interfacial roughness was 0.5-0.7nm, slightly higher for W/on- Co or W/on -Fe interfaces. >From the GIDS spectra vertical correlation of the interfaces across the whole ML stack was obtained. The XRD patterns revealed polycrystalline structure of the Fe, Co and W layers with structural coherency between fcc Co(111) and/or bcc Fe(110) and bcc W(110) lattice planes across the ML stack. The coherency is affected by the lateral waviness of the Fe/W or Co/W interfaces what results in relatively wide angular distribution of the column orientation. The data point at the growth induced mixing and roughness at the ML interfaces. There is no evidence of compound formation at the interfaces even at the deposition at elevated temperatures (<=200C). The miscibility of Co/W and Fe/W systems and the possible formation of magnetically dead layers due to the mixing and/or roughness at Fe/W and Co/W interfaces are discussed.

TF-MoP3 Intermixing Phenomena in Immiscible Ag/Co Bilayers and Co/Ag/Co Trilayers under KrF Laser Annealing*, **S. Luby**, E. Majkova, M. Jergel, R. Senderak,* Institute of Physics SAS, Slovak Republic*; P. Mengucci, G. Majni,* Uni. Ancona, Italy*; E. D'Anna, G. Leggieri, A. Luches, M. Martino,* Uni. Lecce, Italy

The discovery of GMR in multilayers of immiscible pairs of metals or alloys is the stimulus for the progress in the field of microdevices. Consequently, the study of the thermal stability of GMR structures becomes topical. In the last years a couple of papers on excimer laser induced diffusion in layered structures appeared. In one of them we have studied intermixing in Co/Ag/Co trilayers under XeCl laser thermal treatment. In this paper we have employed thermally more effective KrF laser and the processed structures were composed of layers only several nm thick. Bilayers and trilayers were e-beam deposited in UHV at room temperature onto oxidized Si substrates. The samples were processed by fluences F=0.1-0.25 Jcm@super -2@ with number of pulses @<=@1000 directed to the same irradiation spot.The samples were studied by RBS, XRD, grazing incidence XRD, X-ray reflectivity and sheet resistance measurements. The temperature and depth of melting vs. time in irradiated structures was obtained by numerical computations. Using a broad interval of heat treatments we were able to study the intermixing phenomena at various interfaces. At solid- solid interfaces the grain boundary diffusion of Ag into Co layers dominates the intermixing. The preexponential factor and activation energy of diffusion are D@sub 0@ ~ 10@super -10@ m@super2@s@super-1@ and E= 0.4 eV. At solid liquid interfaces the sharpening of previously deteriorated profiles (probably by back diffusion in immiscible systems) was observed at F=0.2 Jcm@super -2@. Here, the value E=1.5 eV was typical. The jumping of Ag clusters seems to be an explanation of the observed value. Using liquid-liquid interactions granular Ag-Co films were obtained. The phenomena in laser treatment are complex, however, they provide more degrees of freedom due to the controlled depth of melting and delivery of energy in well-defined quanta.

TF-MoP4 The Study of Growth of Al on Polyimide Free-standing Films*, **X.-F. Lin**,* Charles Evans & Associates*; D.A. Grove,* Luxel Corporation*; T.F. Fister, L.P. Bisaha, G.S. Strossman, L.-C. Wei,* Charles Evans & Associates*; G. Lefever-Button,* Luxel Corporation*; J.R. Kingsley, I.D. Ward, R.W. Odom, P.M. Lindley,* Charles Evans & Associates

Al thin film growth on polyimide free-standing films has been studied by several different characterization techniques. We focused our attention on investigating Al growth, nucleation, and the resulting surface structures. Atomic force microscopy (AFM) and energy dispersive x-ray spectroscopy

(EDS) were used to monitor surface morphological evolution and variations of stoichiometries of the Al/polyimide complex as a function of the increasing thickness of Al thin films. The chemical bonding states between Al and polyimide complex were obtained by using x-ray photoelectron spectroscopy (XPS); while the local surface electronic density distribution about the Fermi-level was revealed by scanning tunneling spectroscopy (STS) measurements. We found that during the initial interaction between the condensing Al adatoms and the polyimide substrate, the Al adatoms interact with carbonyl groups of the polyimide to form small clusters which conform to the surface morphology of the polyimide film. Further Al growth produces oriented crystallized sub-micron islands that enlarge with additional Al deposition. The STS I-V spectra acquired at different stages of Al growth show variations of local surface electric conductivity which are affected by adsorbate-substrate and adsorbate-adsorbate interactions, as well as external environmental conditions. These results are compared for Al grown on both free-standing and Si substrate-supported polyimide films.

TF-MoP5 Amorphous Silicon Photodiodes for Image Sensing*, M. Ristova,* Texas A&M University and University in Skopje, Republic of Macedonia*; **Y. Kuo**, H.H. Lee, S. Lee, J.Y. Tewg,* Texas A&M University

The aim of this research was to develop amorphous silicon (a-Si:H) thin film photodiodes for image sensing using the He-Ne (632 nm) laser source. Three different kinds of thin film diode structures, i.e., metal-(a-S:H)-metal, n@super +@-(a-S:H)-metal, and n@super +@-(a-S:H)-n@super+@, were prepared. The a-Si:H (between 200 and 1000 nm) and n@super +@ (20 nm) layers were deposited by plasma-enhanced chemical vapor deposition (PECVD) at 250°C. The molybdenum metal was deposited with a magnetron-sputtering gun at 13.56 MHz. All a-Si:H layers, which contain about 10 % of hydrogen, were deposited under the same condition. The n@super +@ layer's conductivity was about 2.3E10 (ohm-cm)@super -1@, while the conductivity of the undoped a-Si:H was about 1-2E9 (ohm-cm)n@super -1@. The complete diode was fabricated using photolithography and reactive ion etching (RIE) methods. Factors, such as electrode geometry, contact resistance, a-Si:H thickness, and the thermal treatment, were studied for their influence on the diode performance. The diode's dark and illumination currents, i.e., I@sub dark@ and I@sub illumination@, were determined from current-voltage (IV) measurement. The following conclusions are summarized from this study: 1) the highest current (in either dark or under illumination condition) can be obtained with the pattern with highest value for the ratio between the illuminated area and the average distance between the gridlines 2) the contact resistance can be the dominating factor in the current path, 3) the thick film has the large light absorption efficiency and the high current ratio, and 4) the annealing step repairs the RIE damaged film and greatly improves the diode performance.

TF-MoP6 Li3PO4:N/LiCoO2 Coatings for Thin Film Batteries*, **M.E. Gross**, P.M. Martin, D.C. Stewart, J.W. Johnston, C.F. Windisch, G.L. Graff,* Pacific Northwest National Laboratory*; P.L. Rissmiller, E.L. Dudeck,* Mine Safety Appliances Company

Li@sub 3@PO@sub 4@:N/Li@sub 1.04@CoO@sub 2@ thin film battery structures were deposited by reactive RF magnetron sputtering. Li@sub 3@PO@sub 4@:N (LIPON) thin films up to 1 µm thick were deposited using a 6" diameter Li@sub 2.9@PO@sub 3.5@ pressed powder target. Li@sub 1.04@CoO@sub 2@ thin films were deposited using a 6" diameter LiCoO@sub 2@ pressed powder target. LIPON films were deposited in He + N@sub2@ mixtures and LiCoO@sub 2@ films were deposited in Ar + O@sub 2@ mixtures. Total chamber pressure during deposition ranged between 10 and 20 mTorr and RF power to the sputtering targets ranged from 100 W to 400 W. Because XPS gave ambiguous compositional results, the films were optimized for AC and DC conductivity. Electrical conductivity was extremely sensitive to deposition conditions (deposition rate, sputtering gas pressure, and reactive gas partial pressure). AC conductivity measurements were made at a frequency of 10 kHz, and were correlated to DC conductivity measurements. LIPON films had highest conductivities in the 130 S.cm@super -1@ range and the highest AC conductivity of Li@sub 1.04@CoO@sub 2@ films was near 0.24 S.cm@super -1@. The most conductive films were deposited at 20 mTorr pressures and 100 W target power. X-ray diffraction analysis showed that the films were mostly amorphous. Films deposited under these conditions were transparent at visible wavelengths with a refractive index of 1.6. Lower conductivity films were brownish in appearance and less transmissive than films with high conductivity. The rechargeable battery structures consisting of a gold cathode, 0.4 Âµm LIPON, 0.6 Âµm Li@sub 1.04@CoO@sub2@, Li metal anode, and Cu substrate are currently under test. The thin film batteries have been cycled successfully. Performance results are correlated with film properties and reported. Future work will involve optimization of battery performance on a large scale and scale up of the deposition process.

TF-MoP8 Degradation Mechanisms of Low-Temperature Poly-Si Thin-Film Transistors with PECVD TEOS Oxide*, **H.W. Zan**, P.S. Shih, T.C. Wu,* National Chiao Tung University, Taiwan*; T.C. Chang,* National Sun Yat-Sen University, Taiwan, Taiwan, R.O.C.*; C.Y. Chang, D.Z. Peng,* National Chiao Tung University, Taiwan

For being applied on low temperature poly-Si AMLCD, we fabricate poly-Si TFTs with PECVD TEOS oxide as gate insulator. It is found that the output characteristics of our devices are well enough with mobility as 37 cm2/V.s and quite low leakage current. However, due to the high density of trap states localized within the grain boundaries, the electric fields across the grain boundaries near the drain side are considerably high even under moderate biases. The hot-carrier effects are therefore more pronounced in poly-Si TFTs than in MOSFETs. To investigate the reliability issues of poly-Si TFTs, we carefully apply several kinds of electrical stresses on our devices and study their degradation phenomena. Two different degradation mechanisms can be concluded. For the stress under linear region, stress-induced defects are located in the whole gate insulator and are uniformly distributed from source to drain. These defects are positive fixed oxide charges and the acceptor-type interface states in the upper half of the band gap. It is also noted that the degradation degree depends on the magnitude of gate current and the electric field across the gate oxide. For stress under saturation region, however, additional defects near the drain side are generated. This asymmetric degradation phenomenon is attributed to the presence of avalanche-generated carriers. These defects could be acceptor-type interface states in the upper half of the bandgap and donor-type interface states in the lower half of the bandgap. In addition, stress under saturation region produces severer degradation than that under linear region.

TF-MoP9 Atomic Force Microscopy Observation of TiO@sub2@ Films Deposited by dc Reactive Sputtering*, T. Takahashi, **H. Nakabayashi**, N. Sasai, K. Masugata,* Toyama University, Japan

A bombardment of energetic particles such as secondary electrons and recoiled ions ejected from the target plane is very useful technique for modifying the structure of the film in reactive sputtering. It leads to the interesting effects such as enhancement of reactivity, adatom mobility and atomic peening. Therefore, the state on the surface of the as-deposited film may significantly depend on the bombardment condition. So, in this study, the relationship between the surface morphology and the crystal structure of TiO@sub2@ films has been investigated in detail. TiO@sub2@ films with thickness of about 2-3 µm were deposited by dc reactive sputtering on glass-slide substrates. The crystal structure and surface roughness of films were measured with a X-ray diffractometry and an atomic force microscopy (AFM), respectively. The A(101), A(200), A(112) and A(220) peaks were observed from the X-ray diffraction patterns, where A shows an anatase of TiO@sub2@. With increasing energy and number of bombarding particles, X-ray peak intensities I@subP@ of A(101) and A(200) gradually decreased, and I@subP@ of A(112) and A(220) gradually increased, respectively. A(220) peak was significantly higher than others. The crystallinity of TiO@sub2@ film was highly improved and its crystallite size became larger with an increase of them. The roughness parameter Ra on the surface of TiO@sub2@ films also depended on them. Ra increased in the range of 4 to 51 nm with increasing energy and number of bombarding particles. Consequently, it was found that the surface morphology and the crystal orientation of TiO@sub2@ films strongly affected to the bombardment of energetic particles to the growing film.

TF-MoP10 Effects of Annealing Conditions on Doping Efficiency in the Indium Tin Oxide Thin Films Deposited at Low Temperature*, **J.W. Bae**,* Sungkyunkwan University, Korea, South Korea*; S.D. Park, D.H. Lee,* Sungkyunkwan University, Korea*; Y.J. Lee,* Sungkyunkwan University, Korea, South Korea*; G.Y. Yeom,* Sungkyunkwan University, Korea

Tin-doped indium oxide (ITO) thin films were deposited on glass substrates at low temperature(below 90°C) by a dual oxygen beam assisted evaporator system and the effect of various annealing conditions such as annealing atmosphere and annealing temperature on tin-doping efficiency affecting electrical, physical, and optical properties of the ITO were investigated. The tin composition of the source was varied by mixing indium oxide and tin oxide(0 wt.% ~ 30wt.%). Two rf oxygen sources mounted in the chamber were used for oxygen ion and radical sources, respectively. Atomic percentages of tin in the deposited ITO thin films were investigated by X-ray photoelectron spectroscopy. Carrier density and Hall mobility changed with the doped tin concentration and annealing conditions were measured by Hall effect measurement. Crystallinity, sheet resistance, and optical transmittance were observed by a X-ray diffractometer, a four point probe, and an UV-spectrometer, respectively. Carrier concentration of the undoped indium oxide (0% tin) thin film deposited at the optimum deposition condition of O/In compositions (by controlling the flux ratios of two rf oxygen sources and the evaporation source) was decreased with annealing but Hall mobility was increased from ~20 cm@super 2@/Vs to 105 cm@super 2@/Vs. On the other hand, in the case of tin doped indium oxide (> 0% tin) film deposited at optimum deposition conditions, both the carrier concentration and the mobility were increased with the increase of the annealing temperature and, therefore, the resistivity was decreased from 5 X 10@super -4@ ohm-cm to below 2 X 10@super -4@ ohm-cm due to the increase of tin doping efficiency. Tin atoms located at interstitial sites during the deposition at low temperature appear to move to indium substitutional sites by annealing. It implies that tin atoms in the indium tin oxide deposited at low temperature could act as impurity instead of dopant.

TF-MoP12 Electrical Properties for Si Doped Glass Light Emitter*, T. Ichinohe,* Tokyo National College of Technology, Japan*; S. Nozaki, H. Morisaki,* The University of Electro-Communications, Japan*; S. Masaki,* Tokyo National College of Technology, Japan*; K. Kawasaki,* TDY Co. Ltd., Japan

Nanometer-sized Si ultrafine particle films (the Si nano-structured films) have been studied extensively as a candidate of Si-based photo-electronic coupled devices. Some of the authors have discussed the emission mechanism of the visible light emission and others have emphasized the possibility on the application to light emitters, although the emission intensity of the Si nano-structured films still remains to be quite low at present. The correlation between the light emission and the carrier injection mechanism in the Si nano-structured films should be clarified to realize Si based light emitter. We have studied both photoluminescence (PL) and electroluminescence (EL) of the Si doped glass (Si-DG) films fabricated by the ion beam sputter-deposition. The transmission electron microscopic(TEM) study has shown that the presence of nano-crystalline Si particles formed by annealing at 900 °C in nitrogen-gas atmosphere is essential for the visible light emission. PL spectra have been influenced by the excitation light energy, indicating that the emission is via the emission centers distributed in the interface between the crystallites and the surrounding SiO@sub 2@. EL devices with indium-tin-oxide (ITO) top electrodes have shown the emission peak at 650 nm, which is considerably longer than the PL peaks between 520 and 580 nm. The EL devices have shown the luminescence only when the diode is in forward bias, that is, the Si back contact is positive to the ITO top electrode. The integrated intensity increases almost in proportion to the injection current. When the forward bias voltage exceeded 5 V, EL became to be strong enough to be noticed with the naked eye in dark. We noticed that EL spectra tend to become broad with increasing current. C-V measurement has shown that the reverse bias characteristics are explained by the MOS-like structure with the flat band potential of about -4V.

TF-MoP14 Characterization of Pb(Zr@sub0.52@Ti@sub0.48@)O@sub3@ Films in the Thickness Range of 0.4-6.0µm Prepared by Pulsed Laser Deposition*, M.C. Kim,* Yonsei University, Korea*; J.W. Choi, S.J. Yoon, H.J. Kim,* Korea Institute of Science and Technology*; K.Y. Yoon,* Yonsei University, Korea

The films of nominal composition of Pb(Zr@sub0.52@Ti@sub0.48@)O@sub3@ (PZT) in the thickness range of 0.4-6.0µm were fabricated on Pt/Ti/SiO@sub2@/Si substrate using a pulsed laser deposition (PLD). The PZT films were deposited at 500°C with single process and post annealed at 650°C in oxygen atmosphere because the deposition rate of PLD was fast. The variations in crystallite orientation, microstructure, and ferroelectric and dielectric properties were determined as a function of film thickness. The preferred orientation (111) was changed to (110) above the thickness of 8000Å. As film thickness increased, gain size increased and cross-sectional microstructure showed columnar structure. Remnant polarizations increased from 20 to 40µC/cm@super2@ approximately, and relative permittivity and coercive field decreased from 1800 to 1000 and 45 to 30KV/cm, respectively. The changes of property would be discussed in terms of the presumed influence of interfacial phenomena.

TF-MoP16 The Effect of the Process Parameters on the Electrical Properties of Ni-Cr-Al-Mn-Si Alloy Thin Films*, B.J. Lee,* Inha University, Korea*; C.S. Kim,* Korea Electronics Technology Institute*; G.B. Park,* Yuhan College, Korea*; D.C. Lee,* Inha University, Korea

We have fabricated thin resistor films using the DC/RF magnetron sputtering of 75wt%Ni-20wt%Cr-3wt%Al-4wt%Mn-1wt%Si alloy target and studied the effect of the process parameters on the electrical properties for low TCR(Temperature Coefficient of Resistance) films. In sputtering process, pressure and substrate temperature, are varied as controllable parameters. The films are annealed to 400°C in air and nitrogen atmosphere. We have investigated the microstructure using TEM, XRD, EPMA and EDS and measured the electrical properties, the sheet resistance and TCR. The oxygen content and TCR of the films decreased as the sputtering pressure decreased. The oxygen content were 8.9, 8.5 and 1.5wt%, TCR were 105, 85 and 54ppm/°C for 25, 15 and 5mTorr of the pressure, respectively. The sheet resistance, TCR and crystallinity of the films increases with increasing the substrate and annealing temperature. The sheet resistance and TCR abruptly increased as annealing temperature increased over 300°C in air atmosphere. >From TEM and XRD, it is found that these results are due to the existence of NiO on film surface formed by annealing. As a results of them, it is suggested that the sheet resistance and TCR of thin films can be controlled by variation of sputter process parameter and annealing of thin film below 300°C in nitrogen.

TF-MoP17 Electrical Properties of the Novel Semiconductor Alloy Cu@sub x@Cd@sub 1-x@Te Prepared by rf Sputtering, *E. Garnett-Ruiz, G. Torres-Delgado, O. Jiménez-Sandoval, R. Perez-Castanedo, P. Garcia-Jimenez,* Cinvestav-IPN, Mexico*; B.S. Chao,* Energy Conversion Devices*; **S. Jiménez-Sandoval,*** Cinvestav-IPN, Mexico

It has been demonstrated that the incorporation of Cu into Cd sites at concentrations around 0.3 at% produces high quality films when compared to pure CdTe or to Cu@sub x@Cd@sub 1-x@Te with higher copper concentrations. The improvement on the structural properties produces an important effect on the transport properties of this semiconducting alloy. For instance, we have observed that the resistivity drops 4 to 8 orders of magnitude depending upon copper content. In this work we present the results of a study on the electrical properties of thin films, grown by rf sputtering, of the novel semiconductor alloy Cu@sub x@Cd@sub 1-x@Te as a function of copper concentration. This study is based on the current-voltage characteristics of a capacitor-like structure metal/semiconductor alloy/metal (suitable for measurement of polycrysdtalline materials) which allows to determine the values for electrical parameters when this structure is measured for different thicknesses of the semiconducting material.

TF-MoP18 Characterization of Hydrogenated Amorphous Germanium, a-Ge:H, Thin Films Deposited by a Low Pressure Hollow Cathode Plasma-jet Reactive Sputtering System*, G. Pribil,* *R.J. Soukup, N.J. Ianno,* University of Nebraska, Lincoln*; Z. Hubicka,* Academy of Sciences

Hydrogenated amorphous germanium, a-Ge:H, thin films were deposited by means of a low pressure dc hollow cathode plasma-jet system. A high density plasma was excited in a cylindrical nozzle of polycrystalline Ge working as a hollow cathode. An adjustable magnetic field was used for dc hollow cathode discharge stability and for partial confinement of the reactive plasma at the cathode outlet. The germanium nozzles were reactively sputtered in this high density hollow cathode discharge. Only nontoxic gases, argon and hydrogen, were used as a working gas mixture. Different conditions for the dc hollow cathode system were used for deposition. The a-Ge:H thin films were characterized by FTIR spectroscopy, Tauc band gap measurements, measurements of conductivity in the light and in the dark, and thickness measurements. The growth rate achieved was in the range of from 2 to 6 µm/h. This system has already been used for the deposition of high quality hydrogenated amorphous silicon, a-SiH, thin films using silicon nozzles. These experiments lead to the deposition of hydrogenated amorphous silicon/germanium alloy films, a-SiGe:H, without the use of silane or germane, using co-sputtering of Si and Ge nozzles in a multi-hollow cathode plasma jet system.

TF-MoP19 Metal-insulator Transition in Ultrathin Copper Film Observed By Impedance Spectroscopy*, X. Jin,* *Y. Zhou, Y.H. Hyun, T.-U. Nahm, C.O. Kim, Y.P. Lee,* Hanyang University, Korea

Ultrathin Cu films with a thickness of 0.3- 9 nm were thermally evaporated on a glass at room temperature in an ultrahigh vacuum chamber. The simultaneous in-situ monitoring of the complex impedance spectrum and the electrical resistance of the growing films was carried out. A metal-insulator transition was observed at a percolation onset thickness of 2.5

nm. The complex impedance of the films could be described by a parallel R-C equivalent circuit when the film thickness is smaller than the percolation onset thickness. With the further growth of film, the complex impedance undergoes a transition to an inductive equivalent circuit. A change in the electrical resistance at the percolation onset thickness follows a scaling law R ~ (d-d@sub c@)@super -t@ where t is an exponent, and are consistent with the observed transition.

TF-MoP20 In-situ Buried Multiquantum Well Structures Studied by Photoreflectance and Photoluminescence Spectroscopy*, **A. Perez-Centeno**, M. Lopez-Lopez, M. Melendez-Lira, M. Tamura,* CINVESTAV-IPN, Mexico*; T. Ishikawa,* OTL, Tsukuba, Japan

In this work we present the optical and structural characteristics of AlGaAs/GaAs multiquantum wells (MQWs) that were in-situ etched into mesa-stripe structures and then buried avoiding air-exposure of the active region at the sidewalls. The samples were fabricated using the following steps: First, by conventional photolithography and etching techniques mesa stripe-arrays of different widths and along different crystallographic directions were patterned on the surface of a 250nm thick GaAs protective layer of MQWs grown on a GaAs(001) wafer. The mesas depth was 200nm, in order to protect the MQWs a 50nm-thick GaAs layer was left unetched. Next the wafer was introduced into an UHV multichamber system with an MBE chamber and an etching chamber connected through UHV tunnels. The initial pattern was transferred down to the MQWs by in-situ Cl@sub 2@-etching to a depth of ~200nm. Then, the sample was transferred in UHV to the MBE chamber, where an AlGaAs layer was overgrown thus completing the in-situ buried structures. Photoluminescence (PL) studies showed a decrease in the MQWs PL intensity and PL lifetime for mesa stripes of several microns in width, thus showing the effects of carrier trapping and non-radiative recombination at the etched-regrown interfaces on the sidewalls. The PL degradation was stronger for mesas along the [110] direction. In the photoreflectance (PR) spectra the transitions associated to the MQWs were clearly observed for mesas along [1-1 0], however for mesas along [110] we only observed the signal associated to the GaAs band-gap. PR spectra also showed the presence of oscillations above the GaAs band-gap value associated to built-in internal electric fields. The strength of the internal electric fields was in the order of 10 kV/cm, as obtained by the Franz-Keldysh model. We discuss the degraded optical properties for mesas along [110] in terms of the increased difficulties to smoothly overgrow mesa-sidewalls along this direction.

Thin Films
Room 123 - Session TF-TuM
Optical Thin Films

Moderator: J. Verhoeven, FOM Institute, The Netherlands

8:20am **TF-TuM1 Influence of Processing Conditions on Sputter Deposited ZnO:Al Thin Films**, ***L.W. Rieth****, P.H. Holloway,* University of Florida

Thin films of zinc oxide (ZnO) are useful in many applications including transparent conductors, gas sensors, RF filters, varistors, and Cu(In,Ga)Se@sub 2@ (CIGS) based thin film solar cells. Thin films of Al doped ZnO are deposited from a ceramic target of ZnO:Al@sub 2@O@sub 3@ (98wt%:2wt%) using an 8 inch RF diode source onto cleaned soda-lime glass substrates with no intentional heating. RF power and process pressure are varied over the ranges of 250 - 1000 watts and 5 - 50 mTorr, respectively. As deposited and modestly heat treated films (400°C for 1 hour) are characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), four point probe, Hall measurements, and spectrophotometry. AFM micropgraphs indicate the films are polycrystalline with grain sizes between 10 and 100nm. XRD results indicate the films have the wurtzite structure with a strong basal texture (0001). XPS spectra reveal the films have the proper stoichiometry, and a chemisorbed surface oxide species that is sensitive in particular to the gas ambient during the modest heat treatments. Electrical data show that the films have a large range of resistivities, which improve with heat treatment to as low as 10@sup -3@ @ohm@-cm, while maintaining transmission greater than 80% across the visible range. The properties were sensitive to location on the substrate relative to the sputter deposition source, exhibiting the lowest resistivity for off axis deposited films These results are discussed with respect to the hypothesis that negative ion resputtering (NIR) strongly influences the properties of the deposited films.

8:40am **TF-TuM2 Linear Combinatorial Synthesis of Cadmium Tin Oxide Films by Low-pressure Chemical Vapor Deposition**, ***X. Li****, T. Gessert, T. Coutts,* National Renewable Energy Laboratory

Recent work on transparent conducting oxides (TCOs) such as tin oxide (SnO@sub 2@) and cadmium stannate (CTO) has been of great interest because of the relevance of these materials to important technological applications. The electrical and optical properties of these materials are relevant to low-emissivity glass, flat-panel displays, and thin-film solar cells. SnO2 is very durable and appropriate for coatings on low-emissivity windows whereas CdO has exhibited mobilities over 200 cm@super 2@ V@super -1@ s@super-1@. The intermediate alloy, CTO, may be either orthorhombic or spinel, although thin-films are typically spinel. This material has also exhibited high mobilities of 80 cm2 V-1 s-1, although requiring rather specific deposition and annealing conditions. This paper will discuss our early efforts to make this material using a technique that is potentially more suitable for large-scale manufacture. We have deposited films of the individual materials using low-pressure metal organic chemical vapor deposition (LPMODVD) and have also combined the precursors to make films of CTO. We used tetramethyltin (TMT), dimethylcadmium and oxygen as the precursors. The concentrations of the two organic precursors varied along the length of the substrate because of their varying rates of decomposition. In effect, we had established conditions that enabled us to perform linear combinatorial synthesis experiments. Our objective was to make CTO films but the films varied from near-CdO (at the leading edge of the substrate) to near-SnO2 (at the trailing edge). The mobilities varied from less than 1 cm2 V-1 s-1 to about 60 cm2 V-1 s-1. Optical data indicated that the bandgaps varied from 2.75 eV (somewhat characteristic of CdO) to about 3.65 eV (more characteristic of SnO2). We also measured the compositional and structural variations along the length of the substrate and found consistent behavior. Within a limited range of distances, we established material similar to spinel CTO.

9:00am **TF-TuM3 Challenges in the Development of Novel Transparent Conducting Oxides**, ***T. Coutts****, D.S. Ginley, D.L. Young, X. Li, J.D. Perkins,* National Renewable Energy Laboratory **INVITED**

Transparent conducting oxides (TCOs) have been used extensively during the last forty years for a variety of applications including, flat-panel displays, photovoltaic modules, and heat-conserving infrared reflectors on windows. While their performance has been acceptable for these applications, the demands of new developments and the emergence of new applications indicate that this will change in the near future. Changes in the quality of existing TCOs and/or the development of new materials are, therefore, certain to be required. In this paper, we shall review our work at the National Renewable Energy Laboratory in this field. This includes the synthesis of high quality spinel n-type TCOs such as cadmium and zinc stannate, binary oxides of tin, zinc and cadmium, and exploratory research into p-type TCOs such as ZnO:NO and the delafossites CuAlO@sub 2@ and CuInO@sub 2@. Several deposition techniques such as sputtering, pulsed laser deposition, and chemical vapor deposition are used, with combinatorial synthesis, to facilitate investigation of the vast phase-space encompassed by TCOs. In addition, we have extensive methods of characterizing the electrical, compositional, structural and crystallographic properties of the materials of interest.

9:40am **TF-TuM5 Kinetics of Hydrogen Induced Changes of Optical Properties in Smart Coatings**, ***M. Wuttig****,* Aachen University of Technology, Germany

Certain transition metal oxides and hydrides show remarkable changes of their optical properties upon hydrogen exposure, in particular if the film surface is covered by a thin Pd or Pt film. This effect can be used to create window coatings that enable a switching of optical properties. In this study we compare the switching kinetics of several thin film systems including Mg, Gd, MgGd alloys and WO@sub 3@ upon hydrogen exposure. The switching process is studied in-situ by time resolved optical spectroscopy measurements, x-ray diffraction and x-ray reflection as well as mechanical stress measurements. The latter measurements reveal that for the different materials very different stresses arise as a function of hydrogen exposure. The lowest stresses are observed for WO@sub 3@ films, while stresses above 1 GPa were observed for Gd. Nevertheless the value of the stress change alone is insufficient to determine if plastic deformation and degradation of the films upon hydrogen exposure takes place. The influence of the film morphology on switching kinetics is carefully studied. A particularly pronounced correlation between switching kinetics and film density is observed for the WO@sub 3@ films where the time constant varies by more than two orders of magnitude upon a variation in density by 20%.

10:00am **TF-TuM6 Plasma Enhanced Chemical Vapour Deposition of SiO@sub x@N@sub y@ for Large Area Applications in a Matrix Distributed Electron Cyclotron Resonance Reactor**, ***A. Hofrichter****, A. Charaya, B. Drevillon,* Ecole Polytechnique CNRS, France

There is a considerable interest to use high-density plasma sources for plasma enhanced chemical vapor deposition of thin films on large areas. Major issues in this field are deposition uniformity and whether the use of radiofrequency bias is needed to obtain high quality materials. In this work we use the recently developed matrix distributed electron cyclotron resonance concept for the deposition of silicon oxynitride thin films. By using an array of individually tunable ECR plasma sources (5x5 in our case), this concept is easily scaleable by increasing the number of the sources while maintaining the necessary plasma homogeneity. Films were deposited onto glass, crystalline silicon and polycarbonate substrates with a typical uniformity of 1,5 % on 200x200 mm, and 4% on 350x350 mm. The properties of the materials are analyzed with in situ UV-Visible spectroscopic phase-modulated ellipsometry (PME), ex-situ transmission, Infra-Red ellipsometry, RBS and ERDA measurements. Without substrate heating and radiofrequency bias dense, non-absorbing, low hydrogen content stoichiometric films of SiO@sub 2@ and Si @sub 3@N@sub 4@ are grown from the mixture of SiH@sub 4@, O@sub 2@ and N@sub 2@. By changing the nitrogen to oxygen gas flow ratio the refractive index (measured at 632.8 nm) can be smoothly and reproducibly tuned from 1.46 to 1.95. Deposition rates are between 13.0 and 0.5 nm/s for SiO@sub 2@ and Si@sub 3@ N@sub 4@ respectively. The influence of process parameters, such as deposition pressure, microwave power, gas flows and flow ratios are studied and correlated with Langmuir probe measurements and optical emission spectroscopy to obtain better insight into the plasma properties and the mechanisms of the growth.

10:20am **TF-TuM7 High Growth Rate Deposition of a-SiN@sub x@:H Films for Photovoltaic Applications**, ***J. Hong****,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; F.J.H. Van Assche,* Eindhoven University of Technology, The Netherlands*; D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

A new technique has been developed for the deposition of amorphous silicon nitride (a-SiN@sub x@:H) films at deposition rates up to ~200 Å/s by injection of SiH@sub 4@ into an expanding Ar/H@sub 2@/N@sub 2@

plasma. This so-called expanding thermal plasma (ETP) technique is relevant for high-throughput deposition of a-SiN@sub x@:H anti-reflection (AR) coatings on industrial Si solar cells, where the a-SiN@sub x@:H can simultaneously lead to both bulk and surface passivation. Silicon nitride films with different Si/N ratios and hydrogen concentrations have been deposited on different types of Si solar cells. It has been revealed that the optical properties can be fully tuned to obtain an optimized AR matching with the Si substrate while real-time ellipsometry is used as feedback during processing. Film homogeneity measurements revealed less than 5% variation over 10x10 cm@super 2@ cells. Bulk passivation of multi-crystalline Si cells has been suggested by an enhanced red response of the coated cells, although preliminary results on surface passivation have not yet revealed sufficient reduction of the surface recombination on mono-crystalline Si cells. More data on real solar cells will be presented. The plasma chemistry has been studied by threshold ionization mass spectrometry and cavity ring down spectroscopy. These measurements suggest the creation of SiH@sub 3@ radicals by atomic H from the plasma source leading to a neutral-dominated deposition of a Si top layer, followed by subsequent nitriding by atomic N. Real-time attenuated total reflection infrared spectroscopy is applied to extend the insight into this deposition mechanism.

10:40am **TF-TuM8 Electrical Characteristics and Growth of ZrO@sub2@ as a Gate Dielectric***, Y. Kim, Y. Kim, H. Jeon,* Hanyang University, Korea

We have studied ZrO@sub 2@ thin film as an alternative gate dielectric. It was deposited on a Si substrate by RF reactive sputtering system which was optimized to achieve high quality thin film. O@sub 2@ flow and power were modulated to control the interface quality and growth rate. This ZrO@sub 2@ thin film was annealed from 600 °C to 900 °C for 30 sec with rapid thermal annealing (RTA).@footnote 1@ Pt was deposited as a top electrode for metal-oxide-semiconductor (MOS) capacitor by ultra high vacuum evaporation system and this capacitor was annealed at 450 °C for 30 sec with RTA in H@sub 2@ + N@sub 2@ ambient. Capacitance-voltage measurements showed an equivalent oxide thickness of less than 30 Å with no significant dispersion of the capacitance for 1MHz frequency. Current-voltage measurements exhibited the low leakage current at -1.0V. Hysteresis shift in these films was measured to be less than 100mV. Interface state density and reliability were measured. We examined cross-sectional transmission electron microscopy and X-ray diffraction to observe reaction and crystallization of zirconium oxide.@footnote 2@ We also examined the zirconium oxide formation depending on the annealing temperature by in-situ Auger electron spectroscopy system connected with ultrahigh vacuum furnace. @FootnoteText@ @footnote 1@B. H. Lee, L. Kang, R. Nieh, W. Qi, and J. C. Lee, Appl. Phys. Lett., vol. 76, p. 1927, Apr. 2000. @footnote 2@G. D. Wilk and R. M. Wallace Appl. Phys. Lett., vol. 76 p. 112, Jan. 2000.

11:20am **TF-TuM10 Effect of Cation Charge State and Site Occupancy on the Dielectric Response of ITCO Spinel Films***, C.F. Windisch Jr.,* Pacific Northwest National Laboratory*; K.F. Ferris,* Pacific Northwest National Laboratory, us*; G.J. Exarhos,* Pacific Northwest National Laboratory

Cobalt-nickel oxide thin films have recently showed promise as infrared transparent conducting oxide (ITCO) materials. In this work, nominal 100 nm thick films with electrical resistivity on the order of 10@super -3@ ohm cm were prepared using both solution and rf magnetron sputter deposition techniques with subsequent post-deposition annealing in air. A combination of XRD, XPS, UV/Vis, Raman spectroscopy, Hall and Seebeck measurements confirmed that a spinel oxide is the primary conducting component of these films and that the conductivity is maximum at or near the NiCo@sub 2@O@sub 4@ stoichiometry, where x = Co/(Co + Ni) = 0.67. Between x = 0.67 and 1.0, i.e. Co@sub 3@O@sub 4@, the conductivity decreases by many orders of magnitude. As x decreases (higher nickel content), conductivity improves somewhat until phase instability drives precipitation of nickel oxide with concomitant loss in conductivity. The reason for this variation has been the subject of much debate in the literature with important questions still unresolved. In this paper, we show, by careful analysis of the XPS and Raman spectra, that the charge state and site occupancy distribution of the Ni cations, as well as the defect structure involving singly charged oxygen anions, vary predictably with composition and conductivity. Electronic structure modeling studies performed in conjunction with the spectroscopy experiments provide a fundamental perspective on the relationship between the optical response and attendant conductivity for this important new class of TCO materials that are being investigated for prospective use in optical limiting and switching applications. This work was conducted under the "Electroactive Coatings and Shutters for Protection of Sensors" Program funded through DARPA contract DAAD19-99-1-0003. Pacific Northwest National Laboratory (PNNL) is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

11:40am **TF-TuM11 Multi-layer Chromium-based Optical Coatings for 157nm Lithography***, P.D. Rack, B.W. Smith, A. Bourov, D. Baiko,* Rochester Institute of Technology*; M.G. Lassiter,* Photronics Corp.

Chromium based multi-layer films have been the dominant masking material for optical microlithography. The next generation optical lithography exposure wavelength is expected to be 157nm from an F2 laser source. Of critical interest for this exposure wavelength is the optical properties of the chromium multi-layer mask. Traditionally the masking film has been ~100-120 nm thick, however for accurate critical dimension control for off-axis illumination sources, it is desirable to thin the masking film thickness. To design a process to deposit a thinned masking material, the composition of the standard masking material was initially confirmed via x-ray photoelectron spectroscopy depth profiling. The composition of the film was determined to be a CrxNy film with a graded CrxOyNz anti-reflecting top layer. To evaluate the thinned materials, a design of experiments was performed to reactively sputter a metallic chromium target in an Ar-N2 and an Ar-N2-O2 ambient, respectively. After successfully reproducing the ~120nm thick multi-layer film, a series of scaled films with a total thickness of 50 and 80 nm were deposited. Vacuum ultra violet (VUV) transmission, reflection, and spectroscopic ellipsometry measurements were performed on each film and the optical constants (n and k) of the individual layers were determined. Finally, the entire multi-layer film stack was modeled with an effective medium approximation and found to correlate well with the experimental reflection and transmission data. In this presentation, we will discuss reactive sputter deposition metallic chromium to form the CrxNy/CrxOyNz multi-layer thin films. The optical characterization results will be presented and discussed in regard to the reflection and optical density requirements necessary for a masking material. Finally the modeling of the spectroscopic ellipsometry will be presented and the effective media approximation of the film stacks will be discussed.

Surface Engineering
Room 132 - Session SE-TuA
Hard and Superhard Coatings

Moderator: I. Petrov, University of Illinois, Urbana

2:00pm **SE-TuA1 Microstructure and Mechanical Properties of Zr-Si-N Films Prepared by r.f.- Reactive Sputtering***, **M. Nose**,* Northwestern University, Japan*; W.A. Chiou,* University of California at Irvine*; M. Zhou,* Osaka University, Japan*; T. Mae,* Toyama National College of Technology, Japan*; M. Meshii,* Northwestern University

ZrN and ZrSiN films were prepared in an r.f. sputtering apparatus which has a pair of targets facing each other (referred to as the Facing Target -type r.f. Sputtering). Films were deposited on silicon wafer without bias application nor substrate heating in order to examine only the effect of silicon addition to transition metal nitride films. The transmission electron microscopy studies were carried out in addition to XRD. For the high resolution TEM observation, the field emission type transmission electron microscope (FE-TEM) was used, which provides a point-to-point resolution of 0.1nm. The samples were observed both parallel and perpendicular to the film surface, which were in-plane and cross-sectional view, respectively. In order to investigate the relationship between mechanical properties and microstructure of films, the hardness was measured by a nano-indentation system at room temperature. The load was selected to produce an impression depth below 60nm (not more than 5% of film thickness) so that the influence from the substrate can be neglected. The contents of zirconium, nitrogen and silicon of the films were determined by ZAF method with EPMA. A study of their microstructure and mechanical properties has provided as follows: (1) The hardness and Young's modulus increase with small Si additions reaching maximum values of 35GPa (at 3%Si) and 370GPa (at 5% Si), respectively; (2) The hardest films containing 3%Si did not consist of nano-crystals but clear columnar crystals in the range of 10 to 25nm; (3) The increment of hardness with small amount of Si atoms can be attributed to the solution hardening by Si to ZrN lattice; (4) In the case of ZrSiN films deposited by r.f. sputtering without bias application nor substrate heating, the available result did not ensure the presence of ZrN nano-crystals embedded in Si@sub 3@N@sub 4@ matrix.

2:20pm **SE-TuA2 Characterization of CrBN Films Deposited by Ion Beam Assisted Deposition***, S.L. Rohde, **S.M. Aouadi**, D.M. Shultze, T.Z. Gorishnyy,* University of Nebraska - Lincoln*; N. Finnegan,* University of Illinois at Urbana-Champaign

This paper reports on the first attempt to grow and analyze CrBN nanocrystalline materials using physical vapor deposition processes. Coatings were deposited at low temperatures (<200 Â°C) on silicon substrates using ion beam assisted deposition (IBAD). These coatings were characterized post-deposition using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), infrared spectroscopic ellipsometry (IR-SE), and visible-light spectroscopic ellipsometry (VIS-SE). The primary phases in the films were identified using XRD. The surface morphology and nanocrystalline nature of the coatings (grain size of 5 - 7 nm) were deduced using AFM. The mechanical properties (wear rate, hardness, elastic modulii) of the coatings were evaluated using a nanohardness test. The chemical composition and phase composition of the samples were determined from XPS and AES measurements and were subsequently deduced from the analysis of the VIS-SE data. The film compositions deduced from both techniques correlated well. Additionally, XPS, AES, and IR-SE were used to reveal the crystal structure of the BN phase in these ternary compounds.

3:00pm **SE-TuA4 Thin Film Growth by Physical Vapor Deposition in the Presence of Residual Gas***, **J.M. Schneider**,* Linkoping University, Sweden **INVITED**

Vacuum based techniques are characterized by the presence of residual gas. Depending on the affinity of the residual gas to the growing film material, chemical reactions may be possible. Residual gas based impurity incorporation during thin film growth has been reported previously.@footnote 1,@@footnote 2@ Here, the state of the art in residual gas - growing film interactions is reviewed. Sources for residual gas incorporation as well as incorporation mechanisms are described. Furthermore the effect of impurity incorporation on the film structure and film properties are discussed. @FootnoteText@ @footnote 1@ J.M.Schneider et al, Appl.Phys.Lett. 74, 200 (1999). @footnote 2@ J.M.Schneider et al, Appl.Phys.Lett. 75, 3476 (1999).

3:40pm **SE-TuA6 Boron and Boron-Based Coatings as Produced by Vacuum Arc Technology***, **C.C. Klepper**,* HY-Tech Research Corporation*; J.M. Williams,* Oak Ridge National Laboratory*; R.C. Hazelton, E.J. Yadlowsky, E.P. Carlson, M.D. Keitz,* HY-Tech Research Corporation

In principle, boron as a material has many excellent surface properties, including corrosion resistance, very high hardness, refractory properties, and a strong tendency to bond with most substrates. However, the potential technological benefits of the material have not been realizable because of difficulty in synthesis of coatings. Boron is difficult to evaporate, does not sputter well and cannot be thermally sprayed. In the present program, a robust system, based on the vacuum (cathodic) arc technology, for generation and delivery of boron plasmas to substrates has been developed. The system produces a fully-ionized boron plasma, which allows use of substrate bias to control the energetics of deposition. Films and coatings have been produced on 1100 Al, CP-Ti, Ti-6Al-4V, 316 SS, hard chrome plate, 52100 steel and other materials. Analyses have been performed by Rutherford backscattering spectrometry. Properties are being evaluated by nanoindentation hardness and other techniques. First results are that the coatings are smooth, highly adherent, and pore free. A number of applications are contemplated. @FootnoteText@ @footnote 1@ Research sponsored in part by the National Science Foundation under contract # DMI-0078385 with HY-Tech Research Corporation. Research at Oak Ridge National Laboratory is sponsored by the U. S. Department of Energy under contract # DE-AC05-00OR22725 with UT-Battelle, LLC.

4:00pm **SE-TuA7 Ion-bombardment Induced Phase Transformation of Cubic Boron Nitride Studied by Reflection Electron Energy Loss Spectroscopy***, **Y.Y. Hui**, K.W. Wong,* Chinese University of Hong Kong, P.R. China*; W.M. Lau,* Chinese University of Hong Kong, P.R. China, People's Republic of China

The phase transformation of cubic boron nitride (c-BN) in the near surface region of a c-BN (111) facet induced by low energy argon ion bombardment has been investigated by reflection electron energy loss spectroscopy (REELS), with the objective of tracking possible growth mechanisms of c-BN in ion assisted vapor deposition. By removing Tougaard background of the REELS spectra, we can quantitatively measure the percentage of different BN phases on c-BN surface after ion bombardment. In addition, varying the energy of the incident electron beam from 250 eV to 650 eV allowed the adjustment of sampling depth of a c-BN surface from 14 Å to 27 Å. It was found that with an ion energy of 500 eV at a fluence of 5 x 10@super 16@ ions/cm@super 2@, 76 % of c-BN was found transformed to h-BN and a-BN in a top surface layer of 8 Å. Lowering down the argon bombardment energy to 200 eV reduced the defective layer thickness to 5 Å. A damage saturation was observed at a fluence of 6 x 10@super 16@ ions/cm@super 2@, at which about 10% of c-BN was transformed into non-cubic phases. Through further investigations on the damage saturation at other ion energies, the effects of ion beam bombardment on a c-BN surface was comprehensively studied. The present work gives, for the first time, a quantitative explanation of the difficulty in growing pure c-BN films with ion assisted deposition and the presence of an upper-bound in ion energy above which h-BN and a-BN are generated.

4:20pm **SE-TuA8 Cubic Boron Nitride Thin Films Deposited on Steel Substrates With Different Interlayers***, M. Ye, **M.P. Delplancke-Ogletree**,* Universite Libre de Bruxelles, Belgium

Cubic boron nitride thin films were deposited on steel substrates using electron cyclotron resonance plasma enhanced chemical vapor deposition. Different interlayers, such as BCN, TiBN, Ti, TiN, and hexagonal boron nitride, were investigated regarding to the promotion of cubic boron nitride growth and the improvement of the film mechanical properties. A systematic optimization procedure for the cubic boron nitride formation was carried out regarding the deposition conditions, including the gas composition, substrate temperature, bias voltage. The films were characterized using Fourier transform infrared spectroscopy, transmission electron microscopy, x-ray photoelectron spectroscopy, and atomic force microscopy. It was found that among the different interlayers, hexagonal boron nitride gives the best results.

4:40pm **SE-TuA9 Industrial Laser-Arc Coater for the Deposition of Superhard Amorphous Carbon Films (Diamor)***, **T. Schuelke**, H.J. Scheibe, P. Siemroth, B. Schultrich,* Fraunhofer Institute for Materials and Beam Technology

Thin amorphous carbon films (Diamor), deposited through laser-assisted cathodic arc evaporation (LaserArco process), have shown unique properties of great relevance to engineered surfaces for wear and corrosion protection. The high-modulus (> 600 GPa) coatings are superhard

(80GPa) with a low coefficient of friction (0.1 dry against steel). The vast variety of potential applications includes cutting and forming tools as well as components in rolling or sliding contact situations. The LaserArco plasma source and the Diamor deposition process have proven to be consistently reliable on the laboratory scale. Extended application development yielded to an increasing demand for the Diamor coating. Subsequently, the further development aimed at scaling up the technology to industrial dimensions. This development included the design of a flexible and compact plasma source module, which was then integrated into a high volume production coater. The paper discusses the equipment design and capabilities, integration and process transfer issues, and first deposition results obtained in an industrial environment.

5:00pm **SE-TuA10 Deposition of Diamondlike Carbon by Magnetic Pole Enhanced Inductively Coupled Plasma***, T. Meziani, P. Colpo, G. Ceccone, P. Leray, P.N. Gibson, D. Summa,* ***F. Rossi****,* Joint Research Center, Italy*; P. Ranson,* GREMI, CNRS-Universite d'Orleans, France

The ICP sources are particularly interesting for the deposition of amorphous carbon since they offer the possibility to control independently the ion energy from the ion flux bombarding the substrate, in contrast to capacitively coupled discharge. Diamondlike carbon coatings (a-C:H) were deposited with a novel inductively coupled plasma source (the Magnetic Pole Enhanced ICP or MaPE-ICP) designed and characterized in our laboratory. The MaPE-ICP uses a magnetic pole to concentrate the magnetic flux on the load (i.e. plasma) and shows very interesting features like high plasma density, good plasma uniformity and wide pressure range. Diamondlike carbon coatings were deposited with this source from CH4 and C2H2 precursors. The plasma was studied by Langmuir probe measurements, optical emission spectroscopy and microwave interferometry. Mass spectrometry including ion detection and ion energy distribution measurements have been carried out at the substrate holder surface in order to investigate directly the impinging species on the growing film. The plasma diagnostics and films characterization including FTIR spectroscopy, Raman spectroscopy, and X-ray reflectivity (XRR) were undertaken for various processing parameters. The results were related to the coating properties like hardness and intrinsic stress.

Thin Films
Room 123 - Session TF-TuA
Growth and Properties of Thin Films

Moderator: P. Barna, Hungarian Academy of Sciences

2:00pm **TF-TuA1 Mechanical Properties and Stresses in Ion-Assisted Thin Films***,* ***G.S. Was****,* University of Michigan **INVITED**

Understanding the origin of stresses in thin films is critical to the control of film properties. Experiments were conducted to determine the origin of residual stresses in amorphous Al@sub2@O@sub3@ and crystalline Al and Nb films, and to control the stre sses in multilayer structures using ion-assisted deposition. Monolithic films were deposited during bombardment by Ne, Ar or Kr ions over a narrow range of energies, E, and a wide range of ion-to-atom arrival rate ratio, R. Films were characterized in terms of composition, thickness, density, crystallinity, microstructure, hardness and residual stress. Stress varied strongly with ion beam parameters, and with the resulting gas content. Residual stress and gas content saturated at a normalized energy of ~20 eV/atom or an R of ~0.05. Where residual stress varied linearly with RE@super1/2@, results are consistent with an atom peening model, but saturation at high R or RE@super1/2@ is inconsistent with such a model. The various mechanisms for residual stress control in monolithic amorphous and crystalline solids and the application of residual stress control to multilayered structures will be discussed. In Nb and Al films, the mechanisms for controlling crystallographic texture and the application of texture control for improved film properties are also presented. In both systems, texture developed slowly, but produced remarkable effects on plastic flow in the film. Specifically, examples will focus on crystallographic texture control in order to control the strength of the film/substrate interface and susceptibility to plastic flow in the film.

2:40pm **TF-TuA3 Growth of Highly-Oriented CeO@sub 2@ Layers on Glass Substrates for High-Quality Poly-Si Overlayer Formation***,* ***N. Sakamoto****, T. Inoue, T. Suzuki, S. Shida,* Iwaki Meisei University, Japan*; K. Kato,* Fukushima Technology Centre, Japan

In order to realize high-performance thin-film transistors, tremendous efforts have been made for growth of high quality polycrystalline Si (poly-Si) films on glass substrates. CeO@sub 2@ films on glass substrates have a potential advantage in attaining high-quality poly-Si overlayers without supplementary crystallization processes such as solid phase crystallization, excimer laser annealing and metal induced lateral crystallization. Systematic experiments varying growth temperature (room temperature 750°C) reveal that orientation controlled CeO@sub 2@ layers can be obtained. CeO@sub 2@ layers with strong (111)-tendency grow in low temperature region, whereas those with (100)-orientation grow at higher temperatures. Comparing conventional evaporation and electron-beam-assisted evaporation,@footnote 1@ the latter gives grain size enlargement and crystallization enhancement. For the films grown by electron-beam-assisted evaporation, the grain size estimated from the full width at half maximum of XRD peaks is 1.1-1.4 times larger than those grown by conventional evaporation. It is verified that poly-Si films with strong (111)-orientation are successfully formed on CeO@sub 2@/glass structures grown at room temperature. @FootnoteText@ @footnote 1@ T. Inoue, Y. Yamamoto, and M. Satoh, J. Vac. Sci. Technol. A, Vol. 19, Jan/Feb (2001) 275.

3:20pm **TF-TuA5 Thin Film Growth of Reactive Sputter Deposited Tungsten-Carbon Thin Films***, P.D. Rack,* Rochester Institute of Technology*;* ***J.J. Peterson****, J. Li,* Advanced Vision Technologies*; H.J. Rack, A.C. Geiculescu,* Clemson University

Tungsten-carbon thin films have been reactively sputter deposited in various Ar-CH gas mixtures and the growth kinetics of the reactive deposition process have been elucidated. X-ray diffraction data reveal that the films are amorphous as-deposited with partial crystallization of W2C and WC occurring following a 1100oC-1 minute rapid thermal anneal. Peak shape analysis of the W and C x-ray photoelectron peaks show binding energy shifts consistent with carbide formation for the annealed films. Carbon incorporation within the W-C films is attributed to flux of CH3 radicals impinging on the growth surface. Although the CH3 radicals have a significantly lower concentration (~0.1%) than the CH4 molecules contained within the plasma, the sticking coefficient of CH3 is significantly larger than that of CH4. In addition, the change in the incorporation rate of carbon in the W-C films at higher CH4 (and subsequently CH3) concentrations has been shown to be due to the changes in the growth surface; as the CH3 flux increases, the growth surface becomes carbon terminated decreases the incorporation of carbon because of the low CH3-C sticking coefficient. This presentation will demonstrate the experimental procedure used in growing the W-C thin films. Compositional analysis as a function of the CH4 concentration will be presented and the growth process will be shown to follow Langmuir-type growth.

3:40pm **TF-TuA6 Reactive Sputter Deposition of Tungsten Nitride Thin Films***,* ***C. Baker****, S.I. Shah,* University of Delaware

Tungsten nitride (WN@sub x@) thin films were deposited by reactive sputtering in an Ar/N@sub 2@ atmosphere. The partial pressure of nitrogen in the sputtering gas was varied from 2-50% and the effect of the N@sub 2@ concentration variation on the film properties was investigated. Through examination of cathode current and voltage during the film growth, it is determined that cathode poisoning occurs when the nitrogen concentration in the chamber is increased above 2-5%. This poisoning reduces the film growth rate. Films were characterized by X-ray Photoelectron Spectroscopy. XPS analyses show that the films are composed of ~30% nitrogen when the nitrogen concentration in the chamber is greater than 10%. X-ray diffraction analyses confirm that the predominant phase in the reactively sputtered films is W@sub 2@N, with the characteristic (111) peak found near 2@theta@=37.7Â°. Slight shifts in this peak position are thought to be the result of nitrogen incorporation in interstitial positions, thus distorting the lattice. A post-deposition anneal was carried out which shifted the peak back to its characteristic position confirming that the extra nitrogen was indeed accommodated as interstitial.

4:00pm **TF-TuA7 The Impact of Residual By-Products from Tungsten Film Deposition on Process Integration due to Non-Uniformity of the Tungsten Film***,* ***A. Sidhwa****,* STMicroelectronics, Inc. and University of Arkansas*; C. Spinner, T. Gandy, S. Melosky,* STMicroelectronics, Inc.*; W. Brown, S. Ang, H. Naseem, R. Ulrich,* University of Arkansas

The effects of residual by-products from a tungsten film deposition process and their impact on process integration due to the non-uniformity of the tungsten film were investigated in this work. The tungsten film deposition process involves three steps: nucleation, stabilization, and tungsten bulk fill. Six experiments were conducted in search for a solution to the problem. The resulting data suggest that excess nitrogen left in the chamber following the tungsten nucleation step, along with residual by-products, causes a shift in the tungsten film uniformity during the tungsten bulk fill process. Data reveal that, due to the residual by-products, an abnormal grain growth occurs causing a variation in the tungsten thickness across the wafer during the bulk fill step. Although several possible solutions were revealed by the experiments, potential integration problems limited the acceptable solutions to one. The solution chosen was the introduction of a 10 second pumpdown immediately following the nucleation step. This choice did not create any integration problems as confirmed by subsequent studies.

4:20pm **TF-TuA8 Thermal Stability of Arc Evaporated Ti@sub 1-x@Al@sub x@N Thin Films***, **A. Hörling**, L. Hultman, M. Odén,* Linköping University, Sweden*; G. Ramanath,* Rensselaer Polytechnic Institute*; P.H. Mayrhofer, C. Mitterer,* University of Leoben, Austria*; J. Sjölén, L. Karlsson,* Seco Tools, Sweden

The thermal stability of Ti@sub 1-x@Al@sub x@N thin films deposited by arc evaporation from cathodes with nominal composition x=0.67 onto substrates kept at 500°C has been investigated by XRD and TEM, and by differential scanning calorimetry (DSC) and 4-point probe measurements. As-deposited films contained 62 at.% Al and were of cubic [NaCl]-structure phase. Annealing of such metastable films results in relaxation of intrinsic compressive stress, together with spinodal decomposition into cubic TiN and AlN-rich phases succeeded by the precipitation of hexagonal AlN. Stress relaxation was observed to take place for all annealing temperatures above the deposition temperature, which implies that point defects or defect complexes become annihilated. For example, DSC showed enthalpy changes at temperatures up to 700°C, and XRD showed a decrease in peak broadening at temperatures up to 800°C. By XRD, the spinodal decomposition stage was revealed as a symmetrical broadening of the cubic (Ti,Al)N (200) peak after annealing at 900°C; by DSC as an exothermic peak starting at 850°C for a heating rate of 27°C min@super -1@; and by 4-point probe measurements as an increased sheet resistance at 500°C with a maximum at 650°C for a heating rate of 5°C min@super -1@. At higher temperatures, the resistivity decreased, and upon cooling and re-annealing showed a reversible behaviour which indicates a parallel-circuit behaviour of a more TiN-like matrix together with emerging AlN phases. Following spinodal decomposition, phase separation of the structure into c-TiN and h-AlN occurred in the temperature range of 900°C-1100°C, being observed by XRD and TEM. The 4-point probe measurements, especially when compared to XRD, indicate that the heating rate has a large effect on the kinetics of phase separation. This observation will be discussed, together with results of activation energies for the various reactions.

4:40pm **TF-TuA9 Evolution of Ti-3Al Film Structures and its Effect on Film Properties***, **C.-F. Lo**, D. Draper, P. McDonald, P. Gilman,* Praxair-MRC

The evolution of Ti-Alx film structure deposited from the Ti-75at%Al (Ti-3Al) sputter targets was investigated. 300nm, 900nm and 9000nm thick films were deposited on three inch diameter silicon wafers at various wafer temperatures from 20°C to 400°C. The films were evaluated for composition, microstructure, crystallinity, hardness and elastic modulus using the FE-SEM, XRD and nano-indentation instrument. In order to understand the effect of the target structure on film properties, the target manufacturing process for the Ti-75 at%Al (Ti-3Al) alloy system was controlled to prepared two four inch diameter targets, one metallic (Ti+3Al) and one intermetallic (TiAl@sub 3@) structures. No effect of target structure and sputtering conditions on the composition of the deposited films was observed. The film compositions were similar to that of the sputtered targets. At a film thickness 300nm and less, the grains showed an equiaxial shape with size about 40nm. The columnar grains generated and grew with increasing of film thickness. The diameter of the columnar grains increased with increasing of film thickness. The target structure showed some effect on the morphology but not on the diameter of columnar grains. XRD analysis showed that TiAl was the major phase existing in all the tested films. The hardness and elastic modulus measurements showed that the mechanical properties of the deposited films were effected by the film microstructure.

5:00pm **TF-TuA10 Surface Structural Anisotropy in Sputter and Electrolytic Deposited Tantalum Films***, **S.L. Lee**,* US Army Armament Research Development and Engineering Center*; D. Windover,* Rensselaer Polytechnic Institute

We studied the growth surface texture of tantalum films generated by sputter and electrolytic deposition processes for high temperature and pressure wear and erosion applications, using conventional and image plate XRD. Electrochemically deposited bcc tantalum coating in eutectic molten salt solution at 800°C on 20mm-diameter 4340 steel cylinder revealed near random grain orientation. Triode sputtered tantalum deposition on steel generally showed weak anisotropy. Example specimens deposited in krypton gas at 200°C-250°C revealed (110) and (211) texture with poles. Planar magnetron sputtered tantalum film on a steel plate with a thin electrolytic chromium interface layer produced bcc tantalum film with (111) fiber texture, following the (111) fiber texture in chromium. Planar magnetron sputter-deposited 200nm film on a (100) silicon wafer, mixed bcc and tetragonal tantalum and (110) fiber texture with azimuth symmetry evolved. Random oriented grain distribution suggests uniform thermal-mechanical properties in polycrystalline solids. Model calculations of Young's modulus and Poisson's ratio for isotropic tantalum crystalline aggregates were made. Evaluation of directional modulus, e.g., E110, E100, E111, from single crystal elastic constants, suggested higher elastic modulus in the out-of-plane direction for (111) fiber-textured films.

Thin Films
Room 134/135 - Session TF-TuP
Microstructure, Oxides, and Optical Properties Poster Session

TF-TuP1 MEVVA Ion-implanted Cr Interlayer on the Microstructure of CrN on Steel*, S. Han,* National Taichung Institute of Technology, R.O.C.*; J.-H. Lin,* National Tsing Hua University, Taiwan, ROC*; Z.C. Chang,* National Chin-Yi Institute of Technology, R.O.C.*; C.J. Yang, F.-S. Shieu,* National Chung Hsing University, R.O.C.*;* ***H.C. Shih,*** National Tsing Hua University, R.O.C., TAIWAN

The effect of MEVVA ion-implantation of Cr on the microstructure and properties of CrN coatings on the steel were investigated in this paper. Two types of CrN-coated specimens (CrN/steel and CrN/Cr/steel) by cathodic arc plasmas deposition were prepared with and without an interlayer deposited by MEVVA ion-implantation of Cr. And the microstructure and microchemistry of chromium nitride has been investigated by using X-ray diffraction (XRD), cross-sectional transmission electron microscopy (XTEM) and selected area diffraction (SAD). Therefore, the coatings exhibit a microcolumnar morphology. The outermost layer of the coating is identifed as CrN. Furthermore, from an estimation of the unrelaxed thermal stresses based on a bilayer model, it is demonstrated that the presence of a Cr interlayer between CrN and steel can dramatically reduced the thermal stress in the CrN coating.

TF-TuP2 Growth of Wide Band Gap MnS Thin Films by rf Sputtering: Substrate Temperature Effects on Structure and Composition*, S.A. Mayen-Hernandez, R. Perez-Castanedo,* ***O. Jiménez-Sandoval****, G. Torres-Delgado, S. Jiménez-Sandoval,* Cinvestav-IPN, Mexico

Manganese sulfide (MnS) is a wide band gap semiconductor that crystallizes in its stable form with the octahedrally coordinated rocksalt structure, presenting as well other metastable structures: cubic(zincblend) and hexagonal (wurtzite). One of the problems that have precluded the application of this semiconductor in devices, has been the little work carried out so far to grow high quality MnS films. To date, most of the work done on MnS has been using chemical bath and thermal evaporation as preparation thecniques. These two methods yielded amorphous and polycrystalline films, respectively. To our knowledge, no report exists so far on the growth of MnS films by rf sputtering due to the technical difficulties involved. In this work we report on the appropriate conditions for the growth of nearly stoichiometric MnS thin films prepared by rf sputtering and the important effects of substrate temperature on film composition and structure. The produced films were polycrystalline with an energy band gap of around 3.47 eV, a value that makes MnS an appealing material for optical windows in applications such as solar cells.

TF-TuP3 Structural Investigations for Amorphous Films Deposited by Simultaneous DC Sputtering of ZnO and In@sub 2@O@sub 3@ Targets*, T. Moriga,* ***A. Fukushima****, K. Tominaga, I. Nakabayashi,* The University of Tokushima, Japan

Oxide films in the ZnO-In@sub 2@O@sub 3@ system were deposited by simultaneous dc sputtering of ZnO and In@sub 2@O@sub 3@ facing targets at the substrate temperature of 150°C. The ratio @delta@ of the ZnO target current to the sum of both the currents was varied. In the @delta@ range from about 0.20 up to 0.67, an amorphous film with one broad diffraction peak at around 2@theta@=33° could be deposited. At the higher substrate temperature of 300°C, the crystallized films with the homologous Zn@sub k@In@sub 2@O@sub k+3@ structure (k=2 for @delta@=0.50, k=3 for @delta@=0.57, and k=5 for @delta@=0.67) were deposited in the range from 0.50 to 0.67, and the bixbyite-type In@sub 2@O@sub 3@ phase was observed in the @delta@ range of 0=<@delta@<0.50. We analyzed the peak position of the amorphous films. For example, we took the amorphous film with @delta@=0.50. The broad peak lies in the center of two peaks. One was the (008) peak which appears strongly in the homologous Zn@sub 2@In@sub 2@O@sub 5@ films. The other was the (104) peak which appears strongly in the bulk Zn@sub 2@In@sub 2@O@sub 5@. The amorphous film with @delta@=0.50 had the atomic ratio of Zn:In=1:1. These facts imply that the amorphous film with @delta@=0.50 would be comprised of NOT-ordered Zn@sub 2@In@sub 2@O@sub 5@ matrix. We will discuss a possibility of existence of ZnIn@sub 2@O@sub 4@ (k=1 in Zn@sub k@In@sub 2@O@sub k+3@), by applying this kind of concept to an amorphous films with @delta@=0.33. The @delta@-value dependence of electrical properties (resistivity, carrier concentration and Hall mobility) suggest the existence of ZnIn@sub 2@O@sub 4@.

TF-TuP5 Micro-crystallites in Mo/Si Multilayer EUV Coatings*,* ***E. Louis****, I.J. Wever, A.E. Yakshin, F. Bijkerk,* FOM-Rijnhuizen, The Netherlands*; J. Verhoeven,* FOM-Amolf, The Netherlands*; E. Ziegler,* European Synchrotron Radiation Facility, France

The reflectivity of 13.5 nm radiation by a Mo/Si multilayer system (periodicity 6.7 nm) depends strongly on the interface roughness and the thickness of the interfacial molybdenum-silicide layers. Ideally, the structure of the constituent layers of these Mo/Si coatings is amorphous. In this work we show results of X-ray diffraction experiments that clearly show the presence of small crystallites in the Mo layers, and, depending on the process parameters during the deposition of the layers, in the molybdenum-silicide interlayers. By varying the incident angle and the energy, we were able to observe a preferential orientation of the crystallites. The crystal orientation was found to depend on the various process conditions during the deposition of the layers and ion beam smoothening of the interfaces. We also observed indications of stress in the Mo-crystallites. The results were obtained using Cu-K radiation in an in-house diffractometer (Philips MRD) as well as 16 keV photons at beam line BM5 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

TF-TuP6 Fabrication of Perforated Thin Films with Helical and Chevron Pore Shapes*,* ***K.D. Harris****, M.J. Brett,* University of Alberta, Canada

We will present a simple method for the fabrication of thin films or membranes perforated by helical and chevron shaped pores. Using the glancing angle deposition (GLAD) evaporation technique highly porous (40-50% of bulk density) SiO@sub 2@ thin films of helical and chevron microstructure were deposited on Si substrates. Typical thin films have thicknesses on the order of 2µm and are composed of 1 to 20 turns. The thin films produced by this technique were filled with photoresist and, subsequently, etched to remove the helices, leaving a continuous photoresist cast of the original film. It has been found possible to produce these perforated photoresist films from microstructures distributed either randomly over the substrate, or from structures grown on well defined, periodic arrays of micrometer or sub-micrometer spacings. The perforations have been produced in both chevron and helical shapes, and both photoresist and spin-on-glasses have been successfully used to fill the template. In addition, it has been found possible to electroplate back up through the perforated thin film, reproducing the structure of the original template with an alternate material. The fabrication processes will be discussed along with the results of optical and magnetic characterization of the films.

TF-TuP7 Influence of the Deposition Conditions on the Growth and Structure of Fe Films on Cu(001)*,* ***S.K. Clowes****, L.V. Goncharova, B.J. Hinch,* Rutgers University

We have undertaken an in-depth study into the growth and structure of Fe/Cu(001) films using helium atom scattering, AES and SPA-LEED. This is a system which has been extensively studied during the last two decades, but which has produced a number of contradictory conclusions for the growth mode of the Fe films. This study has paid particular attention to the effects that the specific conditions during deposition have on the growth and quality of the films. These include the rate-of-deposition, surface defects, substrate temperature and contaminants such as oxygen. It is known that oxygen allows the formation of a single, well ordered, monolayer by reducing the surface free energy when it is adsorbed in the fcc hollow site. In a similar manner, it is suggested that under certain conditions oxygen can behave as a surfactant during the deposition of thicker films, promoting layer-by-layer/bilayer growth.

TF-TuP8 Engineering of Porous Thin Films by Modification of Substrate Topography*,* ***B. Dick****, D. Vick,* University of Alberta, Canada*; T. Smy,* Carleton University, Canada*; M.J. Brett,* University of Alberta, Canada

A unique class of evaporated porous thin films has been developed using the technique of glancing angle deposition (GLAD). High porosity in the films is achieved by in situ control of the substrate orientation during deposition. At sub-micron scale lengths, the structure of the films consists of a "forest" of isolated columns that can be engineered into a variety of shapes. For certain envisioned applications, a regular arrangement of uniformly shaped columns may be desirable. Previous work suggests that these requirements may be difficult to achieve on planar substrates due to the column competition, extinction and thickening that occurs during growth of the film. These related phenomena arise from the fact that the advancement of the film - vacuum interface is an inherently non-linear process in which the self-shadowing mechanism plays a predominant role. We are currently investigating the degree to which order may be imposed on the film growth by means pre-patterned substrate topography. Using lithographic and embossing techniques, substrates with patterned seed arrays have been created, onto which GLAD films are then deposited. The elevated seeds serve as nucleation sites for the columns by exploiting the self-shadowing mechanism. After deposition, the films can be analyzed using atomic force and scanning electron imaging, with the dual aim of determining scaling behaviour and identifying appropriate choices of substrate and deposition parameters to produce stable column growth. Results from an experimental study supplemented by 3D-FILMS ballistic simulations will be presented. Recent examples of metal and oxide films deposited by electron beam evaporation and sputtering onto patterned and planar topography will be shown, together with a summary of our present understanding of the growth behaviour of GLAD films.

TF-TuP9 Composite Tantalum Nitride-Silicon Nitride Thin Films for 193nm Embedded Attenuated Phase Shift Masks*, **M.G. Lassiter**, M. Cangemi,* Photronics Corporation*; P.D. Rack, B.W. Smith,* Rochester Institute of Technology

As semiconductor device dimensions continually decrease in size, the ability to print these dimensions using 248nm light from a KrF excimer laser is becoming increasingly more difficult. According to Lord Rayleigh's resolution criteria the minimum resolution on the wafer is proportional the exposure wavelength divided by the numerical aperture of the objective lens. Thus resolution can be improved by using smaller wavelengths, which has brought about the development of exposure systems that use the 193nm ArF excimer laser. The use of a new exposure wavelength requires the development of new materials for the photomasks used in such an imaging system. Image contrast has been significantly improved in the past due to the use of embedded attenuated phase shift masks (EAPSM). An EAPSM induces a 180-degree phase shift and limited transmission in the regions that are traditionally opaque in a binary mask. The result is a phase induced contrast enhancement at image edges at the expense of higher background intensity compared to a binary mask. New materials are needed to construct such a mask for 193nm wavelength. This paper explores the use of a composite TaN-Si3N4 for the purpose of providing both the radiation attenuation and the relative phase shift on an EAPSM for use at 193nm wavelength. The TaN and Si3N4 were each reactively rf sputter deposited and their respective optical constant spectra were determined using a Woollam VUV-Variable Angle Spectroscopic Ellipsometer. An effective media approximation (EMA) was used to combine the constituents to tune the optical properties to the desired values for an EAPSM film. Finally, a matrix of composite thin films of varying the TaN-Si3N4 composition were co-deposited and the optical constants of the composites were determined using the ellipsometer to verify the EMA. The composition was iteratively tuned to provide the optimum optical constants at 193nm for a 20% transmission EAPSM.

TF-TuP10 Electrical, Optical and Structural Properties of Sol-gel Deposited Tantalum Oxide Thin Films*, **M.J. Alam**, D.C. Cameron,* Dublin City University, Ireland*; M.S.J. Hashmi,* Dublin City University

Because of its wide field of applications in semiconductor sciences, tantalum oxide (Ta@sub2@O@sub5@) has been extensively studied both experimentally and theoretically over the past three decades. Tantalum oxide films are of considerable interest in optical and optoelectronic technology. Tantalum oxide film is a promising candidate as a capacitor dielectric in high-density dynamic random-access memories (DRAMs) and in ultra-large-scale integrated devices (ULSI) due to its high dielectric constant (about 25) compared with that of only 3.9 for SiO@sub2@. @paragraph@ To date, tantalum oxide films have been deposited using a variety of deposition techniques, such as, thermal oxidation, electron beam evaporation, reactive evaporation, reactive sputtering, pulsed laser deposition and chemical vapor deposition, as well as the sol-gel method. Recently, the preparation of tantalum oxide films by a sol-gel process has received increased attention. This technique has many advantages, such as low temperature processing, simple and compact equipment, deposition on a substrate of large area and a complex structure and high homogeneity of the deposited films. @paragraph@ Thin homogeneous tantalum oxide films have been prepared on silicon and glass substrates using a sol-gel process. The coating solutions were prepared using Ta(OC@sub2@H@sub5@)@sub5@ as a precursor. X-ray diffraction studies determined that the sol-gel films, annealed at temperatures below 400°C were amorphous. Films annealed at higher temperatures were crystalline with the hexagonal structure. X-ray photoelectron spectroscopy was employed to examine the elemental content during the process. Ellipsometry, Fourier transform infrared spectroscopy, capacitance-voltage and current-voltage measurements were also employed to characterize the tantalum oxide films annealed at different temperature in different atmospheres.

TF-TuP11 Infrared Emission from Electroluminescent Thin Film ZnS Doped with Rare Earth Fluorides*, **W. Glass**, A.S. Kale, R. Owing, M.R. Davidson, P.H. Holloway,* University of Florida

Alternating current thin film electroluminescent devices (ACTFELDs) are well-known thin film structures used for flat panel displays. A well-known phosphor for such displays is ZnS doped with either transition or rare earth elements. For example, ZnS:TmF@sub 3@ emits blue light, ZnS:NdF@sub 3@ emits orange, ZnS:DyF@sub 3@ emits yellow, and ZnS:ErF@sub 3@ emits green. Each of these materials also emits in the infrared. The infrared emission from these types of materials is often overlooked except in the case of ErF@sub 3@, which has been of interest for fiber optic communications. The infrared intensity of these materials is dependent on the environment of the luminescent centers and can be improved by modification of deposition and processing. In this study, rare earth fluoride doped ZnS films were deposited by RF planar magnetron sputter deposition or thermal evaporation. Deposition temperature and annealing conditions are varied to determine temperature effects during and after deposition. In addition, the rare earth concentration was changed from a maximum of 1.6 mol% to zero by simultaneously sputtering an undoped ZnS target. The devices were then excited by electroluminescence to determine the effects of the deposition variations. These sputtered devices will be compared to those deposited by evaporation. Finally, emission from materials with similar and dissimilar luminescent decay paths will be discussed.

TF-TuP12 Aluminum Flakes with Enhanced Spectral Properties*, **K.E. Coulter**, R.W. Phillips,* Flex Products, Inc.*; T. Mayer,* Optical Coating Laboratory, Inc.*; R.A. Bradley, J.S. Matteucci,* Flex Products, Inc.

A vacuum deposited multi-layer rigid and brittle bright metal flake has been developed that provides favorable planar specular reflective characteristics in the visible wavelength range and application and durability advantages. Two constructs of the 300nm thick by 15micron in diameter brittle flakes have been demonstrated. One design has a central layer of reflective material supported on both sides by dielectric layers at a thickness of 10-100nm. The addition of the dielectric layers theoretically reduces the specular reflectance of the aluminum surface but the addition a dielectric for support increases reflectance 5-10% in the flake form. The second design utilizes the same materials and dimensions but has the dielectric as the central layer with the reflective material on each side. The result for both designs is a sub-micron thick three-layered metal flake that exhibits a uniaxial compressive strength of approximately 8 times a corresponding uniaxial tensile strength. As a result, the metal flake is then afforded the benefits of rigidity and brittle fracture during manufacturing and application processing. In this talk, a review of design, vacuum deposition processes for manufacture, characterization and use of the flakes in applications will be discussed.

TF-TuP13 The Effect of Annealing upon IR Electroluminescent Emission For Zinc Sulphide: Rare Earth Doped Thin Films*, **A.S. Kale**, W. Glass, R. Owings, M.R. Davidson, P.H. Holloway,* University of Florida

Infrared emitters (IR) enjoy a wide market today with a variety of applications ranging from commercial based fiber optic communication devices to remote controls for televisions. ZnS doped rare earth fluoride thin films typically 1µm thick have been fabricated by RF sputter deposition in the conventional metal-insulator-semiconductor-insulator-metal configuration to study a new structure for IR radiation. The current study investigates three different kinds of phosphors namely ZnS:TmF@sub3@, ZnS:NdF@sub3@ and ZnS:ErF@sub3@ for their IR versus visible emission. Electroluminescence has been investigated after different annealing conditions (as-deposited to 650°C) and time (5-60min), to study the effect on emission properties. As annealing improves the crystallinity of the film, the emission improves. The brightness versus concentration of dopant has been measured and optimized. Emission spectra of the devices have been measured from 0.35 to 1.5µm and the films studied for their emission efficiency and decay time. Methods of enhancing the IR output with respect to the visible have also been studied and reported, including codoping and condition of annealing.

TF-TuP14 Fabrication and Optical Properties of SiO@sub 2@ Sol-gel Made Thin Films Modified with Carminic Acid*, L.L. Diaz-Flores,* Instituto Tecnolodico de Saltillo, Mexico*; G. Luna-Barcenas, J. Gonzalez-Hernandez,* ***Yu.V. Vorobiev,*** Unidad Queretaro del CINVESTAV-IPN, Mexico

SiO@sub 2@ sol-gel colored films on the glass slides were prepared by traditional process, using the precursor solution made of water, TEOS and ethanol, with the ratio of the components providing good structural quality of the films, and using the dip-coating apparatus. The carminic acid was introduced in the solution; special mechanical treatment of the solution was made to ensure good dispersion of the colorant. The films with intense and stable red color were obtained. The optical absorption spectra of the films contain all three visible absorption bands mentioned in the literature (494, 520 and 555 nm) as well as the UV band at 330 nm not reported earlier. The quantum mechanical description of energy spectrum of the system was attempted based on the modified FEMO approach, treating the carminic acid molecules as three-dimensional quantum wells and using the Born-von Carman boundary conditions corresponding to the mirror reflection of an electron delocalized inside the molecule, from its walls. Good agreement between the theory and experiment was obtained without any adjustable parameters.

TF-TuP15 Inhomogeneous Optical Thin Films and Filters Based on SiN@sub x@:H Prepared by PECVD in Dual-mode Microwave/Radiofrequency Plasma*,* ***R. Vernhes****, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique of Montreal, Canada

Deposition of inhomogeneous thin films for optical applications offers great advantages in comparison to traditional multilayer structures. Particularly, optical losses and mechanical stresses due to interfaces are considerably reduced, as well as harmonics and side lobes are eliminated from transmission or reflection spectra. In the present work, we used plasma-enhanced chemical vapor deposition (PECVD) to grow amorphous hydrogenated silicon nitride (SiN@sub x@:H) films on glass and silicon substrates using silane and nitrogen. Control of the refractive index was performed by selectively varying the power of microwave and radiofrequency sources without any change in gas composition. In this way, the film properties are strictly controlled by the energetic interactions in the gas phase and at the exposed surface. The films were characterized by spectrophotometry, variable angle spectroscopic ellipsometry, Fourrier transform infrared spectroscopy, and elastic recoil detection in time-of-flight regime. We found that the radiofrequency mode permits one to obtain a higher refractive index, while the microwave mode leads to a lower refractive index. We demonstrated that this variation was related to a change in composition and density. Indeed, films deposited by radiofrequency mode contain larger quantities of Si-H groups and show a denser microstructure while films grown by microwave mode present a higher concentration of N-H groups with a porous microstructure. We proved that it is possible to pass continuously from one composition and structure to another by gradually adjusting the power of each source. This leads to a continuous variation of refractive index from 1.65 to 1.95. Using this refractive index interval, we demonstrate the fabrication of optical filters with an inhomogeneous refractive index depth profile. Optical and mechanical properties of such filters are discussed.

TF-TuP17 Deposition of Transparent Conductive TiN Oxide Thin Films Doped with Fluorine by PACVD*, F. Arefi-Khonsari,* ENCSP-University of P.M. Curie, France*;* ***N. Bauduin****, J. Amouroux,* ENSCP-University of P.M. Curie, France

The conductivity of plasma deposited tin oxide films from a mixture of O@sub2@/Ar/Tetramethyltin (TMT) can be enhanced from 0.01 to 100 @ohm@@super@ -1.cm-1 by biasing the substrate by means of a second generator. In this work an attempt has been made to dope the films by a one step process by introducing a fluorine precursor which was SF6 with the plasma mixture used for the deposition of tin oxide films. Optical emission spectroscopy and mass spectrometry were used to study the plasma phase and the characterization of the films was carried out by different surface diagnostic techniques such as SEM, XPS and FTIR. A two fold increase of the electrical conductivity was obtained for very small flow rates of SF6 introduced in the discharge.For higher flow rates, a sharp decrease of the conductivity was obtained. For high flow rates of SF6, competitive etching and functionalization processes assisted by fluorine atoms present in the discharge took place. Although the conductivity dropped down, the optical transmission of the deposited films remained higher than 90%.Moreover, the morphology of the films was modified by the presence of SF6 with an increase of the grain size and the appearance of clusters on the surface of the films.

TF-TuP18 Development of a New Luminescence Spectrum from ZnS:Mn Films*, T. Hirate, N. Orihara,* ***T. Satoh****,* Kanagawa University, Japan

ZnS Films with a new electroluminescence and photoluminescence spectrum were prepared by the modified chemical vapor deposition method developed by us. The deposition method is a low pressure thermal CVD system basically concerning the synthesis of ZnS matrix except that the metal Mn target is set in the deposition chamber. The two main precursors used to synthesize the ZnS are the metal Zn vapor and H2S. The pulsed Nd:YAG laser beam (wavelength =1.064µm) was used to ablate the Mn target and to dope Mn into the growing ZnS film. The crystal structure of the deposited ZnS:Mn films was analyzed by XRD and the composition was analyzed by EDX and by XPS. The crystallinity of the films was generally poor and it was proven that the deposited ZnS:Mn films consisted only of Zn, S and Mn within the limits of detection by the EDX and XPS analysis. The electroluminescence (EL) spectrum of the ZnS:Mn films hitherto reported has a peak at about 5850Å and the photoluminescence (PL) spectrum has also the main peak at the same wavelength. On the other hand, the EL spectrum of this study has a new peak at 6700Å other than the peak at 5850Å, and the PL spectrum has a strong and wide peak at 7000Å and the intensity at 5850Å is very weak. It was experimentally confirmed that the appearance of these spectra is not due to the concentration of Mn and not due to the interference. We discovered these new spectra and the discrepancy between EL and PL spectrum for the first time. We consider that these may be due to any excited state of Mn generated by the high laser energy density, and that this deposition method has a high probability of development of a new spectrum.

TF-TuP19 Growing Behavior and Luminous Characteristics of ZnGa@sub 2@O@sub 4@ Thin Film Affected by the Substrates and Heat Treatment*, Y.J. Kim,* ***S.M. Jeong****,* Kyonggi University, Korea*; Y.E. Lee,* ETRI, Korea

ZnGa@sub 2@O@sub 4@:Mn phosphor powder has been well known for the green luminescence for flat panel displays because of its good chemical stability and excellent luminescent properties. However, thin film type ZnGa@sub 2@O@sub 4@:Mn has a limitation in a practical application due to its low luminous properties. In this work, the dependence of growth behaviors and luminous properties on the various substrates and heat treatment were examined. Amorphous, polycrystalline, and highly preferred oriented ZnO thin films were prepared by rf magnetron sputtering method on ITO coated glass substrates to investigate the effects of substrates. Thin film phosphors were deposited on these various substrates, and the structural, luminescent, and optical properties were characterized. It will be emphasized that the structural and luminescent properties of ZnGa@sub 2@O@sub 4@:Mn thin-film phosphors are significantly influenced by the crystallinity of the ZnO layers. On (002) highly oriented ZnO thin film, well developed crystalline ZnGa@sub 2@O@sub 4@thin film could be obtained and showed high luminescent intensity as well. Structural relations between wurzite ZnO film and spinel ZnGa@sub 2@O@sub 4@ film were also investigated to determine the growth mechanism of ZnGa@sub 2@O@sub 4@films. By heat treatment, luminous properties were improved and depended on annealing conditions such as temperature and atmosphere. Defects in as-deposited films which deteriorated the luminous properties could be annihilated by defect transportation and solid state reaction during annealing process.

TF-TuP20 Optical Absorption in the Visible and Near Infrared Range of Electron-beam Deposited Metal-dielectric Structures*,* ***F. Sabary****, A. de Winne, P. Hamel,* CEA Le Ripault, France

Metal-dielectric structures were deposited by electron beam evaporation. They consist in a silver island film separated from a smooth silver surface by a dielectric material. These structures exhibit strong optical absorptions in the visible range. The spectral position and the amplitude of these absorptions can be modified by changing the mass thickness of the silver island film, the thickness of the dielectric layer and by performing a post-deposition annealing. With appropriate experimental parameters, quasi-total extinction can be obtained. More complex structures have been fabricated by sequential deposition of silver island films and dielectric layers. These structures exhibit a large band absorption in the visible and near infrared range. A theoretical calculation was carried out, based on an effective medium model taking into account the interactions between the silver islands and the metallic substrate.

Electronics
Room 124 - Session EL-WeM

Si Surface Dynamics and Reactions

Moderator: J.E. Rowe, Army Research Office

8:20am **EL-WeM1 Step Motion and Morphology on Si(111)***, **M.S. Altman,*** Hong Kong University of Science and Technology, Hong Kong **INVITED**

Surface steps are of interest for their role as templates for growth. Step morphology determined by thermodynamics can be influenced through step motion kinetics. Low energy electron microscopy observations of step flow, island nucleation and growth, and spiral growth at screw dislocations are the basis for studying step motion kinetics and the influence of surfactants upon growth. Sb and In surfactants are found to have notable and opposite influence on step kinetics. These results demonstrate that surfactants can be used to controlkinetically driven morphological instabilities, i.e., bunching and meandering, in step flow motion, and support the view that surfactants function at least partially through step passivation. However, surface phase separation is also observed as a consequence of surfactant incorporation during growth, which leads to a distinct step flow instability. Self-organized periodic step bunching patterns on vicinal surfaces will also be discussed.

9:00am **EL-WeM3 Step Fluctuations on a Chemically Heterogeneous Surface: Al/Si(111)-(@sr@3x@sr@3)@footnote 1@***, **I. Lyubinetsky**, D.B. Dougherty, E.D. Williams,* University of Maryland at College Park

Analysis of equilibrium step fluctuations has been extended for an adsorbate-induced reconstruction. The lateral and temporal correlations of single-height step fluctuations has been studied with variable temperature STM at 550-750° C on a vicinal Si(111) surface, miscut by 0.5° in the [2,-1,-1] direction, after formation of the Al-induced (@sr@3x@sr@3) surface phase. From direct measurement of the spatial step-correlation function, the step diffusivity, b@super 2@/a, is found to exponentially increase from 0.7 Å at 550°C to 1.19 Å at 750°C. The effective kink creation energy of 0.14 eV then has been extracted from corresponding Arrhenius plot. Results of analysis of lateral step correlations at elevated temperatures will also be compared with results obtained in traditional way by quenching surface down to the room temperature. The temporal correlation functions in this temperature region are shown to scale as t@super 1/2@, consistent with either step-edge attachment or terrace-crossing diffusion as a rate limiting process. The prefactor of the temporal correlation function also varies exponentially with temperature yielding an effective activation energy of 2.5 eV for the rate-limiting step in surface mass transport. Using both lateral and temporal correlation functions, the kinetic parameters governing mass transport have been extracted for different temperatures, and atomistic models for the step fluctuations will be discussed. @FootnoteText@ @footnote 1@ Work supported by the UMD-NSF-MRSEC.

9:20am **EL-WeM4 Atomic and Electronic Structure of Si Layers on CaF@sub 2@/Si(111)***, **A.A. Bostwick**, J.A. Adams,* University of Washington*; E. Rotenberg,* Advanced Light Source, Berkeley*; M.A. Olmstead,* University of Washington

Many forms of nanocrystalline silicon have been observed to luminesce at room temperature under photon or electron excitation. However, the relative importance of electron confinement and interface compounds is still an open question for many of these materials. Our group recently developed a means to fabricate ultrathin, crystalline, arsenic-terminated silicon quantum wells on calcium fluoride using electron irradiation in the presence of an arsenic surfactant flux.@footnote 1@ With no intrinsic oxygen and a well-defined surface and interface structure, these films make excellent candidates for probing the properties of oxygen-free silicon nanostructures. We have studied such films with angle-resolved valence band and core-level photoemission spectroscopy and diffraction and near-edge xray absorption spectroscopy. Our initial studies show no surface states in the bulk Si energy gap and a flat, weakly dispersing density of valence states. We also discuss growth mechanisms for these films, which are sensitive to the irradiation and arsenic exposure conditions. @FootnoteText@ @footnote 1@ B. R. Schroeder, S. Meng and M. A. Olmstead, Appl. Phys. Lett. 77, 1289 (2000).

9:40am **EL-WeM5 Surface Mass Transport and Island Nucleation during Growth of Ge on Laser Textured Si(001)***, T. Schwarz-Selinger,* Max Planck Institut für Plasmaphysik, Germany*; **D.G. Cahill,*** University of Illinois, Urbana

Shape transitions and coarsening of coherent three-dimensional islands in Stranski-Kranstanow crystal growth have been extensively studied but quantitative descriptions of island nucleation kinetics are hindered by incomplete understanding of surface mass transport on the wetting layer. To gain new insights on wetting layer mass transport, we manipulate the spatial distribution of island nucleation by modifying the substrate morphology with laser texturing: fluid flow in the melt zone created by tightly-focused nsec pulses from a frequency doubled Nd:YAG produces shallow, micron-sized dimples on the Si substrate. We then use gas-source molecular beam epitaxy to deposit Ge and, finally, measure the distribution of three-dimensional Ge islands surrounding the laser dimples by atomic force microscopy. As expected, island nucleation starts at the vicinal surfaces near the rim of the dimple. These initial islands create a denuded zone of suppressed island nucleation on the flat regions of the substrate surrounding the dimple. Nucleation theory predicts that the extent of the denuded zone L should be comparable to the the island-island separation d but, in the limit of slow growth rates, we observe L/d>20. By comparing the denuded zone lengths produced by different growth rates (varied by a factor of 100) and substrate temperatures (500-600°C), we extract an activation energy for surface mass transport.

10:00am **EL-WeM6 Non-thermal SiO@sub 2@ Film Growth on Si(100) using Laser-generated O(@super 1@D) and O(@super 3@P)***, **T.C. Coulter**, A.C. Tuan,* University of Washington*; W.P. Hess, J.W. Rogers, Jr,* Pacific Northwest National Laboratory*; Y. Ono,* Sharp Labs of America

Thermal oxidation of silicon by O@sub 2@ or H@sub 2@O at high temperature (usually 800-1000°C) is currently used to achieve device-quality films for microelectronic applications. These high temperatures can degrade other device characteristics. As device dimensions shrink, it becomes even more important to keep processing temperatures low. Thus, many alternative low-temperature oxidation methods have been explored. A successful low-temperature method must produce thin silicon oxide layers with good uniformity, abrupt interfaces, and device-quality electrical characteristics. In order to develop the best low temperature deposition strategy, it is necessary to understand the details of the oxidation mechanism. High-temperature thermal oxidation studies suggest that atomic oxygen, and not molecular O@sub 2@, may be the oxidizing species diffusing through the oxide to react at the silicon interface. Low temperature plasma oxidation proceeds faster than thermal oxidation, which is often attributed to the presence of charged and neutral atomic species. Recent studies using a modified plasma for SiO@sub 2@ growth suggest that excited oxygen atoms in the @super 1@D state may play an important role in oxidation.@footnote 1@ To elucidate the roles of excited and ground state neutral oxygen atoms in silicon oxidation, we have used photolytically generated ground state O(@super 3@P) and excited state O(@super 1@D) atoms to oxidize Si(100) at low temperature. In contrast to plasma oxidation, where many oxygen species of differing energy and charge are present, we can study the contributions of O(@super 3@P) and O(@super 1@D) individually, and compare their kinetics and oxidation mechanism. The growth rate and oxidation kinetics were studied with in-situ ellipsometry, and oxide stoichiometry and interface quality were determined with XPS. @FootnoteText@ @footnote 1@M. Hirayama, K. Sekine, Y. Saito, and T. Ohmi. IEEE Transactions on Electron Devices. 47(7), 1370 (2000).

10:20am **EL-WeM7 On the Use of Angle-resolved XPS for Resolving Composition Structure of Ultrathin Inhomogeneous Oxide Layers***, **T. Conard**, H. De Witte, W. Vandervorst, J. Petry,* IMEC, Belgium*; R. White, K.S. Robinson,* Thermo VGScientific, UK

With the downscaling of electronic, the industry faces a large number of challenges. Among those, layers with an EOT lower than 1nm have to be engineered for the gate oxide. The materials considered can be silicon oxynitride, ZrO@sub 2@, Al@sub 2@O@sub 3@ as a single layer or as multistack. One common characteristic of all these films is there very limited thickness (a few nm at most) and the inhomogeneous distribution of elements throughout the stack. These films challenge thus most of the analysis techniques used for determining the layer structure and composition such as SIMS. For very thin layers, XPS is a possible alternative to sputtering techniques as it allows a non-destructive analysis through the whole film. The development of angle resolved XPS instruments with the ability to acquire spectra simultaneously over multiple angles should also give the possibility to retrieve the layer composition as a function of depth. This work concentrates on the interpretation of such ARXPS data and its application as an alternative and complementary technique to SIMS profiling. Particular in our experiments is the simultaneous collection of up to 16 emission angles (using a Thermo VG Scientific ThetaProbe) which provides unparalleled capabilities to reconstruct non-homogenous depth profiles in very thin layers. We will present results showing that small differences in the nitrogen distribution (near surface, in film, interfacial) inside thin (~3.5 nm) SiON layers can be determined using simultaneous ARXPS. In addition, the technique can also be used to understand the strong modification observed in the profiling of ZrO@sub 2@/SiO@sub 2@/Si stacks using Ar+ ions at energies between 500 eV and 3keV. The depth profiles reconstructed from the ARXPS provide information on the redistribution of Zr and O in the ion bombarded film allowing to interpret these modifications in terms of oxygen preferential sputtering and sputtering induced oxygen diffusion in the ZrO@sub 2@ layer.

11:00am **EL-WeM9 Silicon-Oxide Formation on Gold***, T. Vdovenkova,* ***A.J. Slavin,*** Trent University, Canada

The Au-Si system has been well studied as a model system for metal-silicon interfaces. In contrast, the present work is one of the few studies of the growth of a silicon-oxide film on a gold substrate. The gold is the electrode, about 200-nm-thick, of a quartz-crystal microbalance (QCM) used for measuring the deposited mass. In early work on the deposition of Si onto a Au film about 10-nm thick, Si was visible in Auger spectroscopy (AES) from the start of evaporation. In contrast, in our study the evaporation of several monolayer-equivalents of Si under UHV conditions at room temperature resulted in the Si dissolving into the gold without the accumulation of any Si on the surface. Subsequent exposure to oxygen gas did not result in the segregation of Si to the surface. However, a layer of oxide from 0.5 to 1.8 nm thick was produced by a series of evaporations of the Si in the presence of O@sub2@ gas at 1 x 10@super -5@ torr with the sample held at 78@super o@C, probably aided by oxygen ions produced at the hot filament of the evaporator. The film growth has been studied by AES and EELS, using the QCM to monitor the amount of silicon oxide deposited. The average stoichiometry of the oxide was roughly SiO@sub 1.75@, based on an AES peak position of 78 eV compared to 92 for elemental bulk Si and 76 for SiO@sub 2@. One atomic layer of Si evaporated in vacuum onto the oxide film gave an AES peak at 90 eV, thought to be elemental Si; this showed that the Si oxide acted as a barrier to Si in-diffusion. This extra Si did not oxidize at 78@super o@C under O@sub 2@ gas at 1 x 10@super -5@ torr with the evaporator filament off. The intensity of the 90-eV peak decreased in comparison with the peak for Si in SiO@sub x@, under prolonged exposure to the electron beam. This research was supported by NSERC, Canada.

11:20am **EL-WeM10 Kinetics of the Selective Oxidation of Si(100) versus W by H@sub 2@O Steam in Hydrogen***,* ***Y. Liu,*** *J. Hebb,* Axcelis Technologies, Inc.

The selective oxidation (SELOX) of Si versus tungsten (W) is an important process to form W gate electrodes on SiO@sub 2@ dielectric in the advanced CMOS devices. The SELOX was studied using a small quartz reactor, a catalytic water vapor generator (WVG), a quadrupole mass spectrometer (QMS), an ellipsometer and a 4-point probe. New kinetics data were obtained for the wet SiO@sub 2@ growth on Si(100) at 1 atmosphere and 900-1150°C, with the steam (H@sub 2@O) in H@sub 2@ percentage being 0 to 80%. A Si(100) or a W-covered Si(100) wafer was rapidly heated to a desired temperature in an inert gas. Fast gas sequencing was carried out to expose the wafer to (1) H@sub 2@ for W passivation, (2) steam+H@sub 2@ for Si oxidation and (3) H@sub 2@ for WO@sub x@ reduction. Gases in the reactor were analyzed with the QMS. The SiO@sub 2@ thickness was measured with the ellipsometer while the W film was characterized by its sheet resistance change. Preliminary results showed that the SiO@sub 2@ thickness is proportional to the steam percentage at a given set of oxidation temperature and time, suggesting that the SiO@sub 2@ growth follows the first-order kinetics. At a 20% steam percentage and during the first 60 sec, the SiO@sub 2@ growth rates at 955°C and 1047°C have been determined to be 0.96 Å/sec and 2.89 Å/sec, respectively. This yields an activation energy of 1.67 eV in agreement with the published values using O@sub 2@ or steam+O@sub 2@. Between 60 and 180 sec, the growth rates decreased to 0.73 Å/sec and 1.81 Å/sec, respectively. Hence, the earlier oxidation stage is kinetically controlled by an interface reaction step while the later stage is limited by a different slow step. Besides the detailed kinetic studies for the wet Si oxidation in the H@sub 2@ reducing ambient, systematic data will be presented for the W oxidation and WO@sub x@ reduction to explore the selectivity window for Si SELOX.

Thin Films
Room 123 - Session TF-WeM
Fundamentals of Deposition

Moderator: J. Colligon, Manchester Metropolitan University, U.K.

8:40am **TF-WeM2 Molecular Dynamics Simulations of Self-bombardment of Compact Clusters on Pt(111)***,* ***D. Adamovic,*** *E.P. Münger, V. Chirita, L. Hultman,* Linköping University, Sweden*; J.E. Greene,* University of Illinois, Urbana

Studies of low-energy bombardment of two-dimensional (2D) close-packed clusters are of great importance and strongly related to thin film growth. We use embedded-atom method molecular dynamics simulations to monitor the kinetics characterizing the self-bombardment of Pt@sub 3@, Pt@sub 7@ and Pt@sub 19@ clusters on Pt(111) at 1000K. Atoms incident perpendicular to the surface with energies between 5 and 50 eV are followed in separate simulations of ~ 20 ps each. Clusters are divided into different sections, outer, rim and core area respectively. Our simulations reveal three major classes of events. They are cluster preservation, i.e. no change in shape or position, cluster reconfiguration, involving edge-diffusion and/or concerted dimer/trimer gliding and cluster disruption (rim atom scattering and/or total disintegration). Two of the most commonly observed events are the formation of three-dimensional (3D) clusters and the hopping and/or push out/exchange mechanism with rim atoms. Other typical processes observed are the permanent or temporary dislodgement of cluster atoms onto the surface as well as the creation of surface vacancies. For Pt@sub 3@ our results suggest that cluster preservation and reconfiguration events primarily occur with incident atom energies below 25 eV, while cluster disintegration prevails at higher energies. Similar effects are observed for larger clusters, however the energy threshold is not as sharply defined.

9:00am **TF-WeM3 On the Relative Motion of Thermal Gas Atoms In the Monte Carlo Simulation of Sputtering***,* ***T. Nakano,*** *S. Baba,* Seikei University, Japan

In this study, we have developed the treatment of gas motion in the Monte Carlo (MC) simulation of sputter deposition process. It has been known well that the mean free path of the sputtered particle depends on the speed of the particle, but the distribution function of colliding gas has been assumed to be the Maxwellian, which is independent of the particle speed.@footnote 1@ We show here that the distribution also depends on it. The collision frequency of the sputtered particle with those gases which belong to some volume in the velocity space is proportional to the product of the density of the gas, the cross section and the relative speed between the sputtered particle and the gas atoms. Therefore, the colliding gas velocity does not obey the stock Maxwellian but the one weighed by the relative speed. This distribution function can be integrated by using the relative speed and the gas speed (in laboratory system) as integrating parameters, hence it is applicable to the MC simulation. Using this method, time evolutions of velocity and positional distributions of sputtered particles are calculated and demonstrated. It is shown that the speed distribution of the sputtered particles after some period of time is described well by the Maxwellian of the same temperature with the gas. It is also shown that this method has enabled the accurate calculation of the resident time of sputtered particles in the chamber, which leads the spatial density of the particle. @FootnoteText@ @footnote 1@G. M. Turner, et al., J. Appl. Phys. 65 (1989) 3671.

9:20am **TF-WeM4 Self-Similar Structure Evolution and Surface Reaction Kinetics in Low Temperature Silicon Deposition***,* ***G.N. Parsons,*** *K.R. Bray, A. Gupta,* North Carolina State University

A current challenge in low temperature thin film deposition is to analyze energetics and kinetics of surface processes to control growth reactions and improve material properties. In this work, surface transport kinetics during silicon plasma deposition are determined by analyzing time and temperature dependent surface topography in comparison to dynamic scaling models. For plasma deposition of silicon using silane or silane/helium mixtures at 25 - 350Â°C, static and dynamic scaling parameters determined from atomic force microscopy are consistent with self-similar fractal geometry. Comparing parameters with those expected from linear continuum models indicates indicate that surface transport is dominated by adspecies diffusion with a diffusion activation barrier of

0.2eV, consistent with previous empirical estimates. However, the elementary steps associated with initial film growth are still not clear. The observed increase in diffusion length with increasing temperature contradicts some current published growth models, and ab-initio analysis of precursor adsorption reactions indicate that silyl radicals do not directly adsorb onto Si-H bonds to form 3-centered bonds, as is commonly proposed. When helium is replace by argon, significant departure from self-similar structure is observed, consistent with excess energy from surface bombardment of heavier Ar ions. Diluting silane with hydrogen results in significant changes in scaling coefficients, indicating that an additional non-linear term is needed in the continuum model to describe surface diffusion. All of the results suggest that atomic hydrogen generated in the plasma plays an important role in assisting surface transport. Possible elementary surface reactions consistent with observed results will be presented and discussed.

9:40am **TF-WeM5 Atomic-Scale Processes in the Growth of Transition-Metal Nitrides***, **D. Gall**, C.-S. Shin, M.A. Wall, I. Petrov, J.E. Greene,* University of Illinois, Urbana

Polycrystalline and epitaxial layers of NaCl-structure transition-metal (TM) nitrides -- TiN, ScN, CrN, and TaN -- were grown on oxidized Si and MgO(001) at 450-1000 °C by ultra-high-vacuum magnetically-unbalanced magnetron sputter deposition in pure N@sub 2@ and N@sub 2@+Ar discharges at 3-20 mTorr. Polycrystalline layers grown under low ion-irradiation conditions exhibit a columnar microstructure with strong 111 preferred orientation which evolves in a kinetically-limited competitive growth mode due to a large anisotropy in adatom mobilities and binding energies. Surface diffusion energies E@sub s@ were obtained from T-dependent nucleation length measurements using STM and by ab-inito density functional calculations. E@sub s@ for (001) and (111) TiN surfaces are 0.8 and 1.7 eV. The much smaller 111 adatom mobility results in preferential 3D growth and, ultimately, in the observed 111-preferred orientation. However, increasing the energy of incident N@sub 2@@super +@ ions during deposition to 20 eV results in layers with purely 001-texture. The high anisotropy in adatom mobilities gives rise to another unique microstructural feature: epitaxial 001-oriented layers exhibit self-organized arrays of 1-nm-wide nanopipes which are formed as a result of periodic kinetic surface roughening and subsequent atomic self-shadowing. While the microstructures of different NaCl-structure TM-nitrides are similar, their electronic and optical properties vary widely. TiN has metallic conductivity, ScN is semiconducting, and CrN is an antiferromagnetic insulator. The color of Ti@sub 1-x@Sc@sub x@N varies continuously with x from golden yellow to orange to burgundy to blue-green to transparent. Measured hardness of single crystal 001-oriented layers are 20, 21, 28, and 31 GPa for TiN, ScN, CrN, and TaN, respectively.

10:00am **TF-WeM6 Low Temperature Synthesis of Fully Textured Highly Oriented AlN Films by RF and Pulsed DC Reactive Sputtering***, **G.F. Iriarte**, F. Engelmark, I.V. Katardjiev,* Uppsala University, Sweden*; H.P. Loebl,* Philips GmbH, Germany

Textured as well as epitaxial thin AlN films are of great interest for a wide range of electro-acoustic and optoelectronic applications. Reduction of the deposition temperature is of vital importance in a number of applications due to thermal budget limitations. In this work we study systematically the influence of the process parameters on the film properties and identify the mechanisms leading to improved film quality as well as reduced deposition temperature with both RF and pulsed DC sputtering in an Ar/N@sub 2@ atmosphere. It is demonstrated that fully textured (0002) films are grown under a wide range of conditions. At the same time the FWHM of the rocking curve of the (0002) XRD peak is found to vary systematically with process conditions - depostion rate, process pressure and gas composition, substrate temperature and bias. The best films show a FWHM of 1.2@super o@. By comparing RF and pulsed DC sputtering we have identified the major mechanisms leading to the synthesis of high quality films. Thus it has been found that by far the most important factor is the arrival energy of the sputtered Al atoms which is primarily controlled by the process pressure. We report for the first time that fully textured AlN films with a FWHM of under 2@super o@ can be grown at room temperature. Other important factors are the ion and electron bombardment of the films, substrate temperature as well as gas composition, although their influence is not as dramatic. Generally, the film quality increases with temperature. Bias and electron bombardment within a certain range also lead to better films. Low Ar/N@sub 2@ ratios also result in improved film quality although the mechanisms are not fully understood.

10:40am **TF-WeM8 A Theoretical Study of the Chemical Vapor Deposition of (100) Silicon from Silane***, **J.K. Kang**, C.B. Musgrave,* Stanford University

We use quantum chemistry to investigate the chemical vapor deposition of (100) silicon from silane. The CVD reaction proceeds through four sequential steps. The first step is activation of surface sites through H2 desorption from the Si (100)-2x1 monohydride surface. We find that H2 desorption proceeds through a two-step pathway. The barrier for the first step is 35.1 kcal/mol while the second step proceeds with a barrier of 31.1 kcal/mol. Next, dissociative adsorption of SiH4 occurs, where SiH3 and H fragments add to two surface dangling bonds. We find the barrier to adsorption to be 4.3 kcal/mol. Then, adsorbed SiH3 transforms directly to SiH2 through simultaneous H migration from adsorbed SiH3 to the dimer and through a dimer-opening and ring-closing reaction with a barrier of 70.7 kcal/mol. We also find an alternative path where adsorbed SiH3 transforms to SiH2 through two sequential steps in the presence of atomic H. One pathway proceeds through hydrogen abstraction from the adsorbed SiH3 on the surface with a barrier of 0.4 kcal/mol followed by a dimer-opening and ring-closing step with a barrier of 23.3 kcal/mol. An alternative path proceeds through abstraction of H from the dimer and has a barrier of 0.2 kcal/mol followed by dimer-opening and ring-closing steps with a barrier of 32.9 kcal/mol. Finally, a dihydride surface with SiH2(a) formed through dimer-opening and ring-closing reactions transforms to a monohydride surface with SiH(a) through two-sequential steps of H2 desorption from one side of dimer followed by H migration from the other side of the dimer. The predicted barrier for this H2 desorption is 47.1 kcal/mol while that for H migration is 2.8 kcal/mol. In addition, we find that the overall theoretical barrier of 60.6 kcal/mol for H2 desorption is in a good agreement with the experimentall barrier (58.2 +/- 2.3 kcal/mol).

11:00am **TF-WeM9 Gas and Surface Reactions of Radicals in Hot Wire CVD of Amorphous Silicon***, **H.L. Duan**, G.A. Zaharias, S.F. Bent,* Stanford University

Hot wire chemical vapor deposition (HW-CVD) is a relatively new growth method that has been shown to produce amorphous and microcrystalline silicon materials of superior quality in comparison to the more conventional plasma enhanced chemical vapor deposit ion (PECVD). By using this technique, the precursor molecule such as silane is dissociated on a metal filament (wire) heated to high temperature. Radical species produced from the filament subsequently either diffuse to the substrate to form the film or react to form secondary products. In this study, a laser-based soft ionization method utilizing the ninth harmonic of a Nd:YAG laser has been applied for the first time to probe various silicon-containing species simultaneously during the growth process. In addition to the detection of gas phase radicals, multiple internal reflection infrared spectroscopy is used to characterize the hydride bonding and film structure. Surface and gas phase species are followed as a function of important growth parameters such as filament temperature, filament material and substrate temperature. It is shown that Si, SiH@sub 3@, and Si@sub 2@H@sub 6@ are the major silicon-containing species evolved upon activating silane with the hot wire. However, even at low gas pressure the filament condition and chamber history are found to influence the radical species produced. Further study of the gas species generated by W and Re filaments at wire temperatures between 1000@super o@C and 2000@super o@ C indicates that heating the fil ament to higher temperatures increases the flux of Si, SiH@sub 3@, and Si@sub 2@H@sub 6@ differently. Above 1800@super o@C, the Si intensity saturates, while SiH@sub 3@ and Si@sub 2@H@sub 6@ show a monotonic increase without saturation up to 2000@super o@C. A growth mechanism consistent with these observations will be discussed.

11:20am **TF-WeM10 In-Situ Determination of the Deposition Chemistry During BPSG Dielectric Thin Film Growth***, **L.D. Flores**, J.E. Crowell,* University of California, San Diego

Dielectric thin film growth of boron and phosphorus doped silicate glass (BPSG) has been studied using the atmospheric pressure reaction between trimethylborate (TMB), triethylphosphite (TEPi), tetraethoxysilane (TEOS) and ozone (O@sub 3@). In-situ gas-phase transmission FTIR spectroscopy was performed between 400-600°C by probing the variable region between the injector, heated Si wafer and exhaust zones. These studies involve low temperature ozone initiated deposition of dielectric thin films using a new atmospheric-pressure chemical vapor deposition (APCVD) reactor utilizing a commercial monoblok vent assembly. We compare the products of N@sub 2@ / O@sub 2@ / O@sub 3@ reactions with BPSG film forming precursors while varying their reactant ratios and corresponding flow rates. The products produced during the reaction of TEOS and ozone are compared to those products measured during dopant reaction and incorporation from TMB and/or TMPi addition. Absorbances due to isolated silanol species (3737 cm@sup -1@) have been quantitatively followed as a function of input reagent concentration and distance from the injector inlet. The silanol groups and their reactions with boron and phosphorus dopant sources has been investigated in order to clarify their role in the oxidation process and to determine the reaction mechanism. Chemical pathways unique to elemental B-P-Si-O-C containing species will be presented with an emphasis placed on their role during the hydrolysis and polycondensation process leading to siloxane formation and BPSG network film growth.

Wednesday Afternoon, October 31, 2001

Organic Films and Devices
Room 131 - Session OF+TF+EL-WeA

Growth of Organic Thin Films

Moderator: T. Fritz, TU Dresden, Germany

2:20pm **OF+TF+EL-WeA2 Resonant Mid-Infrared Pulsed Laser Deposition of Polymer Films***, **R.F. Haglund**, M.R. Papantonakis,* Vanderbilt University*; D.M. Bubb, J.S. Horwitz, J.S. Callahan, R.A. McGill, E.J. Houser, D.B. Chrisey,* Naval Research Laboratory*; M. Galicia, A. Vertes,* George Washington University*; B. Toftmann,* Risoe National Laboratory, Denmark

Resonant, picosecond-pulse, mid-infrared laser irradiation has been shown to ablate glassy and crystalline solids with high efficiency and low collateral damage.@footnote 1@ We have extended this concept to show that resonant infrared (IR) pulsed-laser deposition (PLD) is an effective method for depositing polymer films with physical and chemical structure as well as optical properties virtually identical to those of the bulk starting material. This contrasts sharply with PLD at ultraviolet (UV) wavelengths, where deposited polymer material is sometimes significantly degraded. In our experiments, the organic starting material was ablated by a pulsed infrared, free electron laser tuned into resonance with various vibrational modes; the vapor was collected on a room-temperature substrate. For polyethylene glycol (PEG, MW 1450) the laser was tuned to either C-H or O-H stretching modes at 2.9 and 3.4 µm, respectively. The properties of the deposited film were determined using infrared absorption spectroscopy and mass spectrometry. When the infrared laser was detuned from resonance, the structure and optical properties of the deposited PEG film were significantly altered, showing that the off-resonance ablation process thermally damages the polymer. The potential for generalizing this technique can be seen in the successful deposition of poly(lactide co-glocolide) (PLCA, MW 67,000). PLCA films were deposited using 5.7 µm excitation (1754 cm@super-1@), where the laser excitation is localized by the C=O stretch. The mechanism of ablation appears to be explosive vaporization; in contrast to the photochemical mechanism typical of UV ablation, the ablated material seems to remain in the electronic ground state. The technique appears promising for biomedical and electronic applications of polymeric and organic thin films. @FootnoteText@ @footnote 1@ D. R. Ermer, M. R. Papantonakis, M. Baltz-Knorr, D. Nakazawa and R. F. Haglund, Jr., Appl. Phys. A 70, 633-635 (2000).

2:40pm **OF+TF+EL-WeA3 Synthesizing Thin and Ultrathin Polymer Films by a Two-step Deposition/Polymerization Process***, **J. Bai**, C.M. Snively, W.N. Delgass, J. Lauterbach,* Purdue University

The goal of this work is to understand and further develop an in-situ preparation method for producing high quality polymer thin films. In this two-step vacuum process, a monomer film is deposited onto a cooled substrate, and then the polymerization reaction is initiated; thus the polymerization is confined to the substrate. Compared to other preparation techniques, this process has the major advantages of allowing the fabrication of films from insoluble polymers and providing better control of film quality. This investigation focused on the molecular orientation and packing of the monomer, as well as polymerization kinetics and film quality characterization. In-situ adsorption and polymerization studies were done using Reflection-Absorption Infrared Spectroscopy (RAIRS) and Temperature-Programmed Desorption (TPD). Time resolved FTIR spectra were taken to study the factors controlling the rate of polymerization. GPC, ellipsometry and AFM provided information about molecular weight, film thickness, and morphology characterization of the films. The model systems investigated were styrene and methyl methacrylate (MMA) on platinum. For the styrene/Pt model system, kinetic studies reveal that the polymerization reaction is preferred in amorphous monomer layers. Ellipsometry measurements show that, in the range of 25-200nm, the polystyrene film thickness is a linear function of the monomer dosage. AFM data suggest that the resulting film morphology is influenced by the platinum substrate. Polarized RAIRS spectra of MMA show that, up to 0.2 micron, only p-polarized component of the beam contributes to the spectrum, indicating that RAIRS can be used to determine the molecular orientation of films with sub-micron thickness.

3:00pm **OF+TF+EL-WeA4 Surface Growth Study of Pentacene, Perylene and CuPc***, **S. Zorba**, N.J. Watkins, L. Yan, Y. Gao,* University of Rochester

Pentacene, Perylene and CuPc are widely used organic semiconductors in organic light emitting diode (OLED) and organic thin film transistor (OTFT) applications. It has been well established that the transport properties of these materials are strongly dependent upon the way they are grown as organic thin films. One of the reasons why these materials are so popular is the fact that their electronic properties, such as their mobilities and barrier to charge injection ratios, can be altered and improved by changing their morphologies. In this talk we will present our recent results on the different growth modes of these substances on different substrates and try to relate their observed electronic and transport properties to their morphologies and account for their favorable features.

3:20pm **OF+TF+EL-WeA5 Substrate Controlled Crystallisation of Ultra-thin Films of Perylene***, **Q. Chen**, N.V. Richardson,* University of St Andrews, UK*; P.J. Unwin, T.S. Jones,* Imperial College of Science, Technology and Medicine, UK*; T. Rada, A.J. McDowall,* University of St Andrews, UK

There has been recent interest in the electronic and optoelectronic properties of polyaromatic hydrocarbons, such as tetracene, pentacene and perylene, because of their potential use as organic lasers, OLEDs and OFETs. Device performance is likely to be strongly influenced by the structural quality of crystals or thin films. We have carried out a detailed investigation of the deposition and growth of ultra-thin films (0-30 monolayers) of perylene on a variety of substrates including Cu{110}, H/Si(111), InAs(111) and InSb(111), using STM, TPD, LEED and vibrational spectroscopies. The substrate has a profound influence on growth and subsequent crystallinity of the film. For example, films grown on a hydrogen terminated Si(111) surface show no evidence of layer-by-layer growth and, from the earliest stages, small clusters of randomly oriented molecules are present which eventually cover the surface with a rough polycrystalline film. In contrast, vacuum deposition on a Cu{110} surface leads to large crystalline domains upto one monolayer coverage. Electron energy loss spectroscopy confirms that the molecules are flat-lying and @pi@-bonded to the substrate. Multilayer growth takes place epitaxially layer-by-layer on this first monolayer into a structure which, although commensurate with the underlying copper surface along the direction is incommensurate along and is unrelated to the bulk crystal structure of perylene. The 2D unit cell at all layer thicknesses (to 30 monolayers) is rectangular with dimensions 2nm x 1.9nm containing two, flat-lying molecules per layer at 90° to each other around an axis normal to the substrate surface. The molecular rows along are out-of-phase with each other in the direction from layer to layer, in an ABA packing sequence of rows along the growth direction. The implications for the modification of film properties implied by this control over film structure and crystallinity will be discussed.

3:40pm **OF+TF+EL-WeA6 Probing the Reactivity of Multifunctional Compounds on Semiconductor Surfaces: Pyrrole and its Derivatives on Si and Ge(100)-2x1***, **G.T. Wang**, C. Mui, C.B. Musgrave, S.F. Bent,* Stanford University

While the chemistry of amines has been extensively studied on the Si(100)-2x1 surface, relatively little is known about their reactivity with the Ge(100)-2x1 surface. In this study, the reactions of pyrrole and multiple pyrrole derivatives, including methylpyrrole, pyrrolidine, and methylpyrrolidine, with the Ge(100)-2x1 and Si(100)-2x1 surface were investigated via multiple internal reflection infrared spectroscopy and ab initio quantum chemistry calculations. This series of compounds comprises a model system for examining the competition of multiple functionalities on Ge(100) and Si(100) and the role kinetics and thermodynamics play on selectively controlling growth of organics on semiconductor surfaces. Although these compounds are structurally similar, they each follow different reaction mechanisms on the Si surface, including dative bonding, N-H dissociation, cycloaddition, and electrophilic aromatic substitution. We have also found that the adsorption of pyrrole and its derivatives on the Ge surface is surprisingly different from the Si surface. While the reaction of organics on Si is typically under kinetic control, the experimental and theoretical results show that thermodynamical considerations are also necessary to explain the reaction of organics on Ge. Additionally, aromaticity and charge transfer to the surface are found to have significant effects on the adsorption behavior of these compounds.

4:00pm **OF+TF+EL-WeA7 Chemisorption of Vinylacetic Acid on Si(001) and Its Subsequent Reaction with Iron Pentacarbonyl***, K. An, S.S. Lee, **Y. Kim**,* Korea Research Institute of Chemical Technology, South Korea

Chemisorption of vinylacetic acid (VAA) on clean Si(001) substrate at room temperature and the change of its adsorption with temperature have been investigated by x-ray and ultraviolet photoelectron spectroscopy. It was hoped that the C=C double bond of the chemisorbed VAA may be utilized in the subsequent reaction with the second adsorbate, iron pentacarbonyl, Fe(CO)@sub 5@, in this study. VAA first adsorbs on Si(001) molecularly, and as the substrate temperature is increased to 350°C, loses the acidic hydrogen resulting in the configuration that has two equivalent oxygen atoms according to the change in the O 1s XPS peak. The curve-fitted Si 2p peak indicates formation of the Si@super 2+@ state on the surface. UPS also showed that the photoemission peak due to the OH group of VAA loses its intensity significantly. This surface species is stable up to about 350°C. As the temperature is raised even more to ~450°C, the adspecies are decomposed leaving a mixture of oxidized silicon and silicon carbide. At about 700°C, only tenacious oxygens remain on the carbided substrate surface. Iron pentacarbonyl was introduced into the XPS analysis chamber to 35000 L with the monolayer of the anionic species of VAA at 350°C. The surface, after the introduction of Fe(CO)@sub 5@, was found to consist of the acid anion and an iron species that shows metallic behavior according to XPS and UPS data. The Fe(CO)@sub 5@ molecules must have been completely dissociated since no accumulation of C or O adspecies has been detected. Also the surface iron atoms do not seem to have been oxidized judging from the shape of the Fe 2p level and the appearance of the Fermi level crossing. However, it is not yet clear whether the iron species have formed microscopic structures or not, while the change in the C 1s peak suggests that they may each have a chemical bond with the surface C=C double bond. At the moment a scanning tunneling microscopy experiment is in preparation to examine the surface structure of the iron species.

4:20pm **OF+TF+EL-WeA8 Possibilities of Electron Beam Nanometer-scale Fabrication of Si(111) Using Alkyl Monolayers***, **T. Yamada**, N. Takano, K. Yamada, S. Yoshitomi, T. Inoue, T. Osaka,* Waseda University, Japan

Utilization of monolayer materials covering Si wafer surfaces is prospective in mass-production of nanometer-scale patterns generated by electron beam drawing, maintaining the spatial resolution. This paper presents application or monolayers of organic moieties bonded on Si(111) for electron-beam patterning and successive chemical metal deposition processes over the patterns. For the purpose of passivation and chemical alteration of Si(111) surface, alkyl groups were deposited by contacting H:Si(111)(1x1) with Grignard reagents (C@sub n@H@sub 2n+1@MgX, X=Cl, Br, I, as tetrahydrofuran solutions).@footnote 1@ Vibrational spectroscopy by FT-IR and HREELS indicated that the bonds in alkyl groups delivered as the Grignard reagent remained unbroken, and that most of the terminating H atoms were replaced by the alkyl groups. STM revealed the original step/terrace structure of Si(111) uniformly covered with a monolayer of organics. The alkyl groups were arranged in a rather disordered manner within the monolayer. Auger electron spectroscopy resulted that the number of alkyl groups per a unit area is constant with respect to the chain length n in the range of 1 ~ 18. All these facts indicate that the alkyl groups are covalently bonded to Si(111). Electron bombardment in vacuum did not introduce useful alteration of the adlayer, and patterning by electron beam (incident energy <3 kV) with ambient O@sub 2@ atmosphere (<10@super -6@ Torr) deposited SiOx on the irradiated portions. Metals such as Ni and Cu were deposited only over the patterns by immersion into aqueous solutions including metal ions. The electron beam patterns were even visualized as metal-deposited area limited by the passivation effect of alkyl monolayer. Application of this entire process to the patterns of <100 nm is now attempted to explore the spatial resolution limit on the nanometer scale. @FootnoteText@ @footnote 1@R. Boukherroub, S. Morin, F. Bensebaa and D. D. M. Wayner: Langmuir 15 (1999) 3831.

Thin Films

Room 123 - Session TF-WeA

Nucleation and Growth

Moderator: H. Jeon, Hanyang University, Korea

2:00pm **TF-WeA1 Spectroscopic Ellipsometry Studies on Film Smoothness of Sputtered Thin Films@footnote 1@***, **C. Liu**, J. Erdmann, A. Macrander,* Argonne National Laboratory

For x-ray mirrors, it is very important to have the surface roughness controlled at less than a few @Ao@ rms. Sophisticated polishing techniques have been developed to obtain substrate roughness less than 3 @Ao@. Quite often, x-ray mirrors are coated with various metals for optimum reflectivity at selected energies. One needs to make sure that the coating process will not introduce excess roughness. Spectroscopic ellipsometry has been broadly used for film thickness and morphology measurements. Here we report a new method to study the smoothness for films that are usually too thick for an ellipsometer to measure. We found that a thin C film usually follows the substrate morphology and will not introduce additional roughness. A thin C film was grown on the film to be studied; ellipsometry measurements were then carried out. The ellipsometry data were fit with both a flat-film and rough-film model to obtain the film smoothness information. Results of C/Au, C/W, and C/Cu films on Si and glass substrates will be discussed. @FootnoteText@ @footnote 1@This work is supported by the U. S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-ENG-38.

3:20pm **TF-WeA5 Quantum Size Effects in 2D Pb Islands on Si(111)***, **C.S. Chang**, W.B. Su,* Academia Sinica, Taiwan, ROC*; S.H. Chang,* National Tsing Hua University, Taiwan, ROC*; W.B. Jian,* Academia Sinica, Taiwan, ROC*; L.J. Chen,* National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.*; T.T. Tsong,* Academia Sinica, Taiwan, ROC

When the thickness of a metallic film approaches a few atomic layers, the de Broglie wavelength of its Fermi electrons becomes comparable to film thickness and quantum size effects (QSE) begin to appear. These effects, though originated from the electron confinement, can have a profound effect on various nano scale physical properties. For instance, Schulte@footnote 1@ earlier calculated the film thickness dependence of electron densities, potentials and work functions for free standing metal films and found oscillations in all these quantities. In addition, when the effect of discrete lattice is taken into account, the QSE can invoke the structural variations also. All these findings exemplify the unusual behavior of thin metal films varying with their thickness. However, clear experimental evidence directly relating quantized electronic states to interlayer relaxations of individual islands is still lacking. The first observation of the QSE for individual Pb islands grown on the Si(111) surface has been made by Altfeder et al.,@footnote 2@ and we have extended their work toward thinner films. Also in this study, individual 2D lead (Pb) islands of varying heights grown on the Si(111)7x7 surface at low temperature are investigated concurrently with real-space and local-probe scanning tunneling microscopy and spectroscopy. Quantum size effects, manifested as quantized electronic states and oscillatory relaxations in interlayer spacings are found perfectly correlated to each other. @FootnoteText@@footnote 1@F. K. Schulte, Surf. Sci. 55, 427 (1976). @footnote 2@I.B. Altfeder, K.A. Matveev, and D.M. Chen, Phys. Rev. Lett. 78, 2815 (1997).

3:40pm **TF-WeA6 In situ and Ex Situ Surface Dangling Bond Measurements on a-Si:H by Means of Surface Cavity Ring Down Absorption***, A.H.M. Smets, J.H. van Helden, **M.C.M. van de Sanden**,* Eindhoven University of Technology, The Netherlands

The study of surface dangling bonds during growth of hydrogenated amorphous silicon (a-Si:H) is of great importance because of their possible role as dominant growth sites. In this contribution we will introduce a new technique, surface cavity ring down absorption (SCRDA), which enables us to measure directly small absorptions (10@super -5@ - 10@super -2@) by surface dangling bonds. The sensitive SCRDA technique is based up on the rate of absorption of a light pulse confined between two highly reflective mirrors in an optical cavity configuration. Ex situ single wavelength measurements (@lambda@ = 1064 nm, @tau@@pulse@ = 10 ns, E@pulse in cavity@ = ± 1 µJ) on a-Si:H films (10-3000 nm) on Corning glass show that the SCRDA technique is able to detect the surface dangling bonds. The obtained surface defect density of the a-Si:H oxidized surface is around 10@super 12@ cm@super -2@ and is in agreement with electron spin resonance (ESR) and photothermal deflection spectroscopy (PDS) results. Furthermore, it is demonstrated that the surface roughness, as determined from AFM measurements, correlates with the surface defect density. In situ SCRDA measurements are performed using a mirror - prism (suprasil) - mirror cavity configuration in which the light pulse incidents perpendicular on the two 70° tilted prism surfaces and has a total internal reflection on the backside surface. The initial a-Si:H growth phase (approx. 20 nm) has been monitored. The surface defect density increases up to the not yet saturated value of about 10@super 13@ cm@super -2@ in agreement with reported results using in situ ESR measurements. This value is higher than expected from reported growth models (10@super 9@ - 10@super 12@ cm@super -2@) in which the defect density is determined by the creation and passivation of surface defects by weakly absorbed radicals. The implications for the growth mechanism of a-Si:H will be discussed.

4:00pm **TF-WeA7 Nanostructured Responsive Surfaces***, **J. Liu**,* Lucent Bell Laboratories **INVITED**

This presentation discusses the design and synthesis of nanostructured materials and films with multifunctional responsive surfaces. The electronic, optical, and dielectric properties of various nanostructured films have been widely investigated. More recently, there has been a growing interest in these materials for health and biomedical applications. Two key areas of research have been pursued: (1) the formation of the nanostructures themselves on a multilength scale, and (2) the incorporation of the recognition and responsive properties. On a molecular level, techniques such as molecular imprinting have been explored. On the nano- and sub micrometer length scale, self-assembly and super-molecular templating have attracted wide attention. On the micro- and macrolength scale, micro machining and lithography have been extensively used. In addition, novel synthesis methods have been developed to incorporate active sites and functionalities so that the nanostructured hosts can selectively recognize, or even respond to the change of the environment. For molecular recognition, selective ligands, or size-and-shape selective cage structures, are introduced. For responsive properties, environmental sensitive polymers, or other switchable organic molecules, are investigated. The challenge is to integrate the nanostructured materials and the functionalities on different length scales so that the whole material will have the proper chemical and physical properties, and will detect and respond to the change in the environment. Many examples from our own research, as well as from other groups, will be given to illustrate the potential of the integrated approaches.

4:40pm **TF-WeA9 Connecting the Evolution and Coalescence of 3-dimensional Grain Structures to Reactor-scale Phenomena***, **M.O. Bloomfield**, D.F. Richards, O. Klaas, J. Lu, A.M. Maniatty, M.S. Shepard, T.S. Cale,* Rensselaer Polytechnic Institute

We have created a finite-element based, multiple level-set code to model the evolution and coalescence of grains and atomic scale islands during thin film growth. Our software tool can simulate the evolution of N grains or atomic-scale proto-grains. Grain boundaries are represented implicitly by a set of N+1 scalar fields, phi@sub i@(r,t) expressed on an unstructured mesh, subject to the condition that phi@sub i@(r,t) = 0 for all r on the boundary of grain i at time t.@footnote 1@ By extracting the zero contour, we can recover the grain boundaries at any time. Because each grain is associated with its own scalar field, properties such as lattice orientation can be easily retained on a grain-by-grain basis. The evolution of each grain is computed separately using the usual level set equation. We use an explicit positive coefficient scheme for this evolution. Level sets representing different regions are then reconciled to bring the them into agreement. To address distortions in the scalar fields, we implement a "redistancing" algorithm that corrects these distortions. This step stabilizes the evolution, allowing for simulations that include the coalescense of proto-grains and islands into complex grain structures. Demonstrations of this code are presented, including applications within a multiscale framework. Reactor scale simulations of reactant transport are performed using an FEM code. Reactant data are passed to this scale from the grain scale in the form of boundary conditions. This allows us to establish concentration fields of reactant both on the scale of 0.1 m, and using local refinement, on the 0.1 mm scale. The reactor-scale simulation passes reactant data back down to a grain-scale level set simulation. This allows us to show the interaction of phenomena such as reactor-scale reactant depletion on the resulting grain structure. @FootnoteText@ @footnote 1@Osher, S. and Sethian, J.A., J. Comput. Phys. 79, 12 (1988).

5:00pm **TF-WeA10 Sputter Deposition of Metallic Sponges***, **A.F. Jankowski**,* Lawrence Livermore National Laboratory

The growth of thin-film metallic sponges is of interest in several electrochemical applications, for example, conductive porous electrodes for gas transport and processing.@footnote 1@ Determination of the experimental parameters needed to yield metallic sponges should be tractable for physical vapor deposition processes. The general guidelines on how to stabilize the basic coating morphologies are found in the classic zone model for film growth.@footnote 2@ It's known that morphologies in structure can range from porous columnar to dense polycrystalline as the process conditions are manipulated for either sputter deposition or evaporation. However, there's no reference to the three-dimensional structure of a sponge - that is, a polycrystal with continuous open porosity but without the definitive columnar features characteristic of vapor deposits. Herein, conditions for deposition are resolved that produce the sponge morphology augmenting the classic zone model of structure. For sputter deposition using planar magnetrons, the general conditions are an increased working gas pressure and an intermediate substrate temperature. Example results of the sponge morphology in a 1 to 2 µm thick coating are presented for metals including aluminum, gold, nickel, and silver. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. @FootnoteText@ @footnote 1@ A. Jankowski, et al., J. Vac. Sci. Technol. A, 13 (1995) 658; 18 (2000) 2003. @footnote 2@ J. Thornton, J. Vac. Sci. Technol., 14 (1974) 666.

Organic Films and Devices
Room 131 - Session OF+TF-ThM

Characterization of Organic Thin Films

Moderator: N.V. Richardson, University of St Andrews

8:20am **OF+TF-ThM1 Characterization and Modification of ITO Surfaces: Use of Chemisorbed Probe Molecules as Indicators of Electron Transfer Rates and Their Use in Improving OLED Performance***, **C. Carter**, C.L. Donley, N.R. Armstrong,* University of Arizona

XPS characterization of ITO surfaces, following various pretreatments, shows that the surface coverage of hydroxyl groups, and oxygen defects, can be varied significantly. Probe molecules, such as ferrocene dicaroboxylic acid (Fc(COOH)2) can be chemisorbed to these surfaces through hydrogen bonding interactions, at coverages up to 40% of a compact monolayer. The coverage and electron transfer rates of these chemisorbed molecules vary by up to 100% depending upon pretreatments used. Organic light emitting diodes, prepared by spin coating single polymer layers (PVK), doped with Alq3, and its tri-sulfonamide analog, Al(qs)3, show signficant lowering of onset potentials for electroluminescence for ITO films modified with the Fc(COOH)2 probe, following air plasma cleaning. These differences in onset potential are most significant for devices where electron injection is not the chief limitation to electroluminescence.

8:40am **OF+TF-ThM2 XPS Characterization of Photo-Alignment of Liquid Crystals using Adsorbed Dichroic Materials***, **L. Su**, J.L. West,* Kent State University*; Y. Reznikov,* Ukraine Academy of Science*; K. Artyushkova, J.E. Fulghum,* Kent State University

The alignment layer is one of the most important parts of a twisted nematic (TN) display. Many methods exist for producing alignment, and the quality of the alignment layer directly influences the performance of the display. The most popular alignment method used by the Liquid crystal display (LCD) industry is mechanical rubbing of a polymer film. However, there are many disadvantages associated with this method, such as the introduction of dust particles, formation of electrostatic charges and other defects on the rubbed surface. Photo-alignment of liquid crystals is emerging as one of the most promising substitutes for mechanical rubbing. Photo-alignment generates surface anisotropy through the interaction between the irradiated substrate and the light source. Photo-alignment using adsorbed dichroic materials provides an efficient and versatile way to produce effective alignment of liquid crystals. Successful photo-alignment results from properly matching the adsorbed and substrate materials. In this study, poly(vinyl) alcohol (PVA) and adsorbed dichroic materials, including the dye Brilliant Yellow, are utilized as the alignment layer. We will demonstrate the use of polarized UV-Vis spectroscopy and angle-resolved x-ray photoelectron spectroscopy (XPS) for studying the interaction of the polymer, dye and liquid crystal. Using ARXPS, it is possible to study the distribution of all three organic layers. Both techniques indicate that intermolecular interaction between the adsorbed dichroic molecules and the substrate polymer is critical to the outcome of photoalignment. This work has been supported in part by NSF ALCOM (DMR 89-20147), and the Air Force (DAGSI SN-AFIT-9903).

9:00am **OF+TF-ThM3 An STM , XPS and RAIRS Study of Cobalt(II) Hexadecafluorophthalocyanine (CoF16Pc) and Its Co-adsorption with Nickel(II) Tetraphenylporphyrin (NiTPP)on Au (111)***, **S.L Scudiero**,* Washington State University, US*; D.E. Barlow, K.W. Hipps,* Washington State University

Scanning tunneling microscopy (STM) images show that cobalt(II) hexadecafluorophthalocyanine (CoF16Pc) forms disordered structures when deposited on Au(111) under UHV conditions at 300K, while nickel(II) tetraphenylporphyrin (NiTPP) forms a tightly packed well organized structure under the same conditions. X-ray photoelectron (XPS) and reflection-absorption infrared spectroscopy (RAIRS) data obtained on thin films of the pure compounds confirm that the chemical composition of these films is the same as the starting bulk materials. When CoF16Pc and NiTPP are co-deposited with a monolayer coverage, the resulting surface structure is a well ordered 2D array having a 1:1 ratio and a nearly square unit cell as revealed by high resolution STM images. The composition of the mixture was confirmed by XPS. We believe that this new structure is due to the weak electrostatic interactions associated with the local partial charges and their images, along with differences in Van der Waals forces.

9:20am **OF+TF-ThM4 Solution-Assisted Tribological Modification of Surfaces Using an Atomic Force Microscope***, **F. Stevens**,* Washington State University, USAS*; R. Leach, J.T. Dickinson,* Washington State University

The response of thin polymer films to combined stress and solvent is important for applications such as protective barriers (e.g., various wrappings), in controlled drug release from polymer hemispheres, resists for lithography, and nanometer scale surface modification. Over a wide range of normal forces, when a polymer is scanned by SFM in contact mode in a solvent, material is not worn away, but rather the polymer surface expands forming a nanometer scale "bump" at and surrounding the scanned location. Furthermore, for sub-micron scan areas one often observes a series of parallel ridges (moguls) perpendicular to the fast scan direction. Previous reports of the formation of raised material have nearly all been in air, required long times or very high forces to form; little evidence has been presented for the mechanism of formation. We have engaged in a detailed study of protrusion formation and raised ridges using poly(methyl methacrylate) in alcohol based solvents. In addition to scanning in air, we have scanned the polymer surface in four solvents with dramatic differences in response. We have also observed the effects of varying contact force, and the effect of using cantilevers with different force constants. We present evidence that both plastic deformation and tip induced swelling play major roles in the observed polymer surface modification by SFM. The stresses applied by the tip generate tensile forces around the tip that likely increase the quantity of solvent that can enter the surface. We show that adding Rhodamine 6G dye to the solvent provides us with evidence that indeed solvent is going into the polymer. Using fluorescence microscopy we can monitor the uptake of dye as a function of scanning and solvent parameters. This study also shows the possibility of introducing small quantities of a chemical into the polymer surface in a highly localized (nanometer scale) fashion.

9:40am **OF+TF-ThM5 Viscoelastic Properties of Thin Liquid Crystal Films***, **I. Zori@aa c@**, P. Borchard, T. Carlsson, B. Kasemo,* Chalmers University of Technology, Sweden

Viscoelastic properties of thin liquid crystal (LC) films are strongly affected by the changes in orientational and/or translational order in the system. These changes may be induced via a temperature variation or by a presence of the two phase interface (e.g. a free surface or a LC-solid substrate interface). In this contribution we report the viscoelastic properties of thin (500-7000Å) 5CB films, spin coated on the Au electrode of the quartz crystal microbalance (QCM), with one free surface. The system (LC film) is exposed to a periodic shear force (at 5 MHz respectively 15MHz) and the changes in the QCM oscillator frequency, @DELTA@f, and dissipation factor, @DELTA@D, are measured as a function of temperature while the system undergoes a series of phase transitions (smectic-nematic-isotropic). Both @DELTA@f and @DELTA@D show unusual temperature dependence in the vicinity of the nematic-isotropic phase transition. Two approaches are used to deduce the temperature dependent viscoelastic coefficients from the measured frequency and dissipation factor changes. In both approaches the QCM is treated as a harmonic oscillator and the Navier Stokes equation is used to calculate the velocity profile in the viscous overlayer caused by the periodic shear. Once the velocity profile in the film is known, a frictional force causing a change in the oscillator frequency and dissipation, may be calculated. In the first case the overlayer is treated as a homogenous isotropic thin liquid film (Voight model) while in the second case a proper anisotropic structure of the LC film is taken into account in the hydrodynamic continuum approach (Leslie-Ericksen theory). We compare our results to generalized viscosities obtained using different methods.

10:00am **OF+TF-ThM6 Structure of Ultrathin Pentacene Films***, **S. Lukas**, G. Witte, C. Wöll,* Ruhr-Universität Bochum, Germany

The structure of ultrathin films (1-3ML) of pentacene grown by evaporation under UHV conditions on various copper surfaces has been studied by LEED, STM and NEXAFS. The enhanced binding energy of acene molecules at step edges which was measured systematically by TDS can be utilized to prepare ordered monolayer films on vicinal copper surfaces with close packed terraces while only disordered films grow on the flat Cu(111) surface.@footnote 1@ Highly ordered mono- and multilayer films were also obtained for the Cu(110) surface and their corresponding molecular orientation was determined by NEXAFS as a function of the film thickness. For comparison additional films were grown also on gold and sapphire surfaces. In addition to the geometrical structure the electronical properties of these pentacene films were investigated by UPS. @FootnoteText@ @footnote 1@ S. Lukas et al., J. Chem. Phys. 114 (2001) .

10:40am **OF+TF-ThM8 Photoelectron Spectroscopy of Exciton Dynamics and Interactions in Organic Thin Films: C@sub60@ and Photopolymerized C@sub60@*, J.P. Long***, *S.J. Chase, M.N. Kabler,* Naval Research Laboratory

Of fundamental importance to the operation of many organic electronic devices are the controlling nonequilbrium populations of singlet (S@sub 1@) and triplet (T@sub 1@) excitons and charged carriers. For example, optoelectronic device efficiencies may be depressed if dark T@sub 1@ excitons compete with fluorescent S@sub 1@ states or if annihilation interactions limit excited state population densities. Because pump-probe photoelectron spectroscopy is uniquely capable, in principle, of resolving in energy and time the electrons of all nonequilibrium species, it promises to provide useful insights into the densities, lifetimes, and mutual interactions of the various nonequilibrium populations. Using both synchrotron and laser-harmonic photoemission sources, we have applied this technique to study the dynamics of excitons pumped by visible laser radiation in the model systems of C@sub 60@ and photopolymerized C@sub60@ films prepared in ultrahigh vacuum and studied in situ. We report the unambiguous identification of the transient photoelectron spectra of both S@sub 1@ and T@sub 1@ excitons. Studies on time scales from 100 ps to 10 µs and of exciton concentrations from below 10@super 18@ cm@super -3@ to more than 10@super 19@ cm@super -3@ reveal a rich dynamics. For exciton densities above ~10@super 19@ cm@super -3@, excited-state interactions lead to a surprising excess of T@sub 1@ excitons at the expense of S@sub 1@ excitons for times much less than the intersystem crossing time of ~2.5 ns. Such excess T@sub 1@ generation suggests that interactions among excited species may interfere with the operation of potential devices that would operate at high nonequilibrium densities. A rate-equation model that couples interacting S@sub 1@, T@sub 1@, and carrier populations reproduces the complex dynamics, including non-Markovian decays, and provides evidence for the annihilation of excitons by charged carriers.

11:00am **OF+TF-ThM9 Optical Properties of Highly Ordered Ultrathin Epitaxial Films of PTCDA on Au(111)***, R. Nitsche, S. Mannsfeld, H. Proehl,* ***T. Fritz,*** TU Dresden, Institut fuer Angewandte Photophysik, Germany

Highly ordered organic thin films on a gold single crystal have been prepared by means of organic molecular beam epitaxy and investigated by optical absorption spectroscopy. The organic dye molecule perylene-3,4,9,10- tetracarboxylic-3,4,9,10-dianhydride (PTCDA) has been deposited on Au(111) with submonolayer to multilayer coverage. All films were structurally characterized by combining Scanning Tunneling Microscopy (STM) with Low Energy Electron Diffraction (LEED), clearly indicating epitaxial growth in the point-on-line mode. In order to determine the optical constants of those films, Differential Reflection Spectroscopy (DRS) has been applied. Subsequently, the optical constants have been calculated based on a model dispersion formula, thereby deconvoluting the absorption index k into several molecular transitions. The thickness dependence of the parameters (position, width, strength) of those transitions is discussed. Contrary to a simple discussion of the peak position of the entire spectrum, which would indicate an energetic shift, our thorough analysis reveals that the dominant effect consists of a change in the relative contributions of the several transitions rather than an energetic shift. The results are compared to polycrystalline PTCDA layers of comparable thickness on polycrystalline gold films, exhibiting a larger inhomogeneous broadening.

11:20am **OF+TF-ThM10 Importance of Structural Order for the Low Surface Energy of Perfluoroalkyl Substituted Polymethacrylates*, J. Luning,*** Stanford University*; D.Y. Yoon,* Seoul National University, Korea*; J. Stohr,* Stanford University

Perfluoroalkyl substituted PolyMethacrylate (PFPM) polymers are today widely used as low surface-energy coatings playing an essential role in microelectronics, anti-fogging, and anti-fouling applications, and even have promising medical applications. It is generally believed that the anti-wetting properties -solely determined by the structures present in the surface region- of these and related polymers arise from the segregation of CF@sub 3@ groups to the surface. However, proof of a direct correlation between surface structure and surface energy, and the importance of order in the underlying bulk, is still lacking as most experimental techniques do not have the required surface sensitivity. For preferentially oriented polymers the asymmetry in chain orientation translates to an asymmetry in the electron charge density as the electron orbitals are oriented along the molecular bonds. Such a charge asymmetry can give rise to a dependence of the Near Edge X-ray Absorption Fine Structure (NEXAFS) on the orientation of the electric field vector of the linearly polarized x-rays relative to the sample. Consequently, such a linear dichroism can be used to study orientation phenomena quantitatively. The required surface sensitivity is obtained by recording simultaneously the more bulk sensitive total (TEY) and the more surface sensitive Auger (AEY) electron yield. Our studies of three PFPM's with different bulk order phases reveal a greater order at the surface than in the bulk, and the surface order parameter is found to correlate with the surface energy. Most importantly, temperature dependent NEXAFS measurements covering several bulk phase transitions show that the achievable surface order, and hence the surface properties, is ultimately limited by the bulk order (phase).

Plasma Science
Room 104 - Session PS+MS-ThM
Conductor Etch and Damage

Moderator: A.E. Wendt, University of Wisconsin, Madison

8:20am **PS+MS-ThM1 An Advanced 300 mm Etcher with Tunable Plasma Source for the Etching of <0.15mm Poly-Silicon Gates*, J. Holland,*** Applied Materials, Inc., US*; M. Jain, M. Shen, N. Gani, A.M. Paterson, V. Todorov, M.S. Barnes, K. Fairbairn,* Applied Materials, Inc.

The current requirements for etch performance for 300mm poly-silicon gate can only be met by providing a wide enough process window that is capable of achieving uniform etching for the variety of steps needed to complete this etch. The final dimensions of the polysilicon gate are functions of the many different etch steps, the ARC/DARC open, the main-etch , soft landing step and over-etch steps. In order to achieve < 10 nm CD range for <0.15 um polysilicon features, all of these steps need to be very uniform and the CD loss (or gain) needs to be very controllable. In this next generation 300 mm etcher, a tunable inductively coupled plasma source combined with advanced gas injection technology allows etch uniformity to be optimized for all of these different steps. Results of tuning for etch uniformity will be shown. CD control of <5 nm with a total range of 10 nm is achieved. The tunable source is also combined with a precise wafer temperature control using a dual-zone electrostatic chuck to ensure CD uniformity can be achieved across the entire diameter of the 300mm wafer. The wide process window of this etcher should be capable of addressing both current and evolving applications which require etching of multiple films with multiple etch steps involving varied process conditions.

8:40am **PS+MS-ThM2 Plasma-Based Copper Etch Process - Additive Gas Effects*, S. Lee*[1]***, *Y. Kuo,* Texas A&M University

Copper is an ideal multilevel interconnection material for VLSIC and many other microelectronic devices. However, it is difficult to etch copper into fine lines by the conventional plasma etching method under a mild process condition such as at room temperature or without the inclusion of an extra energy source, e.g., UV, IR, or a high-density plasma source. Recently, authors reported a new plasma-based copper etching method that showed a high etch rate at room temperature using a parallel-plate electrode design.@footnote 1,2@ The success of this method relies on a novel plasma-copper reaction. Instead of removing copper compounds during the plasma processing, copper was converted into a solution soluble compound accumulated on the surface. This reaction product was subsequently removed with a HCl solution. The resulting copper pattern has a vertical profile. In this paper, we are going to discuss the additive gas (Ar, N@sub 2@, CF@sub 4@, and O@sub 2@) effects on the Cl@sub 2@ plasma-based copper reaction process. In addition to the reaction rate, the product's morphology, structure, and the undercut of the photoresist pattern have been studied. The added gas can enhance or hinder the reaction rate and the progress in the radial direction through various mechanisms. Experimental results are interpreted by the plasma phase chemistry, ion bombardment phenomena, and the original copper structure. The composition and chemical states of the reaction product are characterized by EDS and XPS. The film's morphology and structure are examined by AFM, SEM, and XRD. This study enhances our understanding of the unique plasma-based copper etching process that is critical to many microelectronic and optoelectronic applications. Authors would like to acknowledge staffs in the CIMS of Texas A&M University for AFM and XPS analyses. @FootnoteText@ @footnote 1@ Y. Kuo and S. Lee, Appl. Phys. Lett. 78, 1002, (2001) @footnote 2@ Y. Kuo and S. Lee, Jpn. J. Appl. Phys. 39, L188, (2000).

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

9:00am **PS+MS-ThM3 Silicon Gate Etching: Potential Strategies for Future CMOS Devices*, G. Cunge*,** *L. Vallier, O. Joubert, J. Foucher, X. Detter,* CNRS/LTM, France **INVITED**

In less than ten years CMOS devices will operate in the sub-50 nm gate length regime. The fabrication of the gate will be the key issue of the device fabrication process since the variation in gate dimension must not exceed the nominal CD targeted by few nm. In this work, some of the most promising gate strategies are investigated 1) resist mask on SiON antireflective layers versus hard mask approaches 2) standard HBr/Cl@sub2@/O@sub2@ chemistries versus CF@sub4@ (or NF@sub3@) added chemistries. The origin of CD deviation are investigated for each single step of the different strategies: correlations between chemistry and plasma operating conditions analysed by mass spectrometry, passivation layer formation on the feature sidewalls analysed by XPS and CD deviation will be established. Our preliminary experiments show that the passivation layers formed on the mask sidewalls induce very severe CD gain during standard gate etch steps. The objective is first to minimize the CD deviation induced by each individual step of the process (by decreasing the passivation layer thickness). Ultimately, the process has to be tuned so that the CD loss or gain of each individual step compensate each other to maintain the CD in the targeted window. In final, by comparing the impact of mask materials as well as the impact of chemistries (standard or clean) on CD control, we may give some interesting conclusions on the most promising strategy. In parallel to this study, we evaluate the current strategies used to obtain gates smaller than the dimension printed by the lithography (resist trimming or "notched gate approach") and try to draw some clear conclusions on the best approach for manufacturing.

9:40am **PS+MS-ThM5 Sidewall Passivation Mechanism of CF@sub4@ Added Polysilicon Gate Etch Process*, T. Lill,*** *F. Ameri, S. Deshmukh, D. Podlesnik,* Applied Materials*; L. Vallier, O. Joubert,* CNRS/LTM, France

For the traditional HBr/Cl@sub2@/O@sub2@ gate etch process, anisotropy is achieved by forming silicon, oxygen, and halogen containing compounds on the sidewall of the etching structures. These compounds inhibit the isotropic etch and are removed by from the etch front via ion sputtering and ion assisted desorption. The introduction of fluorine via CF@sub4@ to a typical HBr/Cl@sub2@/O@sub2@ polysilicon etch process suppresses the formation of SiOxBry or SiOxCly via formation of volatile SiF@sub4@. Speculations that carbon based polymers play an important role in the sidewall mechanism for the CF@sub4@ polysilicon gate etch chemistry have recently been confirmed by in-situ XPS studies in the Silicon DPS chamber at CNRS/LETI in Grenoble. In this paper we present more detailed studies of the sidewall composition for different CF@sub4@ and O@sub2@ flows. The results suggest the coexistence of silicon oxyhalogenides and carbon polymers on the sidewall for theHBr/Cl@sub2@/CF@sub4@/O@sub2@ gas mixture. The carbon content in the sidewall passivation layer increases strongly when the oxygen flow is reduced. The XPS results will be correlated with findings on chamber wall condition (oxide or carbon mode), change of the critical dimension for dense and isolated lines during gate etching (critical dimension microloading), and etch rate differences between doped and undoped polysilicon. We will present experimental line width data that corroborate the idea of change in sidewall passivation from compounds that are formed on the etching surface (silicon oxyhalogenides) to compounds formed in the gas phase (carbon polymers) when CF@sub4@ is added to the plasma. Typically, profile and critical dimension microloading are significantly reduced for the CF@sub4@ added chemistry as a result of the change in the sidewall passivation mechanism. The superior etch performance and the increased productivity due to clean chamber walls explain the rapid acceptance of this polysilicon gate etch chemistry in high volume VLSI production.

10:00am **PS+MS-ThM6 Manufacturing Viability of the "Notched Gate" Process for sub 0.1µm Technologies*, J. Foucher*[1],** *L. Vallier, G. Cunge, O. Joubert,* CNRS/LTM, France*; T. Lill,* Applied Materials

The development of new integrated circuit generations, at a unique rate in the semiconductor history, imposes the development of new technologies. Recently, Integrated Circuit manufacturers have evaluated new strategies to make gate transistors smaller than the resolution allowed by the lithographic tool available for manufacturing. One of them is to decrease the resist feature dimension before gate etching (resist trimming), the other approach is to design a "notched gate" etch process with a controlled etch rate of silicon in the lateral direction (the bottom of the gate is smaller than its top). We first describe in details the main differences between a notched gate process and a standard gate etch process and introduce the notion of passivation layer engineering. We demonstrate that when the process is accurately tuned, gate dimension of 10 nm can be obtained on a 200 mm diameter wafer. We mainly concentrate on several aspects of the process which determine its industrial viability: - What are the plasma operating conditions and chemistry required to stabilize a "notched gate" process or in other words what are the impact of the wall conditions on notch reproducibility ? - Can we solve the CD control issues of the notched gate process ? We will present experimental data demonstrating clearly that the notch depth rate is strongly dependent on the gate environment. In other words, the lateral etch rate which controls the notch depth is aspect ratio dependent and impacted by the plasma non-uniformity. In conclusion, we clearly demonstrate the strong limitations of the notched gate process for manufacturing.

10:20am **PS+MS-ThM7 Properties of Pulsed ICPs with rf Substrate Biases@footnote 1@***, P. Subramonium,* ***M.J. Kushner,*** University of Illinois

Pulsed inductively coupled plasmas (P-ICPs) are of interest for controlling reactive fluxes to the substrate in microelectronics fabrication. In particular, negative ion fluxes to the wafer can be obtained in electronegative pulsed plasmas. In order to achieve anisotropy of the fluxes, rf substrate biases must also be used with P-ICPs. This is problematic since the increase in plasma potential obtained with an rf bias tends to trap negative ions. A moderately parallel implementation of the 2-dimensional Hybrid Plasma Equipment Model (HPEM) was used to investigate P-ICPs in electronegative gas mixtures having continuous and pulsed rf substrate biases. Electron properties are obtained using a Monte Carlo Simulation. In Cl@sub 2@ at 10 mTorr (PRF=10 kHz, duty cycle 50%), the electron temperature, after falling in the first part of the afterglow, increases in the late afterglow signifying a transition to a capacitive mode. The onset of the increase in T@sub e@ comes earlier with increasing rf bias voltage. The increase can be attributed to progressively larger rates of sheath heating resulting from the decreasing electron density, increasing sheath width and increasing sheath speed. Coincident with the increase in T@sub e@ comes an increase in sheath potential which prevents negative ions from escaping from the plasma. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials.

10:40am **PS+MS-ThM8 Magnetic Field Effects and Electron Shading Damage*, W.W. Dostalik,*** Texas Instruments, Inc.

The use of magnetically enhanced plasma etch systems (MERIE) is widespread in semiconductor manufacturing. A primary concern with such systems is the risk of plasma process induced damage. In this paper, we discuss several of the candidate mechanisms in which magnetic fields may affect plasma damage associated with the electron shading effect (ESE). In particular, we consider for the case of a permanent magnet MERIE reactor the effects of guiding center drifts (e.g., gradient drift and curvature drift) on charged particle fluxes, of magnetic field effects on individual trajectories, and of non-uniformity in a typical magnetic field map. These effects are calculated in a two-step fashion. In the first step, an experimentally measured magnetic field map of a commercial plasma reactor is input into a computer program that calculates the various drift velocities and non-uniformity for typical plasma parameters. In the second step, the results of these calculations are used to affect incoming charged particle fluxes in local scale Monte Carlo simulations including the magnetic field and local topography. Charge accumulation and the resulting Fowler-Nordheim injection current are accounted for in the Monte Carlo simulations.

11:00am **PS+MS-ThM9 Effects of H@sub 2@, D@sub 2@, N@sub 2@ and Ar Plasma on III-V Compound Semiconductor Devices*, B. Luo,*** University of Florida*; K. Ip,* Agere Systems*; F. Ren, K.P. Lee, S.J. Pearton, C.R. Abernathy,* University of Florida*; R.J. Shul,* Sandia National Laboratories*; S.N.G. Chu,* Agere Systems*; C.W. Tu,* University of California, San Diego*; C.S. Wu,* Win Semiconductor*; K.D. Mackenzie,* Unaxis USA Inc.*; C.H. Hsu,* Feng Chia University, Taiwan

The effects of H@sub 2@, D@sub 2@, N@sub 2@ and Ar plasma exposures on the dc and rf characteristics of pseudomorphic AlGaAs/InGaAs high electron mobility transistors (HEMTs), GaAs metal semiconductor field effect transistors (MESFETs), and AlGaAs/GaAs heterojunction bipolar transistors (HBTs) were investigated. The experiments were conducted in a Plasma Therm 790 inductively coupled plasma (ICP) system. The influences of rf chuck power(10-100W), ICP source power(100-800W), chamber pressure(2-10mtorr) and durations(10-240sec) on device performance were studied. To analyze the rf results, a device equivalent circuit model was proposed to realize damage effects on

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

the transistor small-signal elements. Several plasma damage mechanisms were identified for the degradations of device dc and rf characteristics, including creation of surface and bulk deep level recombination centers, preferential loss of As atom from the surface due to energetic ion bombardment and passivation of Si donors by formation of Si-H and Si-D neutral complexes. Auger and atomic force microscopy (AFM) were also used to characterize the atomic ratio and roughness of plasma damaged surface, respectively.

11:40am **PS+MS-ThM11 Plasma Induced Physical Damage and Contamination on the SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Film after Etching in Cl@sub 2@/CF@sub 4@/Ar Plasma***, **D.P. Kim**, C.I. Kim,* Chung-Ang University, Korea*; W.J. Lee, B.G. Yu,* ETRI, Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) have been developed as dielectric materials of capacitor. To fabricate high density FRAM, plasma etching is indispensable process for the anisotropic pattern definition because it has good selectivity and excellent process control. However, the detrimental impact of plasma etching process on device characteristics has been existed. As feature size decreases, the plasma induced damages can decrease the performance of device. The plasma induced damages can be broadly classified as residue contamination, plasma-caused species permeation, bonding disruption and current flow damage. Etching mechanism and damages on SBT thin film during etching process have less reported in the literature. SBT thin films were etched in Cl@sub 2@/CF@sub 4@/Ar plasmas with measuring etch rates at different etching parameters such as gas mixing ratio, rf power, dc bias voltage, and chamber pressure. The maximum etch rate was 1060 Å/min in Cl@sub 2@(10)/CF@sub 4@(20)/Ar(80). The small addition of Cl@sub 2@ into CF@sub 4@(20)/Ar(80) plasma will decrease the fluorine radicals and the increase Cl radical. The etch profile of SBT thin films in Cl@sub 2@/ CF@sub 4@/Ar plasma is over 80°. The chemical reactions on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was used to investigate the surface morphology of SBT thin films exposed in plasma. High-resolution transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS) and x-ray diffraction (XRD) were evaluated in order to investigate physical damages. Electrical properties were characterized by measuring leakage current and hysteresys loop of Pt/SBT/Pt capacitor. From the results, damages in SBT etching was occurred in the near surface and Ar ion bombardment and nonvolatile etching by products caused to change of crystallinity and surface morphology.

Thin Films
Room 123 - Session TF+BI-ThM
Bioactive and Organic/Inorganic Thin Films

Moderator: L. Hultman, Linköping University, Sweden

8:20am **TF+BI-ThM1 Self-aligned Deposition and Patterning of Biologically-active Polymer Thin Films***, **B.H. Augustine**, S.M. Ramirez, O.D. Lees,* James Madison University

High-resolution patterning and microfabrication of polymeric and other soft materials is challenging since traditional photolithographic methods require organic solvents to remove photoresist. These solvents typically also dissolve or degrade biological and polymeric surfaces which one might pattern. We report selective dewetting using microcontact printing (µ-CP), micromolding in capillaries (MIMIC), and solvent assisted micromolding (SAMIM) techniques to pattern thin films of the biodegradable copolymer, poly-3-hydroxybutyrate-co-3-hydroxyvalerate [P(3HB-3HV)] onto glass, silicon, and Au coated silicon substrates. Film thicknesses range from 20 mn to over 700 nm, with minimum feature sizes as small as 3 µm. Dense 100 nm thick films with sub-10 µm features can be patterned in as few as two minutes for the entire processing resulting in potentially high throughput processing. Thin film microstructure can be dramatically changed by controlling deposition parameters such as solvent concentration, feature aspect ratio, and polarity of the solvent. While we report microfabrication techniqes for a specific biodegradable polymer system, we will also comment on extending these techniques to other polymer systems and the issues affecting the profound change in polymer microstructure using these three different patterning techniques.

9:00am **TF+BI-ThM3 Desorption and Processing of Bioactive Thin Films***, **A. Chilkoti,*** Duke University **INVITED**

I will describe methods to micro- and nano-pattern proteins and other biological ligands onto self-assembled monolayers (SAMs) and polymers for application in multianalyte biosensors, patterned biomaterials, and protein chips. These methods include: (1) Light-activated micropatterning (LAMP), which exploits spatially precise, light-activated deprotection of affinity ligands on functionalized SAMs to achieve step-and-repeat patterning of multiple biomolecules. (2) Microstamping onto activated polymer surfaces (MAPS), which involves surface-selective functionalization of polymers, followed by microcontact printing of reactive biological ligands. (3) Thermodynamically addressable reversible patterning (TRAP) which uses patterned domains with different surface energies as a thermodynamic address to direct the attachment of proteins and other biomolecules from solution. TRAP functions by the selective adsorption of nanoclusters of an elastin fusion protein above its phase transition temperature specifically on patterned hydrophobic regions, but not on a hydrophilic background. Unlike other methods for protein patterning, TRAP is reversible, and modulating the solution environment (e.g., T, ionic strength), can erase protein patterns. A theme illustrated by this talk will be the interdisciplinary convergence of surface chemistry and spectroscopic characterization (XPS, TOF-SIMS, and evanescent optical techniques) with molecular biology.

9:40am **TF+BI-ThM5 Nano-scale Fabrication Using Organic Thin Films***, **C.B. Gorman,*** North Carolina State University **INVITED**

We will show how a combination of lithographic methods on organic self-assembled monolayers (SAMs) can be used to form chemically well-defined, patterned surfaces. These surfaces can form the basis of nanometer-scale, molecular electronic devices. The talk will focus on (1)the engineering and the chemistry behind nanometer scale lithography on SAMs including an assessment of its strengths and limitations, (2) why the control of chemical functionality is so important for a true, nanometer-scale process and (3) demonstration of new, molecular electronic behaviors with potential applicability in devices.

10:20am **TF+BI-ThM7 Hot-Filament Chemical Vapor Deposition of Fluorocarbon-Organosilicon Copolymer Thin Films***, **S.K. Murthy**, K.K. Gleason,* Massachusetts Institute of Technology

Hot-filament chemical vapor deposition, a non-plasma technique, has been used to deposit copolymer thin films consisting of fluorocarbon (CF@sub 2@) groups and organosilicon groups (Si(CH@sub 3@)@sub 2@ - O) at rates of approximately 250 angstroms/min. The synthesis of such copolymers by solution chemistry techniques is difficult since one component (PTFE) is normally synthesized by free radical polymerization techniques and the other (PDMS) by ionic polymerization methods. The presence of covalent bonds between the fluorocarbon and organosilicon moieties in the thin films has been confirmed by Infrared, X-Ray Photoelectron (XPS) and solid-state @super 29@Si, @super 19@F, and @super 13@C Nuclear Magnetic Resonance (NMR) spectroscopy. These techniques also indicate retention of methyl groups from the siloxane precursor. The XPS data shows that all of the silicon present in the films is in the +2 oxidation state and that the ratio of silicon to CF@sub 2@ groups is approximately 1:0.86 based on atomic composition. Further, the NMR data suggest that the copolymer films are blocky in nature, consisting of networked chains having multiple fluorocarbon groups interspersed between siloxane groups. Atomic Force Microscopy of the films showed that the roughness of these copolymer films is in-between that of homopolymeric fluorocarbon and organosilicon films made by the same technique.

10:40am **TF+BI-ThM8 Polyatomic Ion Deposition of Gradient Thin Films: A New Method for Combinatorial Materials***, **L. Hanley**, M.B.J. Wijesundara, E.R. Fuoco,* University of Illinois at Chicago

Beams of gaseous ions are used for the growth and modification of interfaces in a wide variety of applications. For example, we have previously shown that mass-selected CF@sub3@@super+@, C@sub3@F@sub5@@super+@, and Si@sub2@O(CH@sub3@)@sub3@@super+@ ions can be employed for the growth and modification of organic thin films on polymer and metal surfaces.@footnote1@We demonstrate here that polyatomic ion beams can also be employed to create chemical gradient thin films by variation of the ion fluence across the substrate. We use mass-selected C@sub3@F@sub5@@super+@ ion deposition in vacuum to create a fluorocarbon gradient film on a polymethylmethacrylate substrate. X-ray photoelectron spectroscopy shows a continuous change in the surface chemistry from that of the native polymer to a fluorocarbon film. The contact angle varies from ~75° to ~95° across the gradient surface. We also examine the production of fluorocarbon films on polystyrene, silicon, and aluminum surfaces from C@sub3@F@sub5@@super+@ ions. Finally, we discuss the general feasibility of producing chemical gradients surfaces from polyatomic ion beams. @footnote1@M.B.J. Wijesundara, Y. Ji, B. Ni, S.B. Sinnott, L. Hanley, J. Appl. Phys. 88 (2000) 5004

11:00am **TF+BI-ThM9 Plasma Sputtering Deposition of Metals on PAMAM Dendrimer Monolayer***, A. Rar, M. Curry, F. Xu, J.A. Barnard,* ***S.C. Street****,* University of Alabama

A number of nanotechnology applications require development of thin, flat surface films with well-regulated mechanical and tribological properties. A promising approach for this is metal layer deposition on PAMAM dendrimer underlayers. Previously, we demonstrated improvement in mechanical and morphological properties for Au, Co, and Cr films deposited by evaporation onto dendrimer self-assembled monolayers. In this paper we will discuss formation of metallic layers on dendrimer by plasma sputtering deposition. We will show the influence of higher incoming kinetic energy of the metal atoms on dendrimer structure and chemical changes at the interface. The evolution of the dendrimer interlayer during metal deposition was analyzed with XRR, the surface morphology of deposited films with AFM, the chemical interaction between deposited metal and dendrimers with XPS and RAIRS. Thin Cr layers obtained by plasma sputtering interact with the dendrimer interlayer in essentially the same way as films deposited by evaporation. Significant differences were found for Cu/dendrimer layers prepared by plasma sputtering deposition compared to less energetic thermal evaporation. In the first case more than 1/3 of the nitrogen atoms in the dendrimer adlayer form nitride-like chemical states. Thermal evaporation shows less pronounced influence on the N1s XPS peak.

Thin Films
Room 123 - Session TF-ThA
Emerging Thin Film Techniques

Moderator: T.M. Klein, University of Alabama

2:00pm **TF-ThA1 Ionized-PVD with Quasi-Stationary High Power Magnetron Sputtering***, **U. Helmersson**, J. Alami,* Linköping University, Sweden*; A.P. Ehiasarian,* Sheffield Hallam University, UK, United Kingdom*; K.M. Macák,* Sheffield Hallam University, UK*; J.T. Gudmundsson,* University of Iceland, Iceland **INVITED**

The development of ionized-PVD by sputtering over the last few years is based on the production of a high-density plasma (10@super 18@ - 10@super 19@ m@super -3@) in front of the source. As the atoms pass through this dense plasma, a large fraction becomes ionized. The high plasma densities can be achieved in several ways, by using an rf-coil, a hollow cathode arrangement, or as in the present case, simply by increasing the power supplied to the magnetron source. To avoid extensive heating of the cathode as well as the development of arcs, in the latter case, the power is pulsed with a duty factor of around 1 %, which maintains the average power at an acceptable level. In the present work, peak power densities of several kW cm@super -2@ with a repetition frequency of 50 Hz was used. This technique has been demonstrated for sputtering a range of different metals, yielding a degree of ionization of 30 to 70 % depending on cathode material and applied power as measured for Cu, Ta, and Cr cathodes. Optical emission studies demonstrate a temporal development of the plasma during the pulse. Initially the emission is dominated by Ar-lines, but later in the pulse lines from cathode-metal ions dominate the emission. This may indicate a transition from Ar-sputtering to self-sputtering during the pulse. That self-sputtering occurs is also supported by the observation that the relative deposition rate (pulsed rate as compared with normal dc rate) scales with self-sputtering yield giving low relative deposition rate for low-yield materials. Film growth by this sputtering technique is demonstrated in trench-filling applications, reactive sputtering of chromium nitrides, and for carbon films.

2:40pm **TF-ThA3 Ionization of Sputtered Titanium Atoms in Radio Frequency Magnetron Sputtering***, **K. Okimura**, T. Nakamura,* Tokai University, Japan

Recently, the ionization of the sputtered flux has received much attention for several aspects such as, assisting effect of low temperature crystallization, filling characteristics to high aspect ratio seed layer and damage in integrated circuits. We have investigated sputtered titanium(Ti) atom densities for both Ar discharge and Ar-O@sub 2@ reactive discharge by means of atomic absorption method.@footnote 1@ As for the ionization of sputtered atom, quantitative measurement is lacking for understanding ion flux incident to substrate. In this study, optical emission spectroscopy for Ti ions were performed using 250 mm monochromater in planar rf magnetron sputtering apparatus with 100 mm diameter titanium target and 35 mm electrodes spacing. Atomic absorption method using a hollow cathode lamp was also applied in order to evaluate concentration of Ti ions. A series of optical emission originated from Ti ion, 336.1 nm, 337.3 nm and 338.4 nm, were observed in a spectrum at argon pressure of 3.5 Pa and radio frequency power of 200 W. We discussed the ionization of sputtered atoms from relative intensities of ionic optical emission to atomic emission in measured spectra. Radial(r) and axial(z) profiles of optical emission intensity of Ti ions at 336.1 nm for different discharge conditions such as rf power, Ar pressure, were presented. At axial directions, z=15 mm, 21 mm, 27 mm, maximum emission of Ti ion located at radial position around r=35 mm where was slightly outward position compared to the position with maximum strength of transverse magnetic field. Absorption measurement of 336.1 nm line showed absorption intensity around 10@super -2@ indicating ionization degree less than several percent for sputtered Ti atom density. Plasma parameters and mass-resolved analyses of incident ions were served for discussion on mechanism of ionization and ion flux incident to substrate. @FootnoteText@ @super 1@T.Nakamura and K.Okimura : to be appeared in JVST-A.

3:00pm **TF-ThA4 High Rate Growth of Cu Thin Films Using New Magnetron Sputtering Source***, H.K. Park,* Sungkyunkwan University, Korea, South Korea*; K.H. Nam, J.G. Han, **J.-H. Boo**,* Sungkyunkwan University, Korea

We have deposited the copper (Cu) thin films on Si(100) and stainless steel substrates in the growth temperature between room temperature and 500 °C using pulsed D. C. magnetron sputtering method. An unbalanced magnetron sputtering source with high current (20 - 120 mA/cm @super 2@) and low voltage (100 - 1000 eV) was designed and constructed for high rate deposition. Based upon the results of magnetic field simulation, we built-up the highest power (120 W/cm @super 2@) Cu magnetron sputtering source to enhance the sputtering yield and film growth rate. The maximum deposition rate and sputtering yield of the newly developed sputtering source are 2.8 µm/min. and 70%, respectively. When an ion extraction grid was adapted between the Cu target and substrate, however, the growth rate was increased over 3 µm/min. This is 10 times higher than that of conventional sputtering method, and the sputtering yield was also reached to 80% due to low voltage and high current Cu-accelerated ions. XRD and XPS showed that highly oriented polycrystalline Cu(111) thin films with no impurity were obtained on the stainless steel substrates. During film deposition, plasma diagnostics was also carried out in situ by optical emission spectroscopy analysis. Electrical conductivity was also measured with four-point probe method.

3:40pm **TF-ThA6 Low Temperature Hollow Cathode Sputter Deposition of Al@sub 2@O@sub 3@ Thin Films***, **A. Pradhan**, S.I. Shah, K.M. Unruh,* University of Delaware

Hollow cathode sputtering offers a novel way of conformally coating three-dimensional objects. It offers the added advantages of uniform sputtered flux and high plasma density. We have characterized a Hollow Cathode Source (HCS) for depositing alumina thin films by reactive sputtering. The target potential decreased sharply in the poison mode. This is contrary to what is observed in most reactive sputtering systems. This was attributed to the large secondary electron emission coefficient for Al@sub 2@O@sub 3@. The hysteresis behavior of planar sputtering was not observed. High growth rates at low power densities were obtained even in the poison mode. This was probably due to the enclosed geometry of the hollow cathode and very high cathode to anode area ratio. The oxidation state of the film was determined using X-ray Photoelectron Spectroscopy (XPS). The alumina content of the films increased sharply with the addition of oxygen to the system. Above a certain oxygen concentration pure Al@sub 2@O@sub 3@ films were obtained. A low cost high deposition rate method for depositing crystalline alumina films will be presented.

4:00pm **TF-ThA7 Influence of the Growth Conditions of AlN Films by Laser Ablation***, **A. Basillais**, C. Boulmer-Leborgne,* GREMI, France*; J. Perriere,* GPS, France

The pulsed laser ablation of targets in vacuum or in a reactive ambient gas (especially for oxide layer) is a very popular method for growing thin films with complex compositions and various properties. But the reliability of the pulsed laser deposition technique needs a wider understanding of thin film growth for nitride films. In this study we report AlN thin film growth by pulsed laser ablation of Al target in N2 reactive ambient gas compared to laser ablation of AlN target in vacuum or N2 gas. An approach of AlN film grown on Si(100) and Al2O3 substrates is studied. The best experimental conditions are defined in relation with film quality deduced from surface analysis (RBS, NRA, XPS, XRD, MEB). The influence of process parameters such as nature of the target, laser energy density and nitrogen partial pressure on the composition, chemical nature and structure of the films has been investigated. The main problem in AlN film growth was the oxygen incorporation. The origin of this contamination and the mechanisms of incorporation were studied, and the crucial parameter was found to be the residual pressure during ablation. Due to the difference in chemical reactivity between O and N, it is necessary to increase the density of atomic nitrogen to obtain pure AlN films. Thus, a RF discharge device was added allowing a better nitrogen molecule dissociation. Finally the hexagonal AlN phase can be formed in the laser deposited films. Highly textured films presenting epitaxial relationships with (001) Al2O3 substrates can be grown with only 5% oxygen contamination. The plasma plume investigation by emission spectroscopy allows the reactive species kinetics study for AlN growth. A secondary discharge device is mounted on the substrate to study the dark zone where there is no more plasma plume emission.

4:20pm **TF-ThA8 Low Temperature and Plasma Damage Free Deposition of Silicon Dioxide on Novel Film Deposition Method Called a Radical Shower-CVD (RS-CVD)***, **A. Kumagai**, K. Ishibashi, X. Ge, M. Tanaka, H. Nogami, O. Okada,* Anelva Corporation, Japan

A novel film deposition method called a Radical Shower-CVD (RS-CVD) has been developed for high quality gate-oxide film formation on low temperature Poly-Si TFT-LCD fabrication. RS-CVD has the advantages of both conventional plasma enhanced-CVD and remote plasma-CVD without having their disadvantages and is characterized by plasma damage free deposition on a large area substrate at a low temperature of about 300°C. As a silicon dioxide film is deposited on the substrate through the diffusion of SiO@sub2@ formed by the reaction of oxygen radical with SiH@sub4@ in the gas phase, oxygen radical quantity, distance from gas injection to substrate, and deposition pressure are very important as a control factor of gas phase reaction. Dependencies of film quality on those factors are investigated to confirm the optimization methods in RS-CVD film deposition process. The calculation of the gas phase elementally reaction have been performed to discussion the formation mechanisms of SiO@sub2@. As a result of this study, it was confirmed to be important in suppressing the contamination of the elements including the OH bonding groups in the films during the deposition itself. The oxygen radical quantity, the distance from gas injection to substrate, and the deposition pressure were useful to control the speed of overall reaction and the elements arriving at the substrate. It was important in the film properties to control the residence time of gases until they reach the substrate by adjusting those factors mutually.

Magnetic Interfaces and Nanostructures
Room 134/135 - Session MI-ThP
Magnetic Thin Films & Surfaces Poster Session

MI-ThP1 Magnetic Spectroscopy at the Elliptically Polarizing Undulator Beamline 4.0.2 at the Advanced Light Source, ***E. Arenholz****, A.T. Young,* Advanced Light Source

Beamline 4.0.2 is the first undulator beamline at the Advanced Light Source equipped with a Sasaki-type elliptically polarizing undulator (EPU). The EPU allows full control of the polarization of the x rays. Variable linear polarization from linear horizontal to linear vertical as well as 100% circular polarization are possible. The undulator in combination with a plane-grating-variable-included-angle monochromator is designed to provide high flux photon beams from 50 eV to 2000 eV, fully covering the L@sub 3,2@ edges of important magnetic transition metals (Fe, Co, Ni, ...) and also the M@sub 5,4@ edges of magnetic rare earth elements of interest (Gd, Tb, ...). We will present first experimental results that illustrate the ability of the beamline to detect small dichroism effects in dilute systems and materials which show only weak magnetic effects (<0.3%), giving us confidence in the suitability of the set up to study novel magnetic systems with high precision.

MI-ThP2 X-ray Magnetic Linear Dichroism of Fe-Ni Alloys on Cu(111), ***T.F. Johnson****, S. Chiang, Y. Sato,* University of California, Davis*; D.A. Arena,* Lawrence Livermore National Laboratory*; S.A. Morton,* University of Missouri-Rolla*; M. Hochstrasser, J.G. Tobin,* Lawrence Livermore National Laboratory*; J.D. Shine, J.A. Giacomo, G.E. Thayer, D.P. Land, X.D. Zhu,* University of California, Davis*; G.D. Waddill,* University of Missouri-Rolla

We have prepared Fe@subx@Ni@sub1-x@ multilayers on Cu(111) in order to learn how to control the structure and magnetism of these thin alloy films, which are relevant to the giant magnetoresistance (GMR) effect used in magnetic disk drive heads. Using the Spectromicroscopy Facility (7.0.1.2) on Undulator Beamline 7.0 at the Advanced Light Source, we have measured X-ray magnetic linear dichroism (XMLD) signals from both Fe and Ni 3p lines for fourteen different thin Ni-Fe alloy films on Cu(111), with Fe concentration ranging from 9% to 84% and for a variety of film thicknesses. The Curie temperature for all of these samples was in the range 200K to 500K. For many of these films, the Curie temperature was considerably lower than was previously seen for similar films deposited on Cu(100). For a particular Fe concentration x, the Curie temperature increases with alloy film thickness. For a specific film thickness, the Curie temperature has a maximum near x=0.4. We have also measured the Fe and Ni asymmetries as a function of Fe concentration.

MI-ThP4 Growth of Mn on Fe(001): Surface Alloy Formation and Multilayer Growth, *T. Yamada, M.M.J. Bischoff, A.J. Quinn,* University of Nijmegen, The Netherlands*; T. Mizoguchi,* Gakushuin University, Japan*;* ***H. van Kempen,*** University of Nijmegen, The Netherlands

A complicated relationship is usually found between the magnetic configuration of a magnetic thin film, the crystallographic structure and the electronic structure. Mn films on Fe(001) are the ultimate example of a system where all these properties are interwoven. Conflicting results are, e.g., reported on the magnetic properties, which suggest a strong dependence on impurities, intermixing, and growth mode. Scanning tunneling microscopy (STM) is the ideal technique to tackle this problem, since it allows studying both the atomic structure in the conventional constant current mode and the electronic structure in the spectroscopic mode. In this contribution, it will be shown that for deposition of submonolayers at temperature s above 400K, Mn atoms are place exchanged with Fe substrate atoms. Locally a c(2x2) MnFe surface alloy is formed. Spectroscopy measurements will be presented for incorporated Mn atoms, pure Mn islands, and the local c(2x2) MnFe alloy structures which all show characteristic features in the dI/dV spectrum. For growth of thicker Mn films at 400K, intermixed Fe atoms can still be observed until the third layer. Analysis of the step heights gives evidence that the structure relaxes after the second layer. From the fourth layer upon, spectroscopy measurements reveal a feature in the dI/dV spectrum which strength oscillates with layer thickness and therefore seems to be related with the reported antiferromagnetic coupling of the Mn layers. The spin-polarized nature of these surface states can be used to study the surface magnetism on a local scale in spin-polarized tunneling experiments. Experiments with Fe covered tungsten tips will be discussed.

MI-ThP6 Epitaxial Growth of Ferromagnetic Ni@sub 2@MnIn Thin Films on InAs (001), ***J.Q. Xie****, J.W. Dong, J. Lu, S. McKernan, C.J. Palmstrom,* University of Minnesota

There has been growing interest in ferromagnetic/semiconductor hererostructures for the development of spintronic devices which utilize the carrier's spin as well as its charge. InAs is the semiconductor of choice because of its high electron mobility and the ease to form an ohmic contact to it. Although no elemental ferromagnet is lattice matched to InAs, the lattice mismatch between the Heusler alloy Ni@sub 2@MnIn and InAs is only 0.2%. In bulk, Ni@sub 2@MnIn is reported to have a cubic (L2@sub 1@) crystal structure with a lattice constant a@sub 0@ = 6.069 Å and a Curie temperature ~ 314 K. Recent theoretical studies showed that the minority spins are situated at the @GAMMA@ point in Ni@sub 2@MnIn and the majority spins are far away from the @GAMMA@ point. Therefore, the band structure alignment between Ni@sub 2@MnIn and InAs would enhance the injection of the minority spins, suggesting that Ni@sub 2@MnIn may be a good choice for spin injection as a ferromagnetic contact. In this talk, we report on the epitaxial growth of Ni@sub 2@MnIn thin films on InAs (001) by the molecular beam epitaxy technique. Both in situ reflection high energy electron diffraction and ex situ x-ray diffraction, Rutherford backscattering spectrometry, and transmission electron microscopy measurements indicate the high-quality epitaxial growth of Ni@sub 2@MnIn films on InAs (001). The films have a Curie temperature ~ 170 K and a saturation magnetization ~ 420 emu/cm@super 3@. The lower Curie temperature, compared to that of bulk Ni@sub 2@MnIn, is believed to result from the growth of Ni@sub 2@MnIn in the B2 structure. Composition has a dramatic effect on the Curie temperature. For Ni@sub 2@MnIn@sub 1.7@, a Curie temperature of ~ 290 K was observed. If ordered films can be grown, significantly higher Curie temperatures may be expected.

MI-ThP7 On the Origin of the Thickness-dependent Dimensional-crossover in Ultrathin Magnetic Films, ***N.A.R. Gilman,*** Penn State University*; M. Hochstrasser,* Lawrence Berkeley National Laboratory*; R. Zhang, R.F. Willis,* Penn State University

We report experimental results that show that the order parameter @beta@, which determines the long-range (spin) ordering in magnetic thin films (M=M@sub o@(1-T/Tc)@super beta@), changes abruptly due to a crossover in dimensionality at different thicknesses in Ni(100), Ni(110) and Ni(111) films. We argue that the different critical thicknesses arise from finite-size quantization energies of the (spin) excitations, which are dependent on the magnitude of associated wavevectors spanning different crystallographic directions of the fcc Fermi surface. Experimental data on nickel alloys support this view.

MI-ThP8 Fabrication of CoCrTa Magnetic Film by RF-sputtering, ***Y. Ohta,*** Fukui National College of Technology, Japan*; K. Ohashi, T. Tsumori,* Shin-Etu Chemical Co., Ltd., Japan

CoCrTa longitudinal media was prepared by sputtering onto Si substrates at substrate temperature of 523 K by RF magnetron sputtering system. The films were fabricated at the substrate temperature of 523K and Argon gas pressure of 3.5 mTorr during sputtering. The film was deposited on surface Si and glass substrates. CoCrTa thin films of several thicknesses were prepared by sputtering. The microstructures and particle size were investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The crystal structure was checked by X-ray diffractometry (XRD) and the magnetic properties were measured by a vibrating sample magnetorometer (VSM). The underlayer thickness dependence of magnetic properties of CoCrTa deposited on Si and glass substrates were investigated. It was known that thickness of underlayer has significant influence the crystallographic texture and magnetic properties of the magnetic layer. CoCrTa layer deposited on the Si substrate revealed small size grain and smooth surface than ones deposited on the glass substrate.

MI-ThP9 Ion-beam Modification of the Physical Properties and the Structure of Fe/Si Multilayered Films, ***Y.P. Lee****, J.S. Park,* Hanyang University, Korea*; Y.V. Kudryavtsev,* Institute of Metal Physics, Ukraine*; J. Dubowik, B. Szymanski,* Institute of Molecular Physics, Poland*; J.Y. Rhee,* Hoseo University, Korea*; G.S. Chang,* Yonsei University, Korea

The influence of ion-beam mixing (IBM) on the strucure, and the magnetic, magneto-optical and optical properties of Fe/Si multilayered films (MLF) was investigated. The IBM was performed with Ar@super +@ ions of an energy of 80 keV and a dose of 1.5 X 10@super 16@ Ar@super +@/cm@super 2@. It was shown that the IBM destroys the layered structure of the MLF down to a depth of about 110 - 150 nm and leads to the formation of a new phase which is characterized to possess a perfect crystalline structure, a low coercivity and a Curie temperature of about 550 K. It is suggested that the phase formed by the IBM is a metastable Fe@sub 2@Si silicide with a B2 type of structure. An annealing of the ion-beam mixed Fe/Si MLF at 720 K destroys further the undisturbed layered structure at the bottom and also leads to a decomposition of the Fe@sub 2@Si phase into a metastable magnetically-hard Fe@sub 5@Si@sub 3@ silicide and, presumably, Fe@sub 3@Si.

MI-ThP10 Suface Magnetic Phase Diagram for a Semi-infinite Ferromagnet*, D.P. Pappas,* National Institute of Standards and Technology, Boulder*; A.P. Popov,* Moscow State Engineering Physics Institute, Russia, Moscow, Russia

The phase diagram for the orientation of the surface region is calculated in the parameter space defined by the surface and bulk anisotropy for semi-infinite systems and thin films. A discrete layer-by-layer approach is developed and compared to the continuum approach. We also consider the 1.5 atomic layer Fe on Gd system, and find that it is a good physical realization of the model. We find that suface magnetic canting always occurs when the magnitude of the surface anistropy is comparable with the interlayer exchange interaction.

MI-ThP11 Low Field Magnetoresistance through Grain Boundaries in Double Exchange Compounds*, D. García, **B. Alascio,*** Instituto Balseiro, Argentina

To model transport through the grain boundary of a manganite bicrystal we study the conductance of a spin chain doped with itinerant electrons which are strongly Hund coupled to the spin at each site. We induce a domain wall in the chain and propose a single site pinning mechanism. At large pinning we find that the magnetoresistance corresponds to that of two uniformly magnetized domains. Assuming uniaxial anisotropy within each grain we use the above results to calculate the magnetoresistance through the grain boundary and obtain remarkable agreement with experiment. Further, our study solves an apparent contradiction between experiments by different authors.

MI-ThP12 Formation of Barriers for Magnetic Tunneling: Ion Embedding vs Diffusion*, **S.O. Demokritov,** B.F.P. Roos, P.A. Beck, B. Hillebrands,* University Kaiserslautern, Germany

A novel type of oxidation technique, the ionized atom beam oxidation, was used to prepare ultrathin insulating aluminum oxide barriers for magnetic tunnel junctions. Thanks to high chemical reactivity of atomic oxygen combined with very low energy (30-50 eV) of the ions the oxide grows fast, homogeneous, and amorphous. The limited oxidation depth reduces the possibility of an overoxidation of the underlaying magnetic electrode. By means of in-situ techniques for monitoring the oxide growth during the oxidation, it was possible to identify two mechanisms which dominate the oxidation at different stages of the process. During the initial stage an ion embedding mechanism controls the oxidation. This mechanism describes the penetration of kinetic O-ions into the target metal layer until they are stopped on their way through the film by elastic and inelastic processes. The ions form chemical bindings with the surrounding metal atoms at their stopping place. The oxidation depth defined by this mechanism depends on the energy of the ions and reaches 1-2 nm. As the oxide layer grows, the incoming O-ions find less and less leftover metal atoms near their stopping place and a diffusion process starts to effect the oxidation. The further oxidation growth is determined by an electrical field controlled diffusion of metal and oxygen atoms. Monte-Carlo-simulations based on the developed "ion embedding with diffusion" model completely describe the formation of thin oxide barriers for magnetic tunnel junctions.

MI-ThP13 Non-monotonic Magnetic Surface Anisotropy of Epitaxial Fe Films Grown on Vicinal Substrates*, S.O. Demokritov, **M. Rickart**, J. Jorzick, B. Hillebrands,* University Kaiserslautern, Germany

The presented work is devoted to the study of the influence of atomic steps at the interface between a magnetic film and a substrate on the magnetic surface anisotropy of the film. Step induced anisotropy contributions appear because of the broken translational invariance perpendicular to the steps. The Fe films were prepared on vicinal MgO(001) substrates with Ag(001) and Au(001) buffers using a molecular beam epitaxy UHV system. Substrates with two different miscut orientations (along [100] and [110]) were used. In-situ characterization was performed by LEED, RHEED and SPM, and chemical analysis by Auger electron spectroscopy. Magnetic anisotropy contributions have been determined from the hysteresis loops and from frequencies of spin waves measured by Brillouin light scattering. In addition to the four-fold anisotropy intrinsic for (001) Fe films the vicinal films demonstrate an uniaxial anisotropy. The strength of the uniaxial anisotropy depends on the miscut angle, the miscut orientation, and the buffer material. Fe films prepared on Au buffers with the miscut orientation along the [100]-direction show an additional uniaxial anisotropy with the easy axis perpendicular to the steps. For the Fe films prepared on Au buffers with the miscut orientation along the [110]-direction a non-monotonic dependence of the anisotropy strength as a function of the miscut angle is observed: the orientation of the magnetic easy axis switches from parallel to perpendicular to the steps, crossing zero value between 1.5 and 2 degrees of the miscut angle. Fe films prepared on Ag buffers with the miscut orientation along the [100] direction shows the same orientation of the uniaxial anisotropy easy axis, as those prepared on Au, however the anisotropy strength is much higher than that observed on Fe/Au system. The properties of the observed uniaxial anisotropies are analyzed on the basis of the Neel pair-bonding model.

Thin Films

Room 134/135 - Session TF-ThP

Thin Film Deposition/Carbon-Containing Films Poster Session

TF-ThP1 Substrate Response During Dual Bipolar Pulsed Sputtering*, P.J. Kelly,* University of Salford, U.K., UK*; J. O'Brien,* University of Salford, U.K., England*; J.W. Bradley,* UMIST, U.K.*; **P.S. Henderson,*** University of Salford, U.K., UK*; R. Hall,* Advanced Energy Industries UK Ltd.

Dual bipolar pulsed sputtering is a highly successful technique for the deposition of dielectric materials. Operating in the mid-frequency range (20-350kHz), each magnetron acts alternately as an anode and a cathode. With the polarity of each magnetron alternating in this manner, target cleanliness is maintained, anode surfaces are preserved, and long term process stability is achieved. Asymmetric bipolar pulsed DC power supplies are commonly used to drive this process. In such instances, the target voltage during each pulse-off period typically reverses to approximately 10% of the nominal pulse-on voltage, i.e., if the pulse-on voltage is â€“400V, then the pulse-off voltage will be approximately +40V. However, as pulse frequencies are increased, particularly to in excess of 150kHz, target voltage waveforms increasingly depart from this idealised "square wave" behaviour. Very significant voltage overshoots are observed in each direction during each half of the pulse cycle. In particular, large positive overshoots are observed at the beginning of each pulse-off period. For example, at a pulse frequency of 350kHz, the target voltage can reach a peak value of +500V. Monitoring of the substrate I-V waveforms during operation has revealed that similar transient "spikes" also occur here. As a result, there is a short burst of high energy ions incident at the substrate during each "spikes", and since two targets are in use, these transients occur at twice the pulse frequency. Clearly, such bursts of high energy bombardment could have a significant influence on the growing film. Consequently, an investigation into the complex processes occurring at the substrate during dual bipolar pulsed sputtering has been carried out. A model is proposed to account for the observed phenomena, and the impact on film properties is considered.

TF-ThP2 Modified HFCVD System for Diamond Coatings on Dental Burrs*, H. Stein, **W. Ahmed,*** Manchester Metropolitan University, U.K.*; C.A. Rego, N. Ali,* Manchester Metropolitan University, U.K., UK

Chemical vapour deposited diamond films grown in a modified hot filament reactor using filament metals such as tantalum and tungsten have been optmised. The non-planar e.g. a small dental burrs or small metal abrading device was used as a substrate. The filament in hot filament chemical vapour deposition "HFCVD" plays an essential role in creating the gas phase species that enable and influence the diamond growth. The modification of HFCVD was such that the coiled filament was fixed vertically within the vacuum deposition chamber as opposed to horizontal position as used in conventional HFCVD systems. The dental burrs were placed within the coiled filament during deposition and this was the distinctive feature of the system. The substrate varied from 0.5mm to 1.25mm in diameter and were as long as 20mm. The as-grown diamond films were found to be polycrystalline, uniform and the film coverage was good. A preferential diamond (111) surface morphology has been obtained which is srongly dependent on diamond growth paramaters, including substrate and filament position in the reactor. Raman spectroscopy and scanning electron microscopy measurements confrimed the good quality of the obtained diamond films.

TF-ThP3 High Rate Deposition of Thick CrNx Films by Unbalanced Magnetron Sputtering*, **K.H. Nam**, J.H. Bin, J.G. Han,* Sungkyunkwan University, Korea

The high rate deposition processes such as high current arc, laser arc, hollow cathode discharge ion plating and magnetron sputtering method have been developed for cost effective industrial applications. Especially magnetron sputtering is emerging a very efficient method for high rate deposition of dense thin films. In previous works, we have synthesized CrNx films by magnetron sputtering. The deposition rate was reached to be about 0.6µ/min. and the microhardness was evaluated up to 2200kg/mm2. And then phase and microstructure were controlled by change of N2 partial pressure and pulsed DC bias. In this study, high rate deposition of thick CrNx films was carried out by magnetron sputtering for the special application such as piston ring employed in automobile engine. For the high rate deposition of CrNx films with thickness of 30µ, residual stress in films was controlled by various N2 partial pressure, target power density and bias in processing. The microstructure was analyzed by X-ray Diffraction(XRD) and Scanning Electron Microscopy(SEM) and mechanical properties were evaluated by microhardness test, residual stress and adhesion tests.

TF-ThP4 Comparison of Poly-Si Films Deposited by UHVCVD and LPCVD and Its Application for Thin Film Transistors*, **D.Z. Peng**, H.W. Zan,* National Chiao Tung University, Taiwan*; T.C. Chang,* National Sun Yat-Sen University, Taiwan, Taiwan, R.O.C.*; C.Y. Chang, P.S. Shih,* National Chiao Tung University, Taiwan

The ultra high vacuum chemical vapor deposition (UHV/CVD) system can deposite poly-Si film without any laser or furnace annealing at lower temperature (550C). The uniformity of threshold voltage and mobility is superior to that deposited by low pressure chemical vapor deposition (LPCVD) system. The threshold voltage and mobility deviation for UHV/CVD are 0.16V, 10%, respectively and 0.23V, 21% for LPCVD system. However, due to the deposition in polycrystalline phase for UHV/CVD, the film surface is rough and results in low field effect mobility (27 cm2/VS, after plasma passivation, p-type device) compared to that (103 cm2/V-s, after plasma passivation, p-type device) obtained by low pressure chemical vapor deposition (LPCVD) using disilane (si2H6) in amorphous phase followed by solid phase crystallization (SPC). It can be shown that poly-Si film thickness will influence the leakage current. In this thesis, NH3, N2 and N2O were used to passivate the devices. They have obvious improvement on device performance after plasma passivation, in addition, NH3 passivation will result in the smallest leakage currrent and highest on/off current ratio. However, N2O needs a longer passivation time compared to the other two. After passivation, the devices show a poor stress endurance compared to unpassivated devices.

TF-ThP5 Oxygen Partial Pressure Effect on the Properties of the Novel Semiconducting Alloy Cu@sub x@Cd@sub 1-x@Te Grown by rf Sputtering*, J. Santos-Cruz, **G. Torres-Delgado**, O. Jiménez-Sandoval, R. Castanedo-Pérez,* Cinvestav-IPN, Unidad Querétaro, Mexico*; B.S. Chao,* Energy Conversion Devices, Inc.*; P. García-Jiménez, S. Jiménez-Sandoval,* Cinvestav-IPN, Unidad Querétaro, Mexico

High quality thin films of the novel semiconductor alloy Cu@sub x@Cd@sub 1-x@Te have been succesfully grown by rf sputtering from a single target made of a mixture of high purity Cu and CdTe powders.@footnote 1@ Micro Raman experiments carried out on the Cu powder particles showed the existence of a CuO overlayer. However, the presence of such oxide, or of oxygen molecules, have not been detected as important components in the films. The role that oxygen plays during the growth and properties of the Cu@sub x@Cd@sub 1-x@Te films is unknown to date. In this work we report the results of a study about the effects of incorporating controlled amounts of oxygen during the growth of Cu@sub x@Cd@sub 1-x@Te thin films, on their crystalline structure, composition, and optical and transport properties. This study was carried out in a two-target sputtering system, in which one target is made of Cu and the other of CdTe. The native oxide on the Cu target surface was removed previously by presputtering for a few minutes before opening the deposition shutters. The controlled incorporation of oxygen into the chamber was achieved by using an electronic mass flow controller and the elemental composition profiles obtained by Auger spectroscopy. @FootnoteText@ @footnote 1@J. Vac. Sci. Technol. A 17, 1958 (1999); Thin Solid Films 342, 1 (1999); Microelectronics Journal 31, 429 (2000).

TF-ThP6 Reactive Dual Magnetron Sputtering Technology for Oxide Dielectric Film Deposition*, **S. Xu**,* HIVAC Technology(GROUP) CO. LTD, P.R. China*; X. Hou,* Tsinghua University, P.R. China*; C. Fan,* HIVAC Technology(GROUP) CO. LTD, P.R. China*; L. Zhao, L. Cha,* Tsinghua University, P.R. China

A study on oxide dielectric film deposition by medium frequency (MF) reactive dual magnetron sputtering (DMS) is reported in this paper. A continuous system for large-area deposition by DMS has been developed more than two years ago. The operation state of the DMS depends on the hysteresis curve of the target voltage with respect to the reactive gas (O@sub 2@) flow rate. The process was controlled by adjusting O@sub 2@ flow based on the target voltage in the closed-loop. Possible mechanism of physical and chemical processes on the target/substrate surface has been discussed. Based on the detailed experimental studies, criteria of the operation point according to the hysteresis were summarized. It was shown that magnetic field profile, distance between the two targets, structure of the shield, arrangement of the pipes for reactive gas supply and direction of the O@sub 2@ flow have strong influence on the time constant and film quality as well as the precision and stability of the feedback closed-loop. Characteristics of deposited SiO@sub 2@, Al@sub 2@O@sub 3@ and TiO@sub 2@ films have been evaluated, including thickness, uniformity, surface topography, crystal structure, stoichiometric composition, refractive index and transmittance, etc. Long term operation confirmed that uniform, dense and amorphous optical film could be deposited rapidly and stably.

TF-ThP7 Copper Metallization for ULSI Using 90°-bend Magnetic Filtered Cathodic Arc Evaporation Plasma System*, **J.-H. Lin**,* National Tsing Hua University, Taiwan, Taiwan, ROC*; U.-S. Chen, W.-J. Hsieh, H.C. Shih,* National Tsing Hua University, Taiwan

The cathodic arc evaporation plasma generated the highest plasma density compared with other PVD systems, but is known to be contaminated with macroparticles. In order to produce high quality defect-free copper films, a 90X-bend magnetic filter is suitable for ULSI interconnects metallization application. Macroparticle contamination has been alleviated by magnetic filter, the copper ions in the fully ionized copper plasma were accelerated and deposited on the wafer with a negative pulsed bias voltage. The fully ionized copper plasma flux was highly directionally deposited on the patterned and blank wafers, the filling of trenches/vias as narrow as 0.2 µm, with an aspect ratio as high as 7, FESEM and TEM images showed conformable copper step coverage ability. Both XRD and SEM/EBSD spectra showed that the FCAE-deposited copper film has an obvious Cu(111) preferred orientation. The result of this process as made, by scratch tests, showed that higher substrate bias and 50% pulse bias duty cycle can effectively enhance the adhesion strength of copper film on TaN layer.

TF-ThP8 Velocities and Ionization Degree of Vapor Stream Produced from Evaporation Source using Porous Rod by Electron Beam Heating*, **H.M. Ohba**,* Japan Atomic Energy Research Institute, Japan*; T. Shibata,* Japan Atomic Energy Research Institute

A metal vapor was produced by electron beam heating with high thermal efficiency using a hearth liner and a porous rod for copper and cerium. While the top surface of the porous rod was heated by electron beam, the molten evaporation material surrounding the rod was transferred to the top surface by capillarity; then the atomic vapor stream was produced from the top surface. The ionization degree and the vapor velocities were measured with Langmuir probes, and a microbalance or laser induced fluorescence. The vapor characteristics were compared by evaporation from the bare water-cooled copper crucible. The ionization degree in the metal vapor is proportional to the electron beam current of the electron gun. In the case of evaporation from the porous rod, so a large amount of vapor flux can be produced at low electron beam current that the degree of ionization of metal vapor in the vicinity of the source is very low. The velocities of vapor produced from the porous rod were lower than that from the bare crucib le even at high vapor flux. The lower velocity for the porous rod was explained as follows. The excitation and ionization energies of the atoms evaporated by electron impact are converted to the kinetic energy of the vapor atoms by atom-atom collision. In the case of the porous rod, the rate of electron impact ionization of the evaporated atoms is lower than that of the bare crucible.

TF-ThP9 Effects of Plasma Exposure on Structural and Optical Properties of TiO@sub2@ Films Deposited by Facing Targets Sputtering

__T. Takahashi__, H. Nakabayashi, N. Sasai, K. Masugata, Toyama University, Japan

In sputtered films, it is very important to investigate the influence of plasma exposure to the substrate because the properties of films strongly depend on the plasma state. So, in this study, TiO@sub2@ films have been deposited at different substrate positions using the facing targets sputtering which can easily vary the degree of plasma exposure. The plasma was confined sufficiently between two Ti targets faced each other. The substrates were placed at a certain distance from the middle of a straight line connecting the centers of the targets' planes. TiO@sub2@ films with thickness of about 2-3 µm were reactively deposited on glass-slide substrates. The crystal structure, and optical properties of films were measured using a X-ray diffractometry and a Raman spectroscopy, and a spectrophotometer, respectively. The A(101), A(200), A(112) and A(220) peaks were observed from the X-ray diffraction patterns, where A shows an anatase of TiO@sub2@. With increasing plasma exposure, X-ray peak intensities I@subP@ of A(101) and A(200) gradually decreased, and I@subP@ of A(112) and A(220) gradually increased, respectively. I@subP@ significantly depended on the substrate position in this study. Moreover, A(220) peak was significantly higher than others and the TiO@sub2@ crystallites became larger with an increase of plasma exposure. TiO@sub2@ films also showed anatase from the Raman spectra with Raman shift of 145 cm@super-1@. With decreasing plasma exposure, the changes in the optical transmittance spectra of TiO@sub2@ films were very small at the wavelength of 350-900 nm. However, the transmittance spectra significantly depended on the wavelength with increasing plasma exposure. The transmittance monotonically decreased with decreasing wavelength in the range of 700 to 350 nm. Consequently, it was found that crystal structure and optical properties of TiO@sub2@ films were strongly affected to plasma exposure during deposition.

TF-ThP10 High Rate Deposition of TiO@sub 2@, TiN, and TiO@sub 2@/TiN/TiO@sub 2@ Thin Films Using New High Power Magnetron Sputtering Source and Comparison with Its Optical Characteristics

M.J. Jung, H.Y. Lee, __Y.-S. Sin__, J.G. Han, J.-H. Boo, Sungkyunkwan University, Korea

Thin films of TiO@sub 2@, TiN and TiO@sub 2@/TiN/TiO@sub 2@ were deposited on glass substrates at a temperature below 200 °C using a newly developed pulsed DC magnetron sputtering source with high power (20 - 150 W/cm @super 2@) and unbalanced magnetron. Titanium metal target (4-inch diameter, 99.9% purity) was mounted onto the sputtering sources, and oxygen and nitrogen were used as reactive gases and argon as working gas. Highly oriented, crack-free, stoichiometric polycrystalline TiO@sub 2@(101) and TiN(100) thin films were successfully grown on glass surfaces at 200 °C. In the case of the TiO@sub 2@ deposition, a thin film with high transmittance (90%) in the visible range was obtained while the TiN films showed very high reflectance (70%) in the infrared region. In this study, however, we found that the transmittance and reflectance are strongly influenced by the film thickness and the film surface roughness. For comparison, a multilayer film of TiO@sub 2@/TiN/TiO@sub 2@ was also deposited on glass substrates under the same growth condition as for TiO@sub 2@ and TiN thin films based on computer simulation results. Quite good optical properties can be obtained for the as-grown multilayer films. The most excellent values of transmittance (85%) and reflectance (80%) were found for a thin film with TiO@sub 2@ (380 nm)/TiN (20 nm) /TiO@sub 2@ (440 nm)/glass structure. The high IR reflection indicates that the as-grown multilayer film can be applied for heat mirrors.

TF-ThP11 Deposition of Dielectric Films by Photo Chemical Vapor Deposition using Vacuum Ultraviolet Xe2 Excimer Lamp from Tetraethoxysilane

__N. Horii__, A. Inouye, H. Nishibata, Fukui National College of Technology, Japan*; K. Okimura,* Tokai University, Japan

Dielectric films have deposited by photo-chemical vapor deposition (CVD) using Xe2 excimer lamp as a vacuum ultraviolet light source. Tetraethoxysilane was used as a silicon source. The goal of the research was to obtain insulation films for between layers in LSI fabrication and plasma free environment for sensitive substrate at low temperature. First, photo-chemical dissociation process of TEOS in the gas phase was investigated by in-situ mass spectrometry. We have found that TEOS was dissociated by VUV irradiation while releasing alkyl groups such as CxHy (x=1-2,y=2-5). Moreover, almost all Si-O bonds of TEOS were not broken at the energy of Xe2 excimer light. These are main reaction of the forming precursors for film deposition in the photo CVD process. A structure of films was investigated by FTIR analysis. The film prepared from TEOS at room temperature was SiOxCx like film having large amount of CH groups, however, Si-OH bonds was not included. Investigation of a stability of the films in ambient air was obtained undesirable results such as the Si-OH bonds increased and the film thickness decreased by the day. In order to improve a stability of the films we have irradiated VUV light to deposited films at room temperature. The result from the technique was effective for reducing unstable CH groups contained in the films and obtaining a good chemical and physical stability.

TF-ThP12 Bahaviours of Energetic Oxygen Particles in the Reactive Sputtering of Zr Target in Oxygen Atmosphere

__K. Tominaga__, T. Kikuma, K. Kusaka, T. Hanabusa, The University of Tokushima, Japan

ZrO@sub@2 films were deposited in oxygen atmosphere with conventional planar magnetron sputtering system. In a sputtering of oxide target, energetic negative oxygen ions and energetic neutral oxygen atoms are bombarding the film. Then energetic oxygen ion s are generated in cathodefall in front of an oxide target. Precauser of the energetic neutral atoms is the negative oxygen ions that are accelerated in the cathode fall. These energetic particles bombard depositing oxide film and degrade film qualities s uch as internal stress, insulative characteristics. However, these energetic particles in a reactive sputtering is not so clear, especially in cases of materials such as Zr that is active with oxygen. We investigated the degree of the energetic oxygen particles in ZrO@sub2@ deposition and the generation mechanism of the energetic oxygen particles. Strong energetic oxygen ions generated in the sputtering of the Zr oxide target in O@sub2@ atmosphere were ascribed to the strong oxidization at the Zr surface. The energetic negative oxygen ions were detected using a probe constructed here. At the same time, the photoemission intensity from the sputtered Zr atoms was observed in order to monitor the target surface oxidization. The results show that the Zr targe t is very active with the oxidization of the target surface and drastically oxidized in a metal mode sputtering. The strong negative oxygen ions in an oxide mode sputtering are due to the generation of thick Zr-oxide layer on the Zr target. At the same time, films were prepared by the two sputtering modes and the relation the film properties and the energetic oxygen ions were investigated.

TF-ThP13 In-situ Fabrication of Polycrystalline Thin Film Cathodes for Secondary Thin Film Batteries using Radio Frequency Sputter Deposition

K.-F. Chiu, __F.C. Hsu__, M.K. Wu, T.-P. Perng, National Tsing Hua University, Taiwan

In situ deposition of polycrystalline LiNi0.8Co0.2O2 thin films was performed using radio frequency magnetron sputter deposition on indium tin oxide substrates. Different substrate temperatures, upto 500 oC, were applied during deposition. The films deposited at elevated temperature exhibited a strong preferred orientation (or texture). It was found that varying the substrate temperature resulted in changing in film texturing. As the substrate temperature increased, the film structure changed from non-crystalline to polycrystalline with enhanced preferred orientation. The film texture was examined using X-ray diffraction (XRD) method. The surface morphology was observed using optical microscope and scanning electron microscope. The compositions of the targets and films were characterized by an inductively coupled plasma spectroscopy method (ICP) and were found to be identical. The change of texturing was interpreted by volume strain energy and surface energy minimization. Textured polycrystalline thin films can be deposited by controlling the deposition temperature. The technique was also used to deposit polycrystalline LiCoO2, LiNiO2 and LiMn2O4 thin films, and similar results were obtained.

TF-ThP14 Effects of Deposition Parameters and Physical Properties of Thin NiO Films on Gas Sensing Characteristics

***I. Hotovy**,* Slovak University of Technology Bratislava, Slovakia*; L. Spiess,* Technical University of Ilmenau, Germany*; P. Siciliano, S. Capone,* IME-CNR Lecce, Italy

Our research has been focused on the preparation and characterization of NiO thin films deposited by reactive magnetron sputtering. Small gas sensors on alumina substrate with different NiO thin films were fabricated and then were investigated their physical and sensing properties for application to nitrogen oxide. In order to apply NiO thin films to the nitrogen oxide gas sensor, NiO thin films (2000 Å) were prepared by dc reactive magnetron sputtering from a nickel metal target in an Ar@+@ O@sub 2@ mixed atmosphere in two sputtering modes. Details about the deposition of NiO have been reported in previous papers.@footnote 1@ The oxygen content in the gas mixture varied from 20 to 60 %. The films deposited in the metal-sputtering mode resulted in a polycrystalline (fcc) NiO phase with nearly stoichiometric composition. On the contrary, the films prepared in the oxide-sputtering mode were amorphous and oxygen rich. The post-annealing (500@degreeo@C) of as-deposited NiO thin films changes amorphous to the (fcc) NiO phase for samples prepared in oxide-sputtering mode. TEM observations revealed a dense fine-grained structure with the grain size in the range 40-100 Å. AFM showed that the surface morphology NiO films could be modified by the process parameters as the oxygen content and the pumping speed. SEM observation and EDX analyses revealed uniform morphology and homogenous dispersion of NiO, Pt and Al@sub 2@O@sub 3@ phases. We have investigated the sensitivity (I@sub g@/I@sub o@) versus operating temperature of NiO films when a concentration varied from 1 to 10 ppm of NO@sub 2@. @FootnoteText@ @footnote 1@ Hotovy, I., Huran, J., Spiess, L., Hascik, S.: Sensors and Actuators B 57 (1999) 147-152.

TF-ThP16 Computer Modeling of Thin Metal Films for Advanced Devices*, L He,* San Jose State University

Computer simulation for semiconductor devices and process is becoming more and more important due to the high cost of device fabrication and processing. In recent years, semiconductor optoelectronic device has undergone explosive growth. This growth has fueled a vast expansion of device modeling and simulation. Low temperature (LT) process on metal thin film has been proven effective to increase Schottky barrier height and reduce film resistivity in recent study. For the potential application of LT process in advanced semiconductor devices, a computer simulation program is developed. The computer simulation focus on microstructure and electric properties of the thin metal films. Metal-semiconductor-metal (MSM) photodetectors are widely used in the optoelectronic integrated circuit receivers because of their compatibility with the preamplifier for their planar integration scheme, the minimum number of processing steps, high performance, and low cost. InGaAs/InP is chosen for long wavelength application. In this work, analysis based on the results of computer simulation is presented. The Ag/InGaAs/InP contact formed by LT process showed that the Schottky barrier height is as high as 0.64eV. This value is more than double of the barrier height when processed in room temperature. It is believed that the LT process could greatly enhance the performance of a MSM photodetector. The device simulation includes RC time simulation, frequency response, and efficiency analysis.

TF-ThP18 Structural Stability of Amorphous Al78W22 Thin Films Below Crystallization Temperature*, N. Radic,* Rudjer Boskovic Institute, Croatia*; J. Ivkov,* Institute of Physics, Croatia*; A. Tonejc,* Faculty of Sciences, Croatia*; T. Car,* Rudjer Boskovic Institute, Croatia

In this work the structural stability of Al78W22 amorphous thin films upon isochronal and isothermal heating below crystallization temperature (about 840 K) is reported. The amorphous Al78W22 films were prepared by a magnetron co-deposition onto alumina ceramic, sapphire, and glass substrates, held at four temperatures: LN2, RT, 200 degC, and 400 degC, respectively. Their stability was investigated by a continuous in situ electric resistance measurements during a two kinds of thermal treatment: a) A cycle of isochronous heating of the as-deposited sample up to 790 K, isothermal annealing at that temperature for 6 hrs, followed by cooling to room temperature. A strong irreversible variation of the film electrical resistivity is observed upon first heating. It is less pronounced at higher heating rates, presumably due to the competition between the relaxation of amorphous structure and temperature dependence of the resistivity. Deposition onto substrates held at high temperatures also strongly reduces the amount of resistivity variation. b) Isothermal annealing at high subcrystallization temperatures (803, 813, and 823 K) for several tens of hours resulted in a partial phase transformation of the amorphous alloy into the intermetallic Al4W compound. The Johnson-Mehl-Avrami model analysis of the phase transformation kinetics yields the Avrami coefficent close to 1, suggesting a nucleation as a crystallization mechanism. The above results show that the amorphous Al78W22 films require an initial annealing in order to attain the structural stability against heating, which is then retained in a marked degree even during a prolonged heating at the high subcrystallization temperatures.

TF-ThP19 Composite Ti/C:H Films and Their Potential Application*, H. Biederman, D. Slavinska, H. Boldyreva, S. Gretchany,* Charles University, Czech Republic*; **S. Kvasnica,*** Boltzmann Inst. for Biomedical Microtechnology and Vienna Univ. of Tech., Austria*; W. Fallmann,* Vienna University of Technology, Austria*; L. Bacakova, V. Stary,* Academy of Sciences of the Czech Republic

Titanium containing carbonaceous thin films have been examined for some time because of their tribological properties@footnote 1-4@ and because of the prospect of their biomedical applications.@footnote 5,6@ Composite Ti/CH films reveal hardness Hv up to 35 GPa and coeficient of friction below 0.3 for Ti concentrations below 40 at % The presence of Ti in C:H matrix causes cellular reactions of bone marrow cells. Therefore Ti/C:H hard coating can be applied for bone implants. Composite Ti/CH films were deposited using an unbalanced dc planar magnetron equiped with Ti target operating in Ar/n-hexane or Ar/methane mixtures. Deposition process is described in relation to composition and structure as well as basic electrical, optical properties and hardness of the films. XPS analysis of the film surface revealed considerable oxidation and static contact angle of a water droplet ranged from 68 to 85 deg. The potential application of these films for bone implants has been assessed. @FootnoteText@ @footnote 1@ N.E. LoBiondo, R. R. Aharonov, R. P. Fontana, Surface and Coatings Technol.,94-95(1997), 652-657 @footnote 2@ C. Donnet, J. Fontaine, T. LeMogne, M. Belin, C. Heau, J.P. Terrat, F. Vaux, G. Pont, Surface and Coatings Technol.,120-121(1999), 548-554 @footnote 3@ T. Krumpiegel, H. Meerkamm, W. Fruth, C. Schaufler, G. Erkens, H. BÃ¶hner, Surface and Coatings Technol.,120-121(1999), 555-560 @footnote 4@ T. Zehnder, J. Ptscheider, Surface and Coatings Technol.,133-134(2000), 138-144 @footnote 5@ R. Hauert, L. Knoblauch-Mayer, G. Francz, A. Schroeder, E. Wintermantel, Surface and Coatings Technol.,120-121(1999), 291-296 @footnote 6@ L. Bacakova, V. Stary, O. Kofronova, V. Lisa: Polishing and coating carbon fibre-reinforced carbon composites with a carbon-titanium layer enhances adhesion and growth of osteoblast-like MG63 cells and vascular smooth muscle cells in vitro, J. Biomed. Mater. Res. in press 2001.

TF-ThP20 The Effect of Substrate Bias and Nitrogen Incorporation on the Diamond-like Carbon Film Depositions by 90°-bend Magnetic Filtered Cathodic Arc Evaporation Plasma*, W.-J. Hsieh,* National Tsing Hua University, Taiwan*; J.-H. Lin,* National Tsing Hua University, Taiwan, Taiwan, ROC*; P.-S. Shih, X.-W. Liu, H.C. Shih,* National Tsing Hua University, Taiwan

The properties of nitrogen incorporated diamond-like carbon (DLC) films were deposited on silicon (111) wafers by a 90°-bend Magnetic filtered cathodic Arc Evaporation Plasma system. The structure and properties have been studied by TEM/EELS, Raman spectra, Vickers hardness, RBS, and SIMS spectra. For the DLC depositions using highly ionized energetic plasma, carbon ions with varying energies can form different types of carbon bonding in the films. The energies can be controlled by applying a variable bias to the substrate. It has been reported that the DLC films have the highest hardness with a substrate pulsed bias between -100V to -150V, and the maximum sp@super3@ bonding content can be obtained at a pulsed bias of -150V (duty cycle:50%) is up to 85% as measured by TEM/EELS. The DLC films have a higher hardness when the content of sp@super3@ bonds have a higher fraction of sp@super3@ bonding contents. The hardness seems to be related to the Raman I(D)/I(G) ratio. It also founds that nitrogen content increases with increasing substrate bias and the deposition temperature on DLC films. However, the deposition above 400°C causes a sudden loss of sp@super3@ bonding. The maximum incorporation of nitrogen to the DLC films was measured up to 15%(N) by SIMS as well as RBS.

TF-ThP21 DLC Thin Films Characterized by AES, XPS and EELS*, E.C. Samano,* *G. Soto, L. Cota,* CCMC-UNAM, Mexico

DLC films have been grown by laser ablating a graphite target in a UHV system. Two kinds of depositions are processed depending on the experimental conditions, a HOPG film and a DLC film. A relationship of the film microstructure with laser power density and substrate conditions was observed. The films are in situ monitored and characterized during the first stages of the deposition process by means of surface spectroscopic techniques, such as AES, XPS and EELS. The film microstructure is confirmed by SEM. Clear evidence of a SiC interface of two monolayers thick was clearly observed to form due to the reaction of the first carbon species impinging on the substrate surface.

TF-ThP22 Physical Properties of Nitrogen Doped Diamond-Like Amorphous Carbon Films Deposited by Supermagnetron Plasma CVD*, H. Kinoshita,* *N. Otaka,* Shizuoka University, Japan

Diamond-like amorphous carbon films doped with nitrogen (DAC:N) were formed using a supermagnetron plasma chemical vapor deposition (CVD) method.@footnote 1@ The electrical conductive DAC:N films were studied for the fabrication of high performance field emitters. DAC:N films were deposited on Si and glass wafers intermittently using i-C@sub 4@H@sub 10@/N@sub 2@ repetitive plasma CVD. CVD duration was selected to be 40sec or 60sec, and several layers were deposited repetitively to form one film. Physical properties such as deposition rate, hardness, resistivity and optical band gap were measured at lower-electrode temperature of 100 °C as a function of upper- and lower-electrode rf powers (200W/200W-1kW/1kW) and N@sub 2@ concentration (0-80%). With increase of rf powers supplied to two electrodes, resistivity, hardness and optical band gap decreased monotonously. Refractive index, however, was almost constant to 2.0-2.1. With increase of N@sub 2@ concentration at rf powers of 1kW/1kW, deposition rate, hardness, resistivity and optical band gap decreased monotonously. With increase of plasma CVD duration from 40sec to 60sec, resistivity decreased to 0.032@ohm@cm and optical band gap decreased to 0.02eV, at N@sub 2@ concentration of 80%. FT-IR spectroscopy measurements revealed that, with increase of N@sub 2@ concentration, absorption peak intensities of NH single and CN triple bonds increased and that of CH single bond decreased. @FootnoteText@@footnote 1@H.Kinoshita and M.Yoshida, J.Vac.Sci.Tecnol.A 19, July (2001).

TF-ThP23 Fabrication of Diamond Photocathode of Transmissive Type*, K. Kato*, *K. Ito, M. Hiramatsu, M. Nawata,* Meijo University, Japan*; C.H. Lau, A. Bennett, J. Foord,* University of Oxford, UK*; R. Jackman,* University College London, UK

Diamond is attractive as a "visible-blind" photocathode material for UV imaging, in view of its wide band gap and optical absorption properties, electrical transport characteristics and chemical stability. Under the negative electron affinity (NEA) condition, when the photon energy is higher than the band gap, the electrons are excited to the conduction band as a result of UV absorption, transported to the surface and then escape into vacuum. In order to realise the efficient diamond photocathode, it is n ecessary to optimise the optical absorption coefficient, the electron diffusion length in the bulk, and the surface escape probability. An investigation of these parameters is the purpose of the current work. Two types of diamond photocathode have been fabricated, for conventional reflective mode (UV photons and electrons interact with the same surface) and, for the first time, the more demanding trasnsmissive mode operation (electrons emitted from the opposite surface to the incoming UV light). The efficiencies of these two designs are compared and discussed in terms of the fundamental optical and electronic properties of the diamond films. In addition, we have investigated systematically the influence of a variety of surface treatments upon the photo-emissive properties of diamond photocathode, with differing levels of hydrogenation and oxidation. As a result of oxygen surface treatment, a drastic decrease in the photocurrent was observed. The use of the alkali metals, caesium and potassium in conjunction with various oxidation treatments is therefore explored in order to stabilise high quantum photo yield.

TF-ThP24 Fabrication of Carbon Whisker Film Using RF Plasma CVD*, K. Ito,* *K. Kato, M. Hiramatsu, M. Nawata,* Meijo University, Japan*; M. Hori,* Nagoya University, Japan*; C.H. Lau, J. Foord,* University of Oxford, UK

In the case of film formation by utilizing the plasma enhanced chemical vapor deposition (PECVD) method, it is desirable to supply selectively reactive species suitable for the film growth onto the substrate. Previously we demonstrated the successful formation of diamond crystals using a unique PECVD system, which has the parallel-plate capacitively coupled radio-frequency (rf, 13.56 MHz) discharge plasma assisted by the hydrogen radical source using the remote microwave (2.45 GHz) discharge plasma.@footnote 1@ In the present work, by using this system with a mixture of C@sub 2@F@sub 6@ and H@sub 2@, carbon films with whisker array were successfully formed on Si (100) substrate at C@sub 2@F@sub 6@/H@sub 2@=0.3/13 Pa, rf power of 100W, microwave power of 100W, and substrate temperature of 600 °C. Deposited films were characterized by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Although fluorocarbon gas was used as a source gas, fluorine was not detected in the deposited film from the XPS analysis. Surface morphology was changed from pyramids to whiskers according to the deposition conditions. Field emission characteristics have been investigated for the fabricated carbon film with whisker array. The V-I characteristics revealed a current density of 750 µmA/cm@super 2@ at an applied field of 60 V/µmm. Corresponding Fowler-Nordheim plot was well fitted by the straight line, indicating that the field emission property can be explained by a tunneling mechanism. @FootnoteText@ @footnote 1@M. Hiramatsu, M. Inayoshi, K. Yamada, E. Mizuno, M. Nawata, M. Ikeda, M. Hori, T. Goto, Rev. Sci. Instrum., 67 (1996) 2360.

TF-ThP26 Effect of Ar Addition on Microstructure and Composition of Nitrogen Containing Carbon Films Prepared by Hot Filament CVD*, Y. Watanabe*, *A. Yamazaki, N. Kitazawa, Y. Nakamura,* National Defense Academy, Japan

Nitrogen containing amorphous carbon (a-CNx) films were synthesized on Si (100) substrates by hot filament chemical vapor deposition method using a carbon filament, which supplies carbon and heat. Deposition was performed in low pressure atmosphere of pure nitrogen and a gas mixture of nitrogen and argon. Effects of argon addition on film microstructures and composition were studied by changing the argon fraction under the total pressure of 100 Pa. The film microstructure was observed by field-emission scanning electron microscope (FE-SEM) and the composition was analyzed by X-ray photoelectron spectroscopy (XPS). FE-SEM observations reveal that films prepared in pure nitrogen atmosphere show a columnar structure, while the films change to tapered structure with argon addition. Spectra of XPS show that the films were composed of carbon and nitrogen, and no contamination was observed except a small amount of oxygen. It is also found that the nitrogen concentration in films increases in dependence on argon partial pressure.

Electronics
Room 131 - Session EL+SE+TF-FrM
Laser Processing of Surfaces

8:20am **EL+SE+TF-FrM1 Laser Creation of 3D Micro- and Nano-objects: Processing, Properties and Applications**, ***M.J. Stuke,*** *M. Koch,* Max-Planck-Institut f. Biophys. Chemie, Germany*; A. Moore,* University of the Pacific*; K. Mueller,* Max-Planck-Institut f. Biophys. Chemie, Germany*; G. Padeletti,* CNR Monterotondo*; K. Williams,* Max-Planck-Institut f. Biophys. Chemie, Germany*; G. Fuhr,* Humboldt University, Germany **INVITED**

Recent results obtained by VUV laser ablation of organic fibers and by laser direct write of 3D microelectrode structures will be described with special emphasis on: (1) creation of a cage on a tip for touch-free trapping, handling and transfer of NEUTRAL objects in solution. Video sequences will give direct evidence for the new possibilities (2) ultraprecise machining of spider fibers, an ultrastrong material.

9:00am **EL+SE+TF-FrM3 Excimer Laser Surface Treatment for Aluminum Carbide Growth***, **F. Fariaut,*** GREMI, France

The excimer laser process reported is developed to enhance the mechanical and chemical properties of aluminum alloys. It would be interesting to use aluminum alloys in the automotive industry widely because of their low density, corrosion resistance and good workability. The motor weight can be reduced by replacing usual materials such as iron-steel by light alloys treated to increase their wear resistance. Ceramic materials generally exhibit great strength, resistance to wear and oxidation. The use of laser beams allows surface treatment to be located at the parts strongly exposed to wear and friction. The surface undergoes a transformation leading to an increase in hardness without changing the dimensions of the piece, thus avoiding no remachining after treatment. The laser process is especially suitable for environment protection as there is no pollution by chemical solvent or emanation. An excimer laser beam is focused onto the alloy surface in a cell containing 1 bar propylene gas. A vapor plasma expands from the surface and shock wave dissociates and ionizes the ambient gas. It is assumed that carbon from plasma in contact with the surface penetrates in depth. Thus it is necessary to work with a sufficient laser fluence to create the plasma, but this fluence must be limited to prevent laser-induced surface roughness. The carbon concentration profiles are determined from RBS and SEM coupled to EDX analysis. Crystalline quality is evidenced by XRD technique. TEM gives the in-depth microstructure. Fretting coefficient measurements exhibit a lowering for some experimental conditions. The polycrystalline cemented layer obtained is several micrometers thick and composed of a pure composition (columnar microstructure) top layer (200-500nm thick) standing on a diffusion layer (grains). This layer allows a significant decrease in the fretting coefficient.

9:20am **EL+SE+TF-FrM4 Laser Surface Treatment for Corrosion Prevention***, **C. Georges,** N. Semmar, C. Boulmer-Leborgne,* GREMI, France*; C. Perrin, D. Simon,* CERI, France

The materials used in electrical contact applications are constitued of a copper alloy (brass or bronze) covered with nickel coating (diffusion barrier) and with a gold coating. There are some porosities in the nickel and gold layers which induced corrosion of the underlying layers. To modify structure of gold coating, some laser surface treatments have been undertaken. An excimer laser is used as the photon absorption coefficient is larger in UV range and because the laser beam homogeneity is available for a surface treatment. The purpose of this surface treatment is to suppress the porosities of the gold layer which are responsible of the corrosion pits and to smooth the surface as the roughness bothers a correct electrical contact. The effects of the laser treatment are studied according to different surface parameters (roughness and composition of the substrate, thickness and composition of the gold coating). The laser beam parameter influence on surface melting is simulated by numerical code. Tests of corrosion are carried out in the humid synthetic air containing low contents of pollutants (NO2, SO2 and Cl2). The technique used to control these effects are : optical microscopy, SEM, grazing X-rays and ESCA. One dimension heat conduction is resolved to simulate the temperature time evolution and the melted depth as a function of the laser parameters (laser fluence, pulse time duration). This modelling helps to the understanding of mechanisms for laser interaction with the connector surface and will allows to determine the laser type to use for this appication.

9:40am **EL+SE+TF-FrM5 Laser Processing Opportunities with a High Average Power Free Electron Laser***, **H.F. Dylla,** S.V. Benson, J. Boyce, G. Biallas, D. Douglas, G.R. Neil, R. Evans, A. Grippo, J. Guebeli, K. Jordan,* Jefferson Lab*; M.J. Kelley,* Jefferson Lab and College of William and Mary*; R. Li, L. Merminga, J. Preble, M. Shinn, T. Siggins, R.W. Walker, G.P. Williams, B. Yunn,* Jefferson Lab

A kilowatt class free electron laser has been operational at Jefferson Lab since 1999. The associated user facility laboratories are being used for laser-materials studies that take advantage of the FEL's high average power, broad tunability and sub-picosecond pulse structure. The presently operating FEL delivers kilowatt level powers over the mid-infrared (3-7 microns). Recently, the device has extended operation through the visible (at the 100 watt level) and the UV (at the 10 watt level) through harmonic generation. A major upgrade is currently under way that will increase the power level in the IR to 10 kW and extend kilowatt operation through 300 nm in the UV. FEL users involved in materials processing have demonstrated unique applications involving: pulsed laser deposition, laser nitriding, laser production of carbon nanotubes, laser ablation and laser micromachining.-This work supported by the Office of Naval Research, the Commonwealth of Virginia, DOE Contract DE-AC05-84ER40150, and the Laser Processing Consortium.

Thin Films
Room 123 - Session TF-FrM
Diamond and Related Materials

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

8:20am **TF-FrM1 Synthesis and Characterization of Highly Conducting Nitrogen Doped Ultrananocrystalline Diamond Films***, **J. Birrell,** O. Auciello, S. Bhattacharyya, J.A. Carlisle, L.A. Curtiss, A.N. Goyette, D.M. Gruen, J. Schlueter, A.V. Sumant, P. Zapol,* Argonne National Laboratory

Diamond has many superior materials properties, yet its application in electronic devices is severely limited due to the difficulty of producing n-type thin films of sufficiently high conductivity. In this work ultrananocrystalline diamond (UNCD) films with up to 0.2% total nitrogen content were synthesized by a microwave plasma enhanced chemical vapor deposition (MPCVD) method using a CH@sub 4@ (1%)/Ar gas mixture with 1-20% nitrogen gas added. CN and C@sub 2@ radicals are identified in the plasma and both their relative and absolute concentrations change as N@sub 2@ gas is added. The morphology and transport properties of the films are both greatly affected by the presence of CN. High-resolution TEM data indicated that the grain size and GB width increase with the addition of more than 5% N@sub 2@ in the plasma. The electrical conductivity of the nitrogen-doped UNCD films increases by five orders of magnitude (up to 143 @ohm@@super -1@ cm@super -1@) with increasing nitrogen content. Conductivity and Hall measurements made as a function of film temperature down to 4.2 K indicate that these films have the highest n-type conductivity and carrier concentration demonstrated for phase-pure diamond thin films. Grain-boundary conduction is proposed to explain the remarkable transport properties of these films, in which nitrogen segregates to the grain-boundaries and promotes sp@super 2@ bonding and the introduction of more states into the fundamental gap, leading to enhanced electron transport. Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

8:40am **TF-FrM2 Probing Surface Species on a Diamond C(111) Surface During the Chemical Vapour Deposition of Diamond***, A. Heerwagen, M.T. Strobel, M. Himmelhaus,* University of Heidelberg, Germany*; **M. Buck,*** University of St Andrews, Scotland

The bottleneck in the accurate modeling of the diamond growth by chemical vapour deposition (CVD) is the lack of knowledge of the surface species and chemistry. In contrast to the gas phase, there is a deficit in experiment data for chemical species and reactions associated with the surface of a growing diamond film. The reason for this striking imbalance between experimental data on the gas phase and the surface lies in the diffculty to probe surface species in situ under the conditions of diamond CVD. Under these conditions, which are prohibitive for other surface science techniques we have applied IR-visible sum frequency generation (SFG) to probe the surface of a natural diamond during the CVD process, using a hot filament (HF) reactor and a gas mixture of hydrogen and methane. Monitoring the range of the C-H stretching vibrations, a single band reflecting a monohydrogen termination of the diamond substrate surface is observed under conditions which yield high quality diamond films. A decrease of the filament temperature from 2000Â°C to 1850Â°C leads to a decrease in intensity of this peak appearing around 2820 cm-1. At filament temperatures below 1800Â°C a new band at 2809 cm-1 emerges while the peak at 2820 cm-1 vanishes. Lowering the substrate temperature has a minor influence on this spectral feature but, instead, a new band at 2855 cm-1 appears. Changing the composition of the gas phase causes the intensity and frequency of the monohydrogen band to vary significantly. In particular, in a pure hydrogen atmosphere it blue-shifts to 2830 cm-1 while a pronounced increase in intensity is detected. Comparison of these results with previous SFG data obtained under ultra high vacuum reveals pronounced similarities. Furthermore, the identification of the species and surface structure associated with the peak at 2855 cm-1 seems to be vital for improving the quality of CVD diamond films grown at lower temperatures.

9:00am **TF-FrM3 Structural, Mechanical and Electrical Properties of DLC Films Deposited by DC Magnetron Sputtering***, **E. Broitman**,* College of William and Mary*; Zs. Czigáni, L. Hultman,* Linköping University, Sweden*; B.C. Holloway,* College of William and Mary

The microstructure, morphology, growth rate, surface roughness, surface energy, electrical and mechanical properties of diamond-like carbon (DLC) films deposited by direct current (d.c.) magnetron sputtering on Si substrates at room temperature were investigated. Film properties were found to vary markedly with the pressure (P@sub Ar@), bias voltage (V@sub B@), and discharge current (I@sub T@). Plan-views HRTEM revealed an amorphous microstructure, however cross-sectional SEM shows a columnar structure at the higher V@sub B@. Film stresses were found to be compressive in all cases, increasing from 0.5 GPa for grounded substrates to 3.5 GPa for films deposited at V@sub B@ = - 90 V and I@sub T@ = 0.3 A. Film stress was not affected by V@sub B@ at I@sub T@ = 0.9 A. The hardness (H), Young's moduli (E) and elastic recovery (R) increased with V@sub B@ to maximum values of H = 27 GPa, E = 250 GPa, and R = 68 %. With an increase in the negative bias, the resistivity @rho@ went through a maximum of 2.2 @ohm@cm at potentials around the floating potential U, while @rho@ decreased with the increase of pressure or discharge current. Langmuir probe measurements of the local electron temperature, density, and plasma potential as a function of Ar pressure and target current were also made at the substrate location. The properties of the films have been correlated in terms of differences in the deposition and plasma parameters.

9:20am **TF-FrM4 Electron Transmission in Thin B-doped CVD Diamond Films***, **J.E. Yater**, A. Shih, J.E. Butler, P.E. Pehrsson,* Naval Research Laboratory

Diamond is a promising cold emitter material for vacuum electron devices because of the negative electron affinity (NEA) observed at specific surfaces. While the NEA properties have been studied extensively, the cold emission process in diamond has not been well characterized. In this study, we inject electrons into thin CVD diamond films using a 0-20 keV electron gun, and we examine the transport and emission of low-energy secondary electrons in transmission measurements. In particular, we measure the intensity and energy distribution of transmitted electrons as a function of incident beam parameters (energy, current) and material properties (film thickness, doping concentration). A series of B-doped CVD diamond films has been grown with thickness between 1 and 7 microns, with the first sample being a lightly-doped, 2.5-micron-thick film with a NEA emitting surface (as indicated by yield measurements of ~20). For beam energies above 13 keV, the transmitted intensity is sharply peaked ~0.60 eV above the emission onset with a FWHM of ~0.60 eV. At constant beam energy (or current), the peak width, position, and emission onset remain constant as the beam current (or energy) is increased, and the peak is very similar to that obtained in reflection measurements. At beam energies below 13 keV, the transmission peak is much broader and less intense. It is possible that the light B doping impacts the transport of electrons to the front surface since a sharp peak was observed at all energies in a previous study of a more conductive 2-micron-thick film. Our ongoing studies continue to examine the role of doping and film thickness on the transmission properties of diamond films.

9:40am **TF-FrM5 Influence of Nitrogen and Temperature on the Deposition of Fluorinated Amorphous Carbon Films***, **L. Valentini**, E. Braca, J. Kenny,* Universita di Perugia, Italy*; R.M. Montereali,* Dip. Innovazione ENEA C.R. Frascati, Italy*; L. Lozzi, S. Santucci,* Universita dell'Aquila, Italy

Plasma deposited hydrogenated amorphous (a-C:H) carbon and fluorinated amorphous carbon films (a-C:H:F) are among the potential candidates considered for the low dielectric constant (k) interconnects. Incorporation of the low-k materials in ULSI integrated structures imposes a lot of requirements to be satisfied, among them stability at the processing temperature of 400Â°C. As deposited a-C:H:F films may be thermally stabilised, in terms of dimensional stability and material loss, by nitrogen incorporation. In this work the effect of nitrogen addition on the properties of a-C:H:F films produced by radio-frequency plasma enhanced chemical vapor deposition has been investigated. The films were studied as a function of nitrogen content and deposition temperature. The structural and optical properties were investigated by x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, UV-VIS transmittance and ellipsometry measurements. The dependence of both fluorine and nitrogen incorporation in the carbon matrix on deposition temperature has been analysed. It was found that the main effect of progressive nitrogen incorporation is a decrease of transmittance and optical band gap of the samples grown at room temperature and at 400Â°C. Raman spectra evidence that for films deposited at 400Â°C a sudden loss of sp3 carbon bonding occurs. In particular, at fixed plasma composition the decrease of the optical band gap is interpreted as a clustering of the existing sp2 carbon sites. The ellipsometry characterization indicates that nitrogen incorporation for the room temperature deposited samples induces an increase of the refractive index and suggested that carrying out a deposition at 400Â°C the films undergo a reduction of the refractive index; this has been correlated to changes in the graphitic cluster size of the network. In particular the increase in the deposition temperature produces an increase in the size of the graphitic clusters.

10:00am **TF-FrM6 Investigation of Nitrogen Bonding in Amorphous Carbon Nitride***, **W.J. Gammon**,* College of William & Mary*; O. Kraft,* Max-Planck-Institut für Metallforschung, Germany*; R.L. Vold, G. Houtson, A.S. Reilly, B.C. Holloway,* College of William & Mary

Previous x-ray photoelectron spectroscopy (XPS) work has shown that the N(1s) spectra of highly elastic amorphous carbon nitride (CN@sub x@) can be resolved into two peaks positioned at ~ 398.5 and 401 eV.@footnote 1@ Furthermore, the exact location and intensity of the two peaks is directly correlated to the mechanical properties of the film.@footnote 2@ Based on XPS data and theoretical calculations, earlier work suggests that the N(1s) peak at 398.5 eV in hard and elastic CN@sub x@, is due to nitrogen bonded to sp@super 3@ hybridized carbon.@footnote 2@ @super -@ @footnote 3@ This interpretation supports the phenomenological model that the mechanical properties of hard CN@sub x@ are due to the cross-linking of graphitic planes through sp@super 3@ bonded carbon.@footnote 2@ However, we present XPS data that suggest the low binding energy N(1s) peak may be due to sp@super 2@ coordinated nitrogen to carbon in an aromatic ring. Also, our data show that the N(1s) peak exhibits bonding over the whole range of possible hybridization. In fact, XPS is not sensitive enough to make unambiguous peak assignments in CN@sub x@, and XPS exhibits no resolvable chemical shift between sp@super 2@ and sp@super 3@ bonded carbon to carbon. However, nuclear magnetic resonance spectroscopy (NMR) provides better discrimination to these bonding types. Therefore, the purpose of this study is to clarify the dependence of chemical bonding on mechanical properties by using NMR data to remove the ambiguity of proposed XPS peak assignments. In this work, we present @super 13@C and @super 15@N NMR, XPS, and FTIR data on CN@sub x@. These films were deposited on a heated Si(001) substrate by DC magnetron sputtering, and nanoindentation was used to quantify the mechanical properties. NMR results are shown for both the hard and elastic phase (deposited at temperatures > 300 @super o@ C) and mechanically poor phase (deposited at ambient temperature). In addition, computational models will be developed concurrently from experimental data to investigate the stability of carbon/nitrogen structures. @FootnoteText@ @footnote 1@ B.C. Holloway, O. Kraft, D.K. Shuh, M.A. Kelley, W.D. Nix, P. Pianetta, and S. Hagström, Appl. Phys. Lett., 74, 3290 (1999). @footnote 2@ N. Hellgren, M.P. Johansson, E. Broitman, L. Hultman, and J. Sundren, Phys. Rev. B, 59, 5162, (1999). @footnote 3@ Å. Johansson and S. Stafström, J. Che. Phys., 111, 3203, (1999).

10:20am **TF-FrM7 Structural and Physical Properties of Carbon Nitride Films with High Nitrogen Content Synthesized by Reactive Pulsed Laser Deposition***, **J.P. Zhao**, Z.Y. Chen, T. Yano, T. Ooie,* National Institute of Advanced Industrial Science and Technology, Japan

Carbon nitride films with high nitrogen content were prepared by reactive pulsed laser deposition in nitrogen atmosphere. The fourth harmonic from a Q-switch Nd:YAG laser with wavelength of 266 nm and pulse duration of 10 ns was focused onto a high purity (99.99%) highly-oriented-pyrolytic-graphite (HOPG) target for producing carbon plume. The laser was pulsed at a rate of 10 Hz. Laser fluence was kept around 12.7 J/cm@super 2@ during deposition. Base pressure of the deposition chamber was lower than 3x10@super -7@ Torr. Nitrogen gas of 99.999% purity was admitted into the chamber during deposition, with pressure varying from 0.1 to 20.0 Torr. It was found that the nitrogen content in the films first increases with increasing the nitrogen pressure, reaches a maximum of 46 at. % at 5.0 Torr, and then decreases to 37 at.% at 20.0 Torr. The almost pure carbon nitride films were systematically characterized by using X-ray photoelectron spectroscopy (XPS) concerning on the core level and valence band structures. With adding the nitrogen incorporation, both the binding energy and peak intensity of the core level and valence band spectra vary systematically as a function of nitrogen content in the films. Structural and physical properties were also studied by using glancing angle X-ray diffractionmeter (XRD), atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, micro-Raman spectroscopy, and UV-visible spectrophotometer. Some fingerprint information that show the role of nitrogen in controlling the electronic structure and physical properties of carbon nitride film were found based on these studies.

10:40am **TF-FrM8 Structure and Properties of Carbon Nitride Thin Films Synthesized by Nitrogen-Ion-BeamAssisted Pulsed Laser Ablation***, **Z.Y. Chen**, J.P. Zhao, T. Yano, T. Ooie,* National Institute of Advanced Industrial Science and Technology, Japan

Carbon nitride films were deposited by pulsed KrF excimer laser ablation of graphite with assistance of low energy nitrogen-ion-beam bombardment. The nitrogen to carbon ratio, bonding state, microstructure, surface morphology, and electrical property of the deposited carbon nitride films were characterized by x-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, micro-Raman spectroscopy, atomic force microscopy (AFM), and four-probe resistance. The irradiation effect of the nitrogen ion beam with various ion currents on the synthesis of carbon nitride films was investigated. XPS and FTIR analyses indicated that the bonding state between the carbon and nitrogen in the deposited films was significantly influenced by the nitrogen irradiation with different ion currents during deposition. The carbon-nitrogen bonding of C-N and C=N was observed in the films. High nitrogen ion current was proposed to promote the desired sp@super 3@-hybridized carbon and the C@sub 3@N@sub 4@ phase. In addition, the tribological properties of the carbon nitride films deposited on TiN coated stainless steel substrates were also studied in both dry and oil environments, which exhibited a low friction coefficient and low wear compared to hard TiN film and commercial stainless steel.

11:00am **TF-FrM9 On the Preparation of Silicon Carbonitride Compounds***, **H. Lutz**, M. Bruns,* Forschungszentrum Karlsruhe, Germany*; E. Theodossiu, H. Baumann,* Universitaet Frankfurt/Main, Germany

Carbonitride as well as Silicon Carbonitride thin films have been the subject of great interest in recent years due to the expected improvement of surface properties for a lot of applications. Various precursor based techniques have been employed to synthezise the pure materials. However, most of these efforts result in amorphous films or tiny crystals embedded in amorphous matrices of deficient nitrogen content and considerable hydrogen and oxygen content, respectively. Very promising approaches to Si-C-N synthesis are R.F. magnetron sputtering and ion implantation providing tailored stoichiometries at high purity. Silicon carbonitrides were reactively sputtered using @super 15@N enriched N@sub 2@/Ar sputter gas and co-sputter targets with different Si/C areas resulting in defined and reproducible Si/C ratios at constant nitrogen concentrations. Alternatively, surface modification by sequential high fluence implantation of C and N ions into silicon allows for tuning the atomic fraction of all elements over a wide range. Both techniques enable us to synthezise ternary systems of more than 52 at.% nitrogen content, which are stable up to 1000°C. @paragraph@ The chemical composition of the Si-C-N films was characterized by means of X-ray photoelectron spectroscopy. In case of the buried implanted layers chemical binding states were attainable after sputter etching using 300 eV Ar ions of a projected range minimized to a negligible part of the XPS information depth. In addition, Auger electron spectroscopy, FTIR spectroscopy, and Raman spectroscopy were used to achieve a comprehensive characterization. For quantification XPS and AES data were calibrated with absolute concentration values from non-Rutherford backscattering spectrometry. Furthermore, both preparation techniques have the advantage that @super 15@N and @super 13@C isotopes can be introduced into the layers enabling non-destructive nuclear reaction analysis for depth profiling.

11:20am **TF-FrM10 The Investigation of Homogeneity of a-SiC:H Thin Films***, B.G. Budaguan,* Moscow Inst. of Electronic Technology, Russian Federation, Russia*; **A.A. Sherchenkov**, E.I. Artemov,* Moscow Inst. of Electronic Technology, Russian Federation

Hydrogenated amorphous silicon-carbon alloy (a-SiC:H)is an important material for device applications because of the possibility to control the optical bandgap by changing the carbon concentration. The physical properties and stability of a-SiC:H as well as device quality strongly depend on material's structural properties and, particularly, on its structural homogeneity. In this paper we determine the local chemical environment of the Si-H bond and the forms of carbon incorporation by analysing with use of chemical induction model the dependence of the Si-H stretching frequency shift on the alloy composition r=[C]/[Si]. a-SiC:H thin films were prepared by decomposition in the low frequency (55 kHz) glow-discharge plasma the gases mixture of silane and methane with varying methane fraction at substrate temperature of 320°C. Si and C atoms can be backbonded to Si-H bond in four possible ways to form HSiSi@sub 3-n@C@sub n@ configurations with n=0-3. So we decomposed the IR absorption band between 1840 and 2300 cm@super -1@ attributed to the Si-H stretching vibrations in monohydride SiH group into four subbands with Gauss distributions. Using the chemical induction model we calculated the dependencies of frequencies for each of four peaks both on the local environments of the Si-H group, and on the medium. In order to estimate the validity of frequency evaluations we calculated the probabilities of HSiSi@sub 3-n@C@sub n@ structures as the functions of r assuming the homogeneous film and random bonding. We observed two slopes on the dependence of the Si-H stretching mode peak position on r. At r0.16 the inhomogeneity in medium is due to carbon clustering in the forms of mentioned above structures with n=2 3. The influence of structural configurations on optical properties was discussed.

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