Thin Films Division
Room 620 - Session TF+VM-MoM

Advances in Hard and Superhard Coatings I

Moderator: F. Sequeda, Universidad del Valle, Columbia

8:20am **TF+VM-MoM1 Advances in Hard and Superhard Coatings for Tribological Applications**, ***A. Matthews,*** *A. Leyland,* University of Hull, UK **INVITED**

Over the past twenty years there has been considerable progress both in the development of advanced coating processes and in the scientific understanding of tribological mechanisms. Typically these developments have occurred completely separately, to the extent that coatings researchers may seek to develop a new coating with a specific extreme property (such as high hardness) driven primarily by scientific curiosity, rather than a desire to fulfil an identified tribological need. Usually that need will (for example) require an enhanced range of properties (such as hardness, toughness and resistance to environmental degradation). Coatings researchers are now increasingly recognising this need and are fulfilling it through several exciting developments. These include multi-layered and nanocomposite coatings which combine high hardness (H) with a relatively low elastic modulus (E) (to provide increased toughness). These coatings thus minimise the E/H ratio - which is known to be a parameter which is closely related to wear resistance. Other developments involve so-called 'hybrid' or 'duplex' combinations of processes to fulfil specific tribological needs. We are now in sight of achieving functionally-graded coating structures which combine tough and stress-equalised bulk properties, together with the extreme hardness, thermal and chemical properties of the exterior. The paper discusses the developments which have been necessary to achieve this - such as optimisation of compound compositions in the case of nanostructured composites based on nitride, carbide and boride phases. Also in the case of hard oxide ceramics, mention is made of growth modelling studies and plasma process developments to achieve the desired phases.

9:00am **TF+VM-MoM3 Ion-Assisted Filtered Cathodic Arc Deposition (IFCAD) Technology for Production of Superhard Thin-Film Coatings**, ***M.L. Fulton,*** Ion Arc Corporation

A new Ion-Assisted Filtered Cathodic Arc Deposition (IFCAD) system has been developed for low temperature production of superhard thin-film coatings. Only ions within a well defined energy range arrive at the substrate surface depositing thin-films with excellent mechanical and optical properties.@footnote 1@ The new IFCAD system consists of a cylindrical rotary deposition chamber with two (or four) Filtered Cathodic Arc (FCA) sources, each associated with an end-Hall Ion-Assisted-Deposition (IAD) ion gun.@footnote 2@ By coupling IAD with FCA the development of cost effective deposition processes for applying superhard advanced thin-film materials such as: Amorphous Diamond-Like-Carbon (A-DLC); Aluminum Oxide (Al2O3); Aluminum Nitride (AlN); Carbon Nitride (C3N3); Titanium Nitrite (TiN); Titanium Nitride Carbide (TiCN); Titanium Oxide (TiO2: Rutile); and others in multi-layer thin-film structures suitable for tribological and electro-optical applications is now feasible. The IFCAD film properties are superior to other processes at elevated deposition temperatures, for example: the A-DLC thin-films have a micro-hardness in excess of 50 GPa (Diamond = 100 GPa); and the amorphous Al2O3 films have a hardness in excess of 20 GPa (bulk sapphire is 35 GPa). This new IFCAD technology has been included in advanced commercial, military and space development programs, such as: EUV mirrors; plastic and glass lens coatings for optical systems; wear resistant coatings on various metal substrates; and ultra smooth, durable, surface coatings for injection molds. @FootnoteText@ @footnote 1@ P. J. Martin, R. P. Netterfield, A. Bendavid, and T. J. Kinder, "The deposition of thin films by filtered arc evaporation," Surface and Coatings Technology, 54/55 (1992) 136-142. @footnote 2@ M. L. Fulton, "Application of ion-assisted-deposition using a gridless end-Hall ion source for volume manufacturing of thin-film optical filters," in Optical Interference Coatings, Florin Abeles, Editor, Proc. SPIE 2253, (1994) 374-393.

9:20am **TF+VM-MoM4 High Rate Reactive DC Magnetron Sputtering of Al Oxide and W Oxide Thin Films; Large Area Coatings**, ***M.K. Olsson,*** Fraunhofer Institute for Solar Energy Systems, Germany*; K. Macák,* Linköping University, Sweden

Recently we reported stable high-rate deposition of Al oxide with any composition, including stoichiometry, utilizing a conventional reactive DC magnetron sputter system in laboratory scale.@footnote 1,2@ Due to the proper system geometry, including large enough target-to-substrate distance, and/or sufficient process gas pressure, it was possible to keep the target in the metallic mode by taking advantage of the scattering of the sputtered Al atoms through the inert gas. Moreover, the relatively high working pressure caused an increase in the back-deposited Al atoms to the non-eroded areas of the target, thus keeping these areas conducting, thereby avoiding arcing, without requiring the use of any other devices. We have applied this concept to a sputtering system considered for large area thin film production. A construction for increasing the cathode-to-sample length was designed with our technical possibilities in mind. After installation the desired O/Al arrival ratio was obtained and it was possible to produce stoichiometric aluminum oxide with an order-of-magnitude higher deposition rate. Choice of a sufficient pressure was crucial for the long-term stability of the process.@footnote 3@ Once the target is in the metallic state one may increase the growth rate linearly by increasing the target current. However, the experiments and analysis of the deposition process based on MC simulation of sputtered particles transport extended by Rossnagel's model of gas heating@footnote 4@ confirmed that the efficiency of the gas scattering process is for heavy elements partially eliminated at high discharge currents. To deal with this, we applied our concept of proper choice of process conditions for sputtering to less reactive materials with relatively high atom mass. It was possible to improve the sputtering condition for making films of stoichiometric amorphous W oxide at relatively high target current.@footnote 5@ @FootnoteText@ @footnote 1@M. Kharrazi Olsson, K. Macák, U. Helmersson, and B. Hjörvarsson, J. Vac. Sci. Technol. 16, 639 (1998). @footnote 2@K. Macák, T. Nyberg, P. Macák, M. Kharrazi Olsson, U. Helmersson, and S. Berg, J. Vac. Sci. Technol. 16, 1 (1998). @footnote 3@M. Kharrazi Olsson, K. Macák, W. Graf, Submitted. @footnote 4@S.M. Rossnagel, J. Vac. Sci. Technol. 6, 19 (1988). @footnote 5@M. Kharrazi Olsson, K. Macák, Submitted.

9:40am **TF+VM-MoM5 Elastic and Plastic Behaviors of Al/TiN Multilayered Thin Films Evaluated by Nanoindentation**, ***E. Kusano,*** *Y. Sawahira, N. Kikuchi, H. Nanto, A. Kinbara,* Kanazawa Institute of Technology, Japan

Elastic and plastic behaviors of multilayer films of Al (Young's modulus:70GPa) and TiN(Young's modulus:350-400GPa) have been investigated for various layer numbers with different total Al thicknesses in order to reveal the role of hard TiN and soft Al layers on nanomechanical properties in multilayered films. Both Al and TiN layers were deposited by dc magnetron sputtering. Aluminosilicate glass was used as substrate. The number of layers prepared was 4, 20, and 40 for the total Al thickness of 100-500nm. The total thickness of TiN layers was kept at 500nm, including the top layer of 250nm. The microhardness and Young's modulus of the films were evaluated by nanoindentation. The energies consumed for elastic and plastic deformations were calculated from the load-displacement curve obtained by the indentation. The microhardness decreased with increasing the total Al thickness. The hardness enhancement by the multilayer structure was observed for 20- and 40-layer films with Al layer thicknesses of 10 or 5nm (the total thickness of 100nm) and TiN layer thicknesses of 26 and 13nm. The energy dissipated during the indentation also increased with the total Al thickness. The dissipated energy for films with 40 layers of Al/TiN was smaller than that for the films with 4 or 20 layers of Al/TiN for all Al thicknesses. In contrary, the elastic energy was independent both of the total Al thickness and of layer numbers. As a result, the ratio of dissipated energy to the loaded energy during the load/unload of the indentation yielded a minimum at an Al thickness of 100nm for 40-layer films. The ratio at the minimum was about 20% smaller than that of the monolithic TiN film. This means that the 40-layer film with a total Al thickness of 100nm is more elastic than the monolithic TiN. It is concluded that the enhancement in the film microhardness for multilayered films with thin Al layers is related to the decrease in the dissipated energy.

10:00am **TF+VM-MoM6 Gas-phase Chemistry in Up-scaled Plasma Enhanced MOCVD of TiN and Ti(C,N) on Plasma Treated Tool Steel**, ***J.P.A.M Driessen,*** *A.D. Kuypers,* TNO Institute of Applied Physics, The Netherlands*; J. Schoonman,* Delft University of Technology, The Netherlands

In this paper, the deposition of TiN and Ti(C,N) in a relatively large scale reactor vessel is discussed. Tetrakis(dimethylamine)titanium (TDMAT) and tetrakis(diethylamine) titanium (TDEAT) were used for the purpose of depositing TiN and Ti(C,N) at low temperatures. In large scale systems, homogeneous reactions dominate the deposition process resulting in non-

uniform and non-adherent coatings. However, in this study, favourable gas-phase conditions for deposition of Ti(C,N) from in a pulsed DC-plasma have been determined, making use of mass and optical spectroscopy. Decomposition of TDMAT in a pure hydrogen plasma results in the favourable cleavage of dimethylamine from TDMAT but prevents the formation of Ti(C,N) due to the lack of nitrogen and carbon. Addition of N@sub 2@ to the hydrogen plasma results in the formation of NH@sub x@ (1@<=@x@<=@4), opening transamination pathways. Results suggest that transamination plays an important role in the gas-phase of our system. Furthermore, these results were compared with those obtained from using ammonia. However, the depletion of TDMAT by interaction with nitrogen in a H@sub 2@(85%) - N@sub 2@(15%) plasma proceeds in a mechanistic step with a rate constant of k = 4.7 x 10@super -14@ cm@super 3@ mol@super -1@sec@super -1@. Nevertheless, seemingly high quality Ti(C,N) coatings were deposited on blank WN1.2370 tool steel and WN 1.2379 treated in a N@sub 2@/H@sub 2@ plasma. XRD analysis of the plasma treated substrate indicates the presence of CrN, among other species in the top surface layer. These multi-layer coatings, deposited at temperatures between 473 K and 698 K, increased in surface roughness, however, showed good adherence and optimum hardness. Hardness values varied from 1600 Hv to 2000 Hv.

10:20am **TF+VM-MoM7 Effect of Ion-to-neutral Ratio and Ion Energy on Structure and Properties of Boron Nitride Thin Films**, ***M.U. Guruz***, *Y.W. Chung, V.P. Dravid,* Northwestern University

Boron nitride thin films were deposited by dc reactive magnetron sputtering using a B@sub 4@C target in a single cathode chamber. The films were grown on Si (001) wafers, held at ambient temperature. The energy of the ions arriving at the substrate surface was determined by the applied bias. Additionally, an external coil assembly was placed outside the chamber, allowing modification of the magnetic field around the substrate. By varying the field strength, the ion flux on the substrate was enhanced. Thus, the ion-to-neutral ratio and the ion energy were independently controlled during deposition. The effects of these two parameters on the resulting film microstructure were investigated by transmission electron microscopy (TEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and nanoindentation. These results and the effects on the formation of cubic boron nitride will be presented.

10:40am **TF+VM-MoM8 Mechanical Properties of Cubic Boron Nitride Thin Films Synthesized by ECR PECVD: Influence of Deposition Conditions**, ***M.P. Delplancke-Ogletree***, *M. Ye,* Université Libre de Bruxelles, Belgium

Cubic boron nitride containing thin films were deposited on (100) Si and steel substrates by electron cyclotron resonance plasma enhanced chemical vapor deposition. The films contain at least 55% of the cubic phase and are 0.5 μm thick. We investigated the dependence of hardness, stress, adherence, friction coefficient and wear resistance as a function of deposition parameters. The studied parameters are substrate bias, gas mixture composition, substrate temperature and processing pressure. These parameters are also correlated to the plasma characteristics measured by Langmuir probe, and mass spectrometer. Nanoindentation, scratch test, cantilever deflection, and ball-on-disk methods were used to evaluate quantitatively the mechanical properties. Films containing 55% of cubic phase are adherent to the two types of substrates, and have stress below 5 GPa.

11:00am **TF+VM-MoM9 Plasma Assisted Physical Vapour Deposition of BN by DC Pulsed Sputtering of a B@sub 4@C Target**, ***L.A. Gea***, *G. Ceccone, F. Rossi,* European Commission Joint Research Centre, Italy

Boron nitride coatings were deposited on Si (100) polished crystals by DC pulsed magnetron sputtering of a B4C target with auxiliary microwave Distributed Electron Cyclotron Resonance (DECR) plasma.The substrates were biased by an independent R.F. source. Characterization of the plasma was undertaken as a function of the total pressure, the nitrogen gas content and the microwave power. The presence of the various species was identified with Optical Emission Spectroscopy.Mass Spectrometry was used to determine the ion energy distribution while the plasma potential and the plasma densities were measured with a single Langmuir probe.The coatings have been characterized by Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES), and Fourier Transformed Infrared Spectrometry (FTIR)

11:20am **TF+VM-MoM10 Field Emission from Flat, Diamond-like Carbon Films Characterized by Scanning Force Microscopy**, *T. Inoue,* Electrotechnical Laboratory, Japan; ***D.F. Ogletree***, *M. Salmeron,* Lawrence Berkeley National Laboratory

Thin films of various diamond-like and carbon based materials on flat cathodes show significant field emission at relatively low voltages, but the exact emission mechanisms are not well understood. Non contact scanning force microscopy with a conductive tip in vacuum, used in the scanning polarization force mode (SPFM) , can detect and characterize emission sites with 100 nm lateral resolution. The SFM tip serves as an anode. It can be scanned over the surface to simultaneously measure local emission currents and local work functions. The tip-sample spacing and the tip bias can be varied to investigate mechanisms. Contact SFM images of emitting regions show local topography, reveal the presence of asperities, and characterize sample conductivity. For one type of CVD cathode material on an Si substrate, the emission sites were found to be (a) ~ 1 micron in diameter (b) not associated with asperities at the cathode-vacuum interface (c) not associated with low work function regions, and (d) semiconducting with a large band-gap. I-Z data indicate that emission takes place within the film, or at the film-substrate interface, rather that at the film-vacuum interface. Single-site emission currents were strongly modulated on a ~ 1 ms time scale, possibly due to charge trapping. Surface potential shifts were correlated with the emission current fluctuations.

11:40am **TF+VM-MoM11 Effect of Nondiamond Carbon on the Electron Transport Path of Field-emitted Electrons from Undoped Polycrystalline Diamond Films**, ***J.Y. Shim***, Yonsei University, Republic of Korea; *K.M. Song,* Konkuk University, Republic of Korea; *H.K. Baik,* Yonsei University, Republic of Korea, KOREA

Diamond has attracted considerable interest recently as a promising field emitter material because of its important properties such as NEA, high thermal conductivity, and low field electron emission. Among the properties, understanding the origin of low field emission is a key factor for the application of diamond to a field emitter. Many investigations have been extensively drawn to clarify the origin of low field emission behavior of diamond. Suggested models explaining the low field emission behaviors up to now are the discontinuous graphitic inclusions in CVD diamond matrix, the defect induced subbands, and the surface emission from metal-diamond-vacuum interface. Besides, there have been several reports on the importance of the electron transport through the substrate/diamond interface. However, the origin of the low field emission behavior is still unclear, and those may be different between diamond crystal and CVD diamond films. It is expected that the field emission mechanism of undoped polycrystalline diamond films can be changed by the structural properties. The present study is mainly focused on the electron transport through the substrate-diamond interface and the diamond layer, and the resulting field emission mechanism of undoped polycrystalline diamond films with different structural properties. In order to examine field emission properties of undoped polycrystalline diamond films, we have prepared the diamond films with different structural properties and/or different substrate-diamond interfaces. It was observed that transport paths of field-emitted electrons could be clearly identified from the spatial distributions of emission sites and the nondiamond carbon content obtained from the diamond films, and the characteristics of the substrate-diamond could modify the field emission properties. From the present study, a possible field emission mechanism for the undoped polycrystalline diamond films is suggested.

Thin Films Division
Room 615 - Session TF-MoM
Fundamentals of PECVD

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

8:20am **TF-MoM1 Investigation of the Plasma Properties and Fluxes in a Hydrogenated Amorphous Carbon Deposition Process**, *B.K. Kim,* ***T.A. Grotjohn***, Michigan State University

The deposition process and conditions used for hydrogenated amorphous carbon (a-C:H) film deposition from acetylene, acetylene-helium, and acetylene-argon gas mixtures in a microwave ECR plasma reactor are studied. This paper quantifies the plasma discharge fluxes to the substrate based on experimental measurements and plasma discharge modeling. The film properties are also correlated to the plasma discharge conditions. The films are deposited on glass and silicon substrates which are placed on an rf biased (13.6 MHz) substrate holder located just at the exit of a multipolar,

permanent magnet ECR plasma source operating at 2.45 GHz. The deposition parameters varied during this investigation included rf induced dc substrate bias voltage (-50 to -300 V), pressure (0.1-1.0 mTorr) and argon/acetylene (or helium/acetylene) gas flow ratio. The properties of the plasma discharge measured include electron temperature, ion saturation current, and residual gas composition. The films deposited with different gas mixtures, pressures and rf biases have substantially different properties including deposition rate, mass density, optical absorption coefficient, optical bandgap and hydrogen content. The use of lower pressures to obtain an increased ion-flux/neutral-flux ratio to the substrate was found to be critical for obtaining dense, low hydrogen content films from acetylene. The addition of argon and helium were found to substantially change the plasma discharge deposition conditions, as well as, influence the deposited film properties.

8:40am **TF-MoM2 Time-resolved Study of C@sub x@N@sub y@ Growth by Means of Fourier Transform Infrared Reflection Spectroscopy**, ***A. de Graaf***, *B. Schreur, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

Fourier transform infrared (FTIR) reflection spectroscopy is used to study the composition of carbon nitride (C@sub x@N@sub y@) films in situ during the early stages of growth and during etching. The C@sub x@N@sub y@ films are deposited from a thermal Ar/N@sub 2@ plasma expanding through a graphite nozzle. The graphite is chemically etched leading to strong CN emission both at the nozzle exit and at the substrate level 65 cm downstream. The observation of C@sub 2@N@sub 2@ in the mass spectrometer gives further support to the idea that CN radicals are formed during deposition. In order to measure small reflection changes on a (sub)monolayer level and on a short enough time scale, a special substrate has been developed which enhances the IR absorption considerably at a specific wavelength. With this substrate the evolution of the different bonds (sp@super 1@, sp@super 2@ and sp@super 3@ C-N) in the film can be followed. The results show a relative increased absorption of the sp@super 1@ C-N bond during initial growth as compared to the absorption in the bulk material. This strongly suggests that CN radicals are indeed involved in the deposition. After film growth the absorption of sp@super 1@ C-N bonds decreases while the absorption of sp@super 2@ C-N bonds increases. Etching of the C@sub x@N@sub y@ films by an expanding Ar/N@sub 2@ or Ar/O@sub 2@ plasma also shows a different response in the absorption signal of sp@super 1@ C-N as compared to sp@super 2@ C-N. The optical constants of the material and growth rate are derived from an optical model and are correlated to in situ ellipsometry measurements performed simultaneously. Based on these findings a tentative growth model is presented. In a next step this model will be extended to describe deposition at different substrate temperatures and bias voltages.

9:00am **TF-MoM3 Surface Reactions of CH@sub x@ and SiH@sub x@ Radicals during Plasma Deposition of a-C:H and a-Si:H Films**, ***A. von Keudell,*** Max-Planck-Institut für Plasmaphysik, Germany **INVITED**

The surface reactions of CH@sub x@ and SiH@sub x@ radicals as the dominant growth precursor during plasma deposition of amorphous hydrogenated carbon and silicon films are investigated by exposing a-C:H and a-Si:H film surfaces to low temperature plasma discharges or to quantified radical beams. The surface reactions are monitored in real time by using in-situ ellipsometry and in-situ infrared spectroscopy. The measurement of the surface reaction probability of various hydrocarbon radicals indicates that the reactivity of larger C@sub x>1@H@sub y@ radicals at the a-C:H surface is much higher than that of CH@sub y@ radicals. This has several consequences for the understanding of a-C:H film growth, which will be described in detail. The deposition of a-Si:H from silane discharges is assumed to be similar to the growth of a-C:H films since in both cases the dominant growth precursor is CH@sub 3@ or SiH@sub 3@, respectively. However, the dominant interaction mechanism of silyl radicals with a-Si:H surfaces, as identified by isotope labeling experiments, is very different to that of CH@sub 3@ radicals on a-C:H surfaces. Whereas methyl radicals can only adsorb at open bonds at the a-C:H film surface, silyl radicals are able to insert into strained bonds at the a-Si:H surface. A comparison of microscopic growth processes during a-C:H growth and a-Si:H growth will summarize this presentation.

9:40am **TF-MoM5 Quantitative Characterization of a Particle Beam Source for Atomic Hydrogen and Hydrocarbon Radicals for Thin Film Growth Studies**, ***Th. Schwarz-Selinger***, *A. von Keudell, W. Jacob,* Max-Planck-Institut für Plasmaphysik, Germany

Hydrocarbon radicals are the dominant neutral growth precursors for the deposition of amorphous hydrogenated carbon films (a-C:H). For the investigation of the growth mechanisms a particle beam source was developed, which is able to produce thermal beams of neutral hydrocarbon radicals. The radicals are produced in a resistively heated tungsten capillary by thermal dissociation at the hot walls of the capillary. The maximum temperature of the capillary, achievable is around 2600 K, which is sufficient to also produce atomic hydrogen from H@sub 2@ with a high yield. A rotatable (@+-@ 20°) quadrupole mass spectrometer in line of sight to the capillary exit was employed to study the emanating particle beam. This setup allows to identify the emitted species and their angular distribution and permits to quantify the emitted fluxes. For hydrogen the degree of dissociation and the total flux of atomic hydrogen as a function of temperature and gas flow is presented. With the same source methyl radicals are produced. Results are presented for the total amount of methyl radicals using different hydrocarbon source gases. First results of surface reactions of these radicals, investigated by monitoring the interaction of the particle beam with a-C:H film surfaces in real time by in-situ ellipsometry and in-situ infrared spectroscopy, complete this presentation.

10:00am **TF-MoM6 High Rate a-Si:H Growth Studied by in situ Ellipsometry**, ***A.H.M. Smets***, *B.A. Korevaar, W.M.M. Kessels, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

In this contribution the results of in-situ HeNe rotating compensator ellipsometry measurements performed on hydrogenated amorphous silicon (a-Si:H) growth using an expanding thermal plasma are presented. This remote thermal plasma technique is developed as a promising tool for high deposition rate (10 nm/s) of a-Si:H on a roll to roll production line of low cost thin film solar cells on a flexible foil. The measurements can be simulated using an optical growth model consisting of a substrate layer, SiO@sub 2@ layer, intermediate layer, a-Si:H bulk layer and a top layer, corresponding to the surface roughness. Using this model the roughness evolution during deposition can be monitored. At deposition conditions at which "device quality" a-Si:H is grown the surface roughness is the smallest, indicating that roughness and material quality are related. The correlation between incorporation of SiH@sub 2@ complexes and the surface structure will be discussed. From the roughness evolution in time at various substrate temperatures the length scales which dominate the high rate a-Si:H growth can be deduced. The activation energy of the diffusion processes is also determined and its significance for the Matsuda-Perrin-Gallagher growth model will be discussed.

10:20am **TF-MoM7 Ab-initio Study of H Abstraction from Amorphous Silicon Surface By Hydrogen and silyl(SiH@sub 3@) Radicals: Implications for Stability of 3-center Bond Formation**, ***A. Gupta***, *H. Yang, G.N. Parsons,* North Carolina State University

Plasma deposition of amorphous and micro-crystalline silicon from silane/hydrogen gas mixtures is widely utilized in the manufacture of solar cells and in thin film transistors (TFT) required in the active matrix liquid crystal displays (AMLCD). A fundamental understanding of the surface reactions that may result in the removal of bonded H will be useful to further optimize the deposition process. The surface H may be abstracted by H or SiH@sub 3@ radicals to form H@sub 2@ or SiH@sub 4@ respectively leaving behind a dangling bond which provides an active site for chemisorption of SiH@sub n@ radicals. It has been proposed that the first step in a-Si deposition is the formation of a stable 3-center (Si-H-Si) bond by the SiH@sub 3@ radicals and the surface hydrogen groups but the energetics of this elementary step are unknown. We have used configuration interaction (CI) and density functional (DFT-BLYP) calculations to compare the abstraction of surface hydrogen by H as well as SiH@sub 3@ radicals. Our results indicate that the H radicals are more likely to abstract the surface H compared to the SiH@sub 3@ radicals. The activation energy for the former reaction was determined to be ~5.5 kcal/mol and the heat of reaction was ~-11 kcal/mol while the latter reaction had an activation energy ~9.4 kcal/mol and an energy change ~-6 kcal/mol. Thus we can conclude that the H radicals are more likely to abstract the hydrogen from the Si(111) surface as compared to SiH@sub 3@ radicals. The potential energy surface for the reaction of SiH@sub 3@ radicals with the surface H generated using the DFT method does not indicate the presence of a stable 3-center bond within the accuracy of the method. The activation energy using this method was ~6 kcal/mol and the

reaction energy was ~-7 kcal/mol. These results indicate that long-standing models for surface and bulk bond structure development need to be re-examined and support the possibility of other reaction schemes viz. SiH@sub 3@ insertion into Si-Si bonds on the surface.

10:40am **TF-MoM8 Impact of Helium Dilution on Low-Temperature Silicon Depositions Using Electron Cyclotron Resonance and RF Plasma Sources**, ***S.H. Bae***, *Y.C. Lee, R.T. McGrath,* Pennsylvania State University

Low temperature silicon films have been prepared at 110° C using electron cyclotron resonance (ECR) plasma, ECR plasma plus RF substrate bias, and RF plasma only. As dilution media, both pure hydrogen and hydrogen mixed helium gases have been employed for these low-temperature depositions. In order to relate the plasmas to the properties of these low temperature Si films, in-situ optical emission spectrum (250 ~ 800 nm) for each plasma condition has been examined. Regardless of the presence of RF substrate bias during ECR plasma depositions, intensity of optical emission of ECR plasma much higher than that conventional RF plasma. In the ECR plasmas, the emission intensities of H radicals much stronger than those in RF plasma mode by two order of magnitude. In both H @sub 2@ and H@sub 2@ +He diluted RF plasmas, H @gamma@ (434 nm) and H @beta@ (486 nm) emissions are not noticeable for 0.6 second integration of optical spectrum while H @alpha@ (656 nm) line is observable in the RF plasma. Addition of He gas in ECR plasma results in strong He radical emission lines (389 nm and 502 nm); i.e., this indicates highly excited hydrogen plasma can be produced by the metastably excited He radicals. X-ray diffraction (XRD) analysis shows that low-temperature pure RF mode Si films do not have any crystallinity regardless of addition of He gas while the Si films prepared with ECR plasmas have high crystallinity. However, these high-crystallnity low-temperature ECR films are very porous and columnar. In terms of micro-etching effect due to hydrogen radicals in high-density plasmas, H @sub 2@+He dilution is more efficient than the case of H@sub 2@ dilution.

11:00am **TF-MoM9 Hydrogenated Amorphous Silicon Surface Growth Mechanism Characterized by Fourier Analysis of the Surface Topography**, ***K.R. Bray***, *A. Gupta, L. Smith, G.N. Parsons,* North Carolina State University

Hydrogenated amorphous silicon (a-Si:H) is widely used for the manufacture of solar cells and for thin film transistors (TFT) in active matrix liquid crystal displays (AMLCD). There have been many studies of the gas-phase reactions occurring in the plasma, but less is known of what takes place on the growing silicon surface. An increased understanding of its growth mechanism is desirable to optimize the quality of the a-Si:H films. Atomic force microscopy (AFM) was used to image the surface topography of PECVD deposited a-Si:H. Surface topography was compared for samples deposited over a wide range of temperatures (25° C - 350° C) and film thicknesses (20 - 2000 Å). The rms surface roughness has been used to characterize surface growth. During the initial 30 seconds of nucleation using 100 sccm of 2% SiH@sub 4@/He, the rms is between 1 - 4 nm. As the deposition continues from 1 to 5 minutes, the rms increases to between 13 and 28 nm. After film coalescence, the rms roughness reduces to between 1 and 4 nm. A Fourier analysis of the surface topography produces an index (i), which has been correlated with different surface growth mechanisms. The Fourier indices for these samples range from i = 3.8 to 4.8, and increase with temperature. These results indicate that surface diffusion (i = 4) is the primary smoothing mechanism during growth. But the deviation from 4 suggests that the actual mechanism is more complex than simple surface diffusion. A shift in i suggests that there is a change in the growth mechanism as the film coalesces. We will discuss correlations between the Fourier index and film quality as deduced from structure and electrical characterizations.

11:20am **TF-MoM10 Deposition of Silicon Oxide Films using a Remote Thermal Plasma**, *M.C.M. van de Sanden,* ***M.F.A.M. van Hest***, *D.C. Schram,* Eindhoven University of Technology, The Netherlands

A cascaded arc (p=0.1 â€“ 0.2 bar) has been used to generate a remote thermal argon plasma, which expands into a vacuum vessel (p=0.1 mbar). In this expanding thermal argon plasma oxygen is injected at the arc nozzle. Downstream HMDSO (hexamethyldisiloxane) is injected as a precursor. The cascaded arc as a plasma source has some big advantages in comparison to the more conventional techniques (i.e. CVD). The first advantage is that the deposition rate obtained is much higher with the use of the cascade arc (>100 nm/s) than with the use of conventional techniques (couple of nm/s). The second advantage is that the deposition rate does decrease with increasing substrate temperature. Therefore it is not necessary to heat the substrate to very high temperatures (>500°C) before the film can be deposited. The deposited films have been analysed using in situ ellipsometry, elastic recoil detection (ERD), and in situ Fourier transform infrared reflection absorption spectroscopy. Ellipsometry shows that the deposited films have good optical properties. FTIR absorption spectrosopy measurements as well as ERD measurements show that the deposited films contain carbon. To get a better understanding of the film growth, in situ FTIR reflection absorption spectroscopy measurements are done. The effect of post deposition plasma exposure is discussed. The gas phase of the depositing plasma has been analysed by means of mass spectrometry and gas phase FTIR absorption spectroscopy. These measurements show that in the gas phase new stable species (i.e. C@sub 2@H@sub 2@) are created.

11:40am **TF-MoM11 Dielectric Properties of Silicon Nitride Deposited by High Density Plasma Enhanced Chemical Vapor Deposition@footnote 1@**, ***J.B.O. Caughman***, *D.B. Beach, G.E. Jellison, W.L. Gardner,* Oak Ridge National Laboratory

The dielectric properties of silicon nitride films have been investigated. The films were deposited on silicon substrates at temperatures <400 degrees C by using a high density inductively coupled plasma source. The plasma source is operated at 13.56 MHz using a flat spiral coil. A nitrogen plasma is formed in the ionization region of the source and 100% silane is injected downstream. Properties of the films are determined by using 2-modulator generalized ellipsometry and FTIR. Growth rates vary from 20-45 nm/min, depending on the processing parameters. For nitrogen/silane gas flow ratios of 0.25 to 10.0, the refractive index of the films (at 350 nm) vary little and are around 1.82. The band gap ranges from 4.5 to 6.2 eV. The addition of hydrogen in the ionization region results in an increase in the refractive index and a reduction in the band gap. For nitrogen/silane ratios of 0.25 to 2.0, the refractive index varies from 2.18 to 1.95 and the band gap varies from 3.1 to 4.4 eV. In addition, the hydrogen content in the film actually decreases with the addition of the hydrogen in the ionization region. A mass spectrometer imbedded in the substrate is used to correlate film properties with processing parameters. It is believed that the addition of the hydrogen increases the reactivity of silane in the gas phase, and that the flux of atomic hydrogen at the surface helps to abstract hydrogen from the growing film. @FootnoteText@ @footnote 1@ORNL is managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract no. DE-AC05-96OR22464.

Thin Films Division
Room 620 - Session TF+VM-MoA

Advances in Hard and Superhard Coatings II
Moderator: B. Holloway, College of William & Mary

2:00pm **TF+VM-MoA1 Characterization of PVD TiN/CN@subx@ and TiN/Si@sub3@N@sub4@ Multilayer Coatings**, ***Y.H. Chen***, *Y.W. Chung,* Northwestern University

TiN coatings are commonly used in various tribological applications for their wear resistance and inertness to steels. However, TiN coatings predominantly grow with a columnar grain structure. The columnar grain boundaries become the usual sites for crack initiation, resulting in earlier failure of TiN coatings (especially thick coatings). In our research, TiN/a-CN@subx@ and TiN/a-Si@sub3@N@sub4@ nanolayered superlattice coatings are developed to suppress the columnar structure. We used a-CN@subx@ and a-Si@sub3@N@sub4@ primarily to periodically interrupt and renucleate the growth of TiN. In addition, the amorphous layers may serve to suppress the transmission of dislocations from one TiN layer to another, thereby enhancing the hardness of the coating. Both coatings have been demonstrated to achieve hardness in the 50 GPa range, consistent with recent reports for high hardness of TiN/a-Si@sub3@N@sub4@ nanocomposites. The correlation between microstructure and mechanical properties of these coatings will be presented.

2:20pm **TF+VM-MoA2 Effects of Interface Mixing on Adhesion of Amorphous Carbon Films Synthesized by Variable-Energy Direct Carbon Ion Beam Deposition**, ***M.H. Sohn***, *S. Kim,* SKION Corporation

Using a variable-energy direct carbon ion beam deposition technique, thin amorphous carbon films were grown on silicon substrate. Interface modification was performed using C@super -@ energies in the range of 300-500 eV prior to the growth of the film to enhance adhesion of the film. By lowering the energy of the C@super -@ beam to 150 eV, amorphous carbon film was continuously grown after the interface modification. High-resolution electron microscopy illustrated that the silicon surface was severely damaged by 500 eV C@super -@ beam and the thickness of damage layer was about 15 nm. Carbon composition profile in silicon investigated by electron energy loss spectroscopy showed that 500 eV C@super -@ beam implanted carbon into silicon up to 30 nm in depth and carbon was mixed with silicon at this implanted region. Silicon L-edge study at the C/Si mixed region found C-Si bonding formation only at the surface of silicon over 2-3 nm-thick layers. The damage layer or C/Si mixing was not observed at 300 eV C@super -@ beam modification. Wear testing found that strong adhesion occurred in samples modified at 500 eV, which indicated complete mixing at the interface. At 300 eV, modified samples exhibited delamination failure, which indicated inferior adhesion of the films.

2:40pm **TF+VM-MoA3 Synthesis of Diamondlike Carbon Films with Superlow Friction and Wear Properties**, ***A. Erdemir***, *O.L. Eryilmaz, G. Fenske,* Argonne National Laboratory

In this study, we introduce a new diamond-like carbon (DLC) film providing friction coefficients of 0.001 and wear rates of 10-9 to 10-10 mm3/N.m in inert gas environments (e.g., dry nitrogen and argon). The film was grown on steel and sapphire substrates in a plasma enhanced chemical vapor deposition system using a hydrogen-rich plasma. Employing a combination of transmission electron microscopy, electron diffraction, Raman spectroscopy, and electron energy loss spectroscopy, we explored the structural chemistry of the resultant DLC films and correlated these findings with their friction and wear mechanisms. The results of tribological tests under a 10 N load (creating an initial peak Hertz pressure of 1 GPa on steel test pairs) and at 0.2 to 0.5 m/s sliding velocities indicated that a close correlation exists between the friction and wear coefficients of DLC films and the source gas chemistry. Specifically, films grown in source gases with higher hydrogen-to-carbon ratios had the lowest friction coefficients and the highest wear resistance. The lowest friction coefficient (i.e., 0.001 on a sapphire substrate) was achieved with a film derived from a gas mixture consisting of 25% methane and 75% hydrogen. The wear-debris particles found in and around the wear scars and tracks were analyzed by Raman spectroscopy and FTIR to elucidate the wear mechanism of DLC films. @FootnoteText@ *Work supported by the U.S. Department of Energy under contract W-31-109-Eng-38.

3:00pm **TF+VM-MoA4 Optical Characteristics of Carbon Nitride: Relationship with Mechanical Behavior and Possible Fullerene-like Microstructure**, ***V. Hajek***, *D. Poitras, D. Dalacu,* Ecole Polytechnique, Canada*; A. Bergeron,* Optical Coating Laboratory Inc.*; L. Martinu,* Ecole Polytechnique, Canada*; K. Rusnak, J. Vlcek,* University of West Bohemia, Czech Republic

Crystalline @beta@-C@sub 3@N@sub 4@ was predicted to exhibit extreme properties, such as hardness, comparable to that of diamond. Although the synthesis of the crystalline metastable phase has not been fully confirmed yet, already prepared "amorphous" CNx films possess very attractive characteristics. In our earlier studies we have shown that these films possess high hardness (up to 30 GPa), high elastic recovery (up to 85 %), and interesting tribological behavior. Such films prepared at temperatures above 200 °C, using magnetron sputtering, are predicted in recent literature to possess a fullerene-like microstructure. In our recent work we suggested to extend this model to account for hydrogen incorporation: Excessive amount (> 1 at. %) of hydrogen in the films is believed to inhibit crosslinking between graphite-like planes containing carbon and nitrogen, and thus to hamper formation of the fullerene-like microstructure. In the present work we focus on the optical properties of CN@sub x@ films studied by spectroscopic ellipsometry and spectrophotometry. Different dispersion relations such as Sellmeier, Cauchy and Drude-Lorenz oscillator were used to determine optical constants n and k. The optical behavior is related to the film microstructure and the film fabrication conditions. CN@sub x@ layers were deposited on Si substrates by reactive DC magnetron sputtering of graphite target in nitrogen plasma at a substrate temperature of 600 °C and at a substrate bias ranging from -300 to -700 V. Films were found substoichiometric in nitrogen (from 12 to 24 at. %), and a concentration of hydrogen between 1 and 5 at. % was revealed by elastic recoil detection (ERD) analysis. Increased hydrogen content was accompanied by lower hardness, elastic recovery and adhesion, by higher electrical resistivity (from 20 to 970 @ohm@cm), by formation of C-H and N-H bonds (FTIR), and by higher optical transparency in the VIS and IR regions. The latter characteristics are related to the variation of optical bandgap which increases with hydrogen incorporation.

3:20pm **TF+VM-MoA5 Preparation and Properties Enhancement of Silicon Carbonitride Films Using Reactive Magnetron Sputtering**, *X.-M. He, K.C. Walter,* ***M. Nastasi,*** Los Alamos National Laboratory

Silicon carbonitride (Si(C,N)) films were synthesized on Si (100) and metal substrates by reactive d.c. magnetron sputtering with Ar as the sputtering gas and N@sub 2@ as the reactive gas. The composition and properties of the films were studied with respect to the influences of the bias voltage applied to substrates, the deposition temperature, and the gas flow ratio of N@sub 2@ to Ar (or F@sub N2@/F@sub Ar@). The Si(C,N) mechanical properties, hardness, fracture, and tribological properties, were observed to be highly depended on the processing conditions such as substrate temperature, the arrival ratios of ion to deposition atom, J@sub i@/J@sub a@, the negative bias voltage and F@sub N2@/F@sub Ar@. Under optimum conditions amorphous coatings with high wear resistance and harnesses as high as 40 GPa were prepared. The role of synthesis parameters on the structure, compositions, and mechanical properties will be discussed in detail.

4:00pm **TF+VM-MoA7 Bonding Structure and Optical Properties of Si-doped Diamond-like Films Synthesized by Plasma Immersion Ion Processing**, ***X.-M. He***, *K.C. Walter, M. Nastasi,* Los Alamos National Laboratory

Silicon-doped diamond-like carbon (DLC) films were prepared on Si(100), glass, and PMMA (polymethyl methacrylate) substrates at room temperature by using C@sub 2@H@sub 2@-SiH@sub 4@-Ar plasma immersion ion processing (PIIP) and their compositions were modified by changing deposition parameters of the gas composition and the negative bias voltages applied on the substrates. The influence of the Si dopant on the bonding structure and the properties of the DLC films were investigated by using ion beam analysis techniques, Raman shift, infrared spectroscopy, and by analyzing the measured density and hardness. The electrical and optical properties of Si-doped DLC films have been evaluated by the study of the electrical resistivity, the refractive index, the absorption coefficient, and the optical gap energy for the films. It was found that the variation of Si dopant was highly correlated with the changes of chemical bonding structure and properties. The careful control of gas flow ratio of C@sub 2@H@sub 2@ : SiH@sub 4@ : Ar in low pressure PIIP was needed for the growth of DLC films with optimal combinations of increased sp3

bonding structure, high hardness and density, and improved optical properties. The resultant Si-doped DLC films with a Si content up to 28 at % exhibited a higher optical transmittance in the visible light range. The tribological tests of Si-doped DLC films were carried out using a pin-on-disk tribometer in ambient air at about 15% relative humidity. The results shown that Si-doped DLC films exhibited a low friction coefficient of 0.03-0.08 and an enhanced wear resistance despite of deposition of the films on Si (100), glass, or PMMA substrates. The effects of ion impingement during PIIP deposition on the formation of Si-incorporated DLC films were discussed.

4:20pm **TF+VM-MoA8 Surface Acoustic Wave Propagation Properties of Nitrogenated Diamond-like Carbon Films**, ***J.Y. Kim***, *H.J. Chung, H.J. Kim,* Seoul National University, Korea*; H.M. Cho, H.K. Yang, J.C. Park,* Korea Electronics Technology Institute

Surface acoustic wave (SAW) devices have become more important as mobile telecommunication systems need high-frequency, low-loss, and down-sized components. Higher-frequency SAW devices can be more easily realized by developing new high-SAW-velocity materials. The ZnO/diamond/Si multilayer structure is one of the most promising material components for GHz-band SAW filters because of its high SAW velocity above 10,000 m/sec. Recently, DLC films are also considered to have a potential for this application, since their physical properties, such as hardness and elastic modulus, are comparable with those of diamond. However, the residual stress during deposition is an obstacle to this application, because the film having high residual stress could not sustain during the full fabrication process of SAW devices. Recently, there have been many reports of the nitrogenated DLC films, which is mainly driven by the possibility of realizing the superhard @beta@-C@sub3@N@sub4@ phase. Some researchers reported the residual stress reduction by nitrogen incorporation without any other significant change in film mechanical properties. In this study, nitrogenated (a-C:N) films were deposited by reactive sputtering method. The a-C:N film properties were investigated using Raman spectroscopy, FT-IR, AES, and x-ray reflectivity (GIXR). To investigate the SAW propagation characteristics of the a-C:N films, SAW filters were fabricated using interdigital transducer electrodes between the ZnO layer and a-C:N/Si(100), which were used to excite surface acoustic waves. SAW velocities were calculated from the frequency-response measurements of SAW filters. A generalized SAW mode with velocities between 5,000 m/s and 7,000 m/s were observed as well as a high velocity Pseudo-SAW mode with 14,000 m/s. We also calculated the film elastic constants from SAW propagation velocities in the layered structure.

4:40pm **TF+VM-MoA9 High Deposition Rate Diamondlike Carbon Films Deposited using Permanenet Magnet Electron Cyclotron Resonance Plasmas**, ***C. Doughty***, *J.B. Bailey,* ASTeX PlasmaQuest

We report deposition of hard diamondlike carbon films at deposition rates exceeding 500 nm/min using permanent magnet ECR plasma CVD. These films are characterized by high hardness ~10-20 GPA and stresses ~300-500 MPa. The deposition rates obtained exceed typical values for plasma CVD deposition by a factor of 10-50 and enable a range of novel applications including economically attractive deposition of >10-um-thick films. These films have electrical resistivities ~10^12 ohm cm at 1 MV/cm, and optical bandgaps ~2 eV. Index of refraction can be controlled over the range 1.7 - 2.2 by manipulation of the deposition parameters. Film hardness has been measured by nanoindentation and will be reported as a function of deposition parameters. Adhesion promoting processes have been developed and films exceeding 5 um thickness have been deposited on silicon, glass and stainless steel substrates without delamination failures. Thin films (

5:00pm **TF+VM-MoA10 Polymerization in Remote Hydrocarbon Deposition Plasmas**, *A. de Graaf, M.F.A.M. van Hest,* ***M.C.M. van de Sanden***, *K.G.Y. Letourneur, D.C. Schram,* Eindhoven University of Technology, The Netherlands

The chemistry of expanding argon plasmas into which either methane (CH@sub 4@) or acetylene (C@sub 2@H@sub 2@) is injected for fast deposition of a-C:H, DLC and diamond films was studied by means of mass spectrometry, Fourier transform infrared absorption and in situ ellipsometry. The measurements reveal that the plasma chemistry of the expanding Ar/C@sub 2@H@sub 2@ and Ar/CH@sub 4@ plasmas is dominated by argon ion induced dissociation of the precursor gas. For acetylene injection the ion-induced dissociation is very efficient leading to complete depletion under certain conditions. For methane injection however, even under conditions of highest reactivity 100% dissociation of the precursor gas can not be reached. In an Ar/CH@sub 4@ plasma under certain conditions up to 40% of the injected precursor flow is transformed into C@sub m@H@sub n@ (m>1) polymers. In an Ar/C@sub 2@H@sub 2@ plasma the polymerization is much less (maximum 4%) and preferentially C@sub 2m@H@sub n@ polymers are formed. This suggests that in an Ar/C@sub 2@H@sub 2@ plasma the C@sub 2@H radicals are the main building blocks in the polymerization process and that they are probably also the dominant radicals in the deposition process. In the case of acetylene injection the deposition rate as measured in situ by ellipsometry is proportional to the depletion of the precursor gas. For methane injection however this proportonality does not hold even when the polymerization is taken into account. The difference in the polymerization rate and the dependence of the deposition rate on the gas depletion for the two plasmas is attributed to the different loss probabilities of the radicals formed in the dissociation. It is suggested that the large amount of C@sub 2@H@sub 2@ formed in the Ar/CH@sub 4@ plasma may lead to formation of radicals which, due to their relatively high loss probability, may become the dominant growth precursors.

Thin Films Division
Room 615 - Session TF-MoA
Fundamentals and Applications of Ionized PVD

Moderator: F.K. Urban III, Florida International University

2:00pm **TF-MoA1 Plasma Interaction Effects in Ion-Beam Assisted Pulsed Laser Deposition of Al-O-N Films**, ***A.A. Voevodin***, *J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory

Interactions between plasmas produced by a nitrogen ion-beam source and pulsed laser ablation of Al@sub 2@O@sub 3@ were studied. Plasma fluxes from both sources intersected on the substrate surface in a typical arrangement for ion-beam assisted pulsed laser deposition (AIPLD). The study was focused on the detection of temporal and spatial plasma distributions, excitation states, and chemical reactions in the substrate vicinity, which were not present when operating each of the plasma sources separately. Plasma emission imaging and spectroscopy analyses using an ICCD camera and a spectrometer were used to investigate plasma development and chemistry in real time using the initial laser pulse for synchronization. In the study, the N@sub 2@ background pressure was varied in the range from 0.08 to 4 Pa and X-ray photoelectron spectroscopy was performed for Al-O-N films. Film elemental compositions were correlated with plasma chemistry. Two significant plasma interaction effects were discovered. One resulted in a considerable activation of N and O and formation of NO in a near substrate region, which then reacted with Al to from Al-O-N. A maximum plasma excitation was observed at reduced 0.1-0.2 Pa N@sub 2@ pressures and provided the highest amount of N in the films. Above 1 Pa of N@sub 2@, the Al-O-N films had lower nitrogen content, even though more nitrogen was available for the deposition. Another interaction effect was observed in the 2-4 Pa pressure region, when formation of short lived plasma channels connecting ion-beam and laser ablated plasmas were detected. These channels resulted in plasma bending and shifting from the substrate surface, affecting film composition and influencing ion beam current extracted from an ion beam-source. The study suggested that the interaction of ion-beam and laser ablation plumes in IAPLD might considerably affect plasma chemistry, excitation stages, and spatial distribution, providing new opportunities for the control of resulting film properties. @FootnoteText@ Key words: ion-beam assisted pulsed laser deposition, plasma chemistry, Al@sub 2@O@sub 3@ ablation, aluminiumoxynitride.

2:20pm **TF-MoA2 Time-of-Flight Measurements of Sputtered Species using Novel Pulsed High Plasma Density Magnetron Discharge**, ***K. Macák***, *V. Kouznetsov, J.M. Schneider, U. Helmersson,* Linköping University, Sweden*; I. Petrov,* University of Illinois, Urbana

Time resolved plasma probe measurements of a novel high power density pulsed plasma discharge are presented. Extreme peak power densities in the pulse (on the order of several kW.cm@super -2@) result in a very dense plasma with ionic flux densities of up to 1 A.cm@super -2@ at source-to-substrate distances of several cm and at a pressure of 0.13 Pa. The pulse duration was ~50 µs with a pulse repetition frequency of 50 Hz. The plasma consists of metallic and inert gas ions, as determined from time resolved Langmuir probe measurements and in situ optical emission spectroscopy data. The influence from the process parameters on the temporal development of the ionic fluxes is discussed. Deconvolution of metal ion probe current pulse waveform allowed for the calculation of the average ion energy. The ionized portion of sputtered metal flux was found

to have an average energy of 2.6 eV in the absence of gas scattering. The obtained energies of the arriving metal ions conform with the collisional cascade sputtering theory. The degree of ionization of the sputtered metal flux at a pressure of 0.13 Pa was found to be 40±20 % by comparing the total flux of deposited atoms with the charge transferred by metal ions in the pulse.

2:40pm **TF-MoA3 Modeling of I-PVD Systems for TiN Film Deposition in Inductively Coupled Plasmas**, ***M. Li***, University of California at Berkeley, CANADA; *D.B. Graves,* University of California at Berkeley

TiN films are widely used as a diffusion barrier for aluminum, tungsten as well as copper in VLSI fabrication. Recently, ionized metal physical vapor deposition, or IPVD, has been used for TiN film deposition. However, this reactive sputtering process is relatively poorly understood. In this work, a two dimensional hybrid model, including a Monte Carlo treatment of fast sputtered atoms from the target and a fluid plasma simulation, is developed to study TiN film deposition in IPVD tools. The model includes a site balance surface model to describe the film deposition and target sputtering processes. Important issues such as neutral gas heating and rarefaction, the uniformity of film deposition across the wafer, and the film deposition characteristics have been investigated. In particular, the model predicts that the titanium species profiles and target shape are major factors in film deposition and computational uniformity at the substrate. The simulation results have been compared to the available experimental measurements.

3:00pm **TF-MoA4 Origin and Evolution of Sculptured Thin Films**, ***R. Messier***, *V.C. Venugopal, P.D. Sunal, H. Maeda,* Penn State University **INVITED**

Sculptured thin films (STFs) are columnar thin films prepared by directed vapor deposition under low adatom mobility conditions. Since the columns grow in the direction of the incoming vapor, and this column direction can be changed instantaneously, a new class of thin films can be engineered in which the STF nanostructural shapes can be sculptured into useful morphologies such as helices, matchsticks, chevrons, and periodically bent nematics. Wide variations in the exact STF shapes, as well as combinations of these morphologies, are possible through simple rotations of the substrate around two canonical axes. Potential applications include optical retardation layers for use in optical storage and communications systems, optical sensors for fluids of biological, chemical or nuclear significance, templates for biomaterials growth, and low-pemittivity materials for microelectronics. For normal angle deposition the columns generally expand and compete for growth evolution, thereby resulting in a cauliflower-like morphology. This is due to an in-plane, isotropic, atomic self-shadowing mechanism. Fortuitously, for large oblique angle deposition conditions („ 40š vapor incidence angle with respect to the substrate normal), typical for STF preparation, the columns become slanted, separated, and cylindrical due to an anisotropy in the self-shadowing process. Thus, the columns have a constant cross-section with film evolution - a requirement for many practical applications. It has been found experimentally, however, that under conditions of rapid or abrupt rotation of the substrate during oblique angle deposition, the columns expand, a situation which could limit their utility. In order to control STF morphology in the broadest sense, it is necessary to understand the details of the atomic clustering and growth competition process. In this paper a fundamental and yet practical approach will be presented for classifying the atomic self-shadowing processes in STF growth based upon previous experience in morphology evolution modeling and experiments. Recent experiments in STF growth include systematic changes in column growth rate / substrate rotation rate, use of textured substrates, and variations of low energy ion bombardment.

3:40pm **TF-MoA6 Ionized Physical Vapor Deposition (PVD) using Hollow-Cathode Magnetron (HCM) Source for Advanced Metallization**, ***E. Klawuhn***, *G.C. D'Couto, K.A. Ashtiani, P. Rymer, M.A. Biberger, K.B. Levy,* Novellus Systems, Inc.

Ionized Physical-Vapor Deposition (I-PVD) has been recognized as the technology of choice for extending the application of PVD processes to < 0.25 µm device geometries. However, due to the complexity of the conventional RF I-PVD, these sources are not in widespread manufacturing use. The Hollow-Cathode Magnetron (HCM) source is a new and promising technology that maintains the simplicity of the PVD technology and combines it with a very high-density diffused plasma (> 10@super 12@ #/cm@super 3@) for efficient ionization of sputtered metals. The HCM is based on the principle of charged particle magnetic mirror applied to an inverted cup shaped target. As such, it does not require any additional RF or microwave sources for generation of metal ions. The HCM source was used for deposition of Ti(N), Ta(N), and Cu films. Excellent bottom coverage (20 % for Cu, 40% for Ta and 30 % for Ti) in narrow, high aspect ratio vias (0.25µm, 5:1 AR) was obtained without the application of RF bias to the wafer. Since reactive processes were run in a non-poisoned mode, both TiN and TaN films had the same step coverage as Ti and Ta films, respectively. The TiN film resistivity is of the order of 30 µ@ohm@-cm (for a 1000 Å film) and close to the theoretical bulk resistivity of 18 µ@ohm@-cm. The HCM films have strong crystallographic orientation, and for Ti, TiN, Ta, and Cu respectively. RF bias was utilized to increase the bottom coverage and the sidewall coverage of the films, thus extending the technology to higher aspect ratios. In addition, RF bias was used to modify film properties such as grain size, grain orientation, and film texture. In this paper, the HCM theory of operation will be reviewed and results will be presented for the application of this source for deposition of Ti(N), Ta(N), and Cu films. In addition, the effects of RF bias on step coverage and film properties will be discussed.

4:00pm **TF-MoA7 Gas Phase Dynamics of Copper Ionized Metal Plasmas**, ***Y. Andrew***, *I.C. Abraham, Z. Lu, T.G. Snodgrass, A.E. Wendt, J.H. Booske,* University of Wisconsin, Madison; *P.L.G. Ventzek, S. Rauf,* Motorola

Copper ionized metal plasmas are of interest for the Damascene process of interconnect fabrication, in which trench and via structures are filled with copper. Used to deposit seed layers for subsequent electroplating, ionized metal plasmas produce films with enhanced conformality compared to conventional physical vapor deposition (PVD) processes. Improved understanding of the performance potential and limitations of this process motivate this study to characterize discharge properties through experiment and simulation. We examine a system consisting of a DC powered 15 cm D copper sputter source and an RF induction plasma powered by a single turn 36 cm D loop antenna internal to the vacuum chamber, with an argon pressure of 10-50 mTorr. Measurements include plasma parameters, ion and neutral copper flux at the substrate, RF and DC potentials on the antenna and in the plasma, and spectroscopic measurements of ground state and metastable copper as well as argon metastable concentrations in the gas phase. The simulations have been done using the Hybrid Plasma Equipment Model, a comprehensive plasma equipment modeling tool developed at the University of Illinois. The plasma is treated as a fluid in this model except for thermal copper neutrals sputtered from the target, for which a Monte Carlo simulation is used. The extensive data set includes some surprising observations. For example, both experiment and simulation show that for some operating conditions, the copper metastable density is substantial compared to that of the ground state population. Measurements and simulation will also address electrical measurements on the system, including a substantial but unexpected DC self-bias voltage on the antenna. Finally, by comparing copper fluxes measured directly and computed from spectroscopically determined gas phase concentrations, we can infer the temperature of the copper in the gas phase, which is found to increase substantially with RF power to the plasma.

4:20pm **TF-MoA8 Effects of Copper Seedlayer Deposition Method for Electroplating**, ***E.C. Cooney III***, *D.C. Strippe, J.W. Korejwa,* IBM Microelectronics

We have investigated copper seedlayer deposition using both ionized PVD and collimation methods by depositing similar films into agressive dual damascene structures. Step coverage measurements using TEM indicated that ionized PVD seedlayers exhibited better bottom and sidewall coverage than collimated seedlayers. Subsequent electroplating of contact structures did not indicate differences in the quality of the filling when observed using SEM. However electrical testing of 68000 dual damascene via chains did show improved chain yield for the ionized PVD deposited films. Cross-sections of the chains revelaed small voids at the bottom of the vias deposited using collimated seedlayers while no voiding was observed for the ionized PVD copper films. Finally SEM examinations of unfilled dual damascene cross-sections indicated the ionized copper seedlayers to be rougher as compared to copper films sputtered using collimation.

4:40pm **TF-MoA9 Steel Coating by Self-induced Ion Plating, a New High Throughput Metallization Ion Plating Technique**, ***P. Vanden Brande***, *A. Weymeersch,* Cockerill Sambre - RDCS, Belgium

Ion plating techniques present major advantages for continuous steel coating in terms of throughput and product quality when compared respectively to sputtering and vacuum evaporation techniques. However, the ion plating systems available on the market today are still cumbersome and present technological difficulties for immediate implementation in high

throughput air-to-air continuous steel coating plants. To address these difficulties we have developped a new ion plating technique referred to as self-induced ion plating in order to produce continuous coating on flat products. This technique is essentially based on the generation of a magnetron discharge in the sputtered and evaporated vapour produced by a tin cylindrical target. Very high deposition rates were achieved (220µm/min) with moderate values of the electrical mean power density (45W/cm@super 2@) applied to the tin target. The magnetron configuration used allowed the reduction of material side losses. This was achieved by reducing the metal escape zone area on the target side. Another feature of this technique is that the control of the heat transfer between the target and its backing plate allows the control of the target surface temperature and hence the control of the sputtered and evaporated material fractions.

5:00pm **TF-MoA10 Analysis of Mode Transistions in I-PVD and Conventional PVD Reactive Sputtering of Refractive Diffusion Barrier Materials**, *D.R. Juliano, R. Ranjan, D.N. Ruzic,* ***J. Norman,*** University of Illinois, Urbana-Champaign

I-PVD techniques have shown to be effective for the deposition of contact, barrier, adhesion and seed layers. For copper metallization such layers include Ti, Ta, TiN and TaN. In conventional PVD processes, reactive sputtering techniques have shown two important deposition modes, namely, metallic and poison modes. In the metallic mode the nitration occurs on the substrate whereas in the poison mode it occurs on both the target and the substrate. There are advantages and disadvantages of each. Mode transitions are compared between I-PVD and conventional PVD sputtering processes. The analysis includes measurements of plasma temperature and density using Langmuir probe techniques, as well as ionization fractions and deposition rates. A dc planar magnetron with a 33-cm diameter target is coupled with a secondary plasma source to ionize the sputtered metal neutral flux to control the angular distribution of the flux arriving at the surface of the substrate. The secondary radio-frequency (rf) plasma is created between the sputtering target and the substrate by a multi-turn coil located in the vacuum chamber. The rf plasma increases the electron temperature and density, which results in significant ionization of the neutral metal flux from the sputtering target. By applying a small negative bias to the substrate, metal ions are drawn to the substrate at normal incidence. A gridded energy analyzer and a quartz crystal microbalance (QCM) are embedded in the substrate plane to allow the ion and neutral deposition rates to be determined.

Thin Films Division
Room 4C - Session TF-MoP
Poster Session

TF-MoP1 Effect of HCl Catalyst in the Formation of Flat Structures of Ta@sub 2@O@sub 5@ Thin Films by Sol-Gel Technique, *S. Santucci,* ***C. Cantalini,*** *A.R. Phani,* University of L'Aquila, Italy

Stoichiometric Ta@sub 2@O@sub 5@ thin films have been successfully deposited on Si (100) substrates by sol-gel technique using tantalum ethoxide as precursor. The films were annealed at different temperatures. The compositional and structural characteristics of the films were systematically examined with the aid of X-Ray Diffraction, Atomic Force Microscopy and X-ray Photoelectron spectroscopy. We demonstrate that upon using Hydrogen chloride (HCl) as catalyst, we obtained uniform flat like structures of Ta@sub 2@O@sub 5@ as observed in tapping mode atomic force microscopy, when compared to the samples without it. X-ray Photoelectron spectroscopy measurements have shown the small presence of SiO@sub 2@ interface layer in the deposited films. A plausible mechanism to obtain flat structures is also explained.

TF-MoP2 Mechanical Properties and Residual Stresses in AlN Films Prepared by Ion Beam Assisted Deposition, ***Y. Watanabe,*** *N. Kitazawa, Y. Nakamura,* National Defense Academy, Japan*; C. Li, T. Sekino, K. Niihara,* Osaka University, Japan

Aluminum nitride (AlN) thin films were prepared on silicon single crystal substrates by ion-beam assisted deposition method, and the influence of the nitrogen ion beam energy on mechanical properties and residual stresses was studied by changing the nitrogen ion beam energy from 0.1 to 1.5 keV. Mechanical properties were examined by a nano-indentation method and residual stresses were evaluated by film curvature measured by an optical cantilever system. The films show elastic behaviors during loading and unloading processes, but the residual depth after the unloading process increases with increasing the ion beam energy, resulting in decreasing in the returned energy ratio. All the films are found to be in compressive stress state and the values of the stress decrease with increasing the ion beam energy. Decreasing tendency is also observed in the relationship between the ion beam energy and film hardness. So as to study the effect of thermal treatment on relaxation of residual stresses, the films were annealed in nitrogen atmosphere at 723 K, and it is found that the films prepared with the high energy ion beam are relaxed more easily than those prepared with the low energy ion beam. These results suggest that rearrangement of AlN occurs readily in the films prepared with the high energy ion beam. It is proposed that the mechanical properties and residual stresses are closely related with each other and they can be controlled by the ion beam energy.

TF-MoP3 The Effects of Temperature and Morphology on the Electron Stimulated Desorption of H@super -@ from Thin Hydrocarbon Films, ***A.D. Bass,*** *L. Parenteau, F. Weik, L. Sanche,* University of Sherbrooke, Canada

In recent years, low energy electron impact techniques have been used to study thin molecular solids under ultra high vacuum (UHV) and have provided valuable information on the electronic interactions that underlie such phenomena as radiation damage to biological materials, dielectric aging and surface mediated photo-chemistry.@footnote 1@ Measurements of the electron stimulated desorption (ESD) of molecular and atomic anions have in part revealed the importance in radiation damage of such processes as dissociative electron attachment (DEA) and dipolar dissociation (DD). In general, the molecular films used in these studies are formed by vapor deposition under UHV conditions. Until very recently,@footnote 2@,@footnote 3@ little consideration was given as to how film preparation and morphology affected ESD measurements and we address questions of this type in this work. We present measurements of the ESD yield of H@super -@ from pure films of n-hexane, ethyl-benzene and benzene as a function of incident electron energy (0 - 20 eV) at various film temperatures between 20 K and their respective sublimation points. The three molecules were chosen as their films display contrasting degrees of porosity, crystallinity etc., Our measurements reveal the variation in the ESD yield from DEA and DD processes as a function of film temperature (and hence morphology). These changes are correlated to others seen in the low energy electron transmission spectra for films of the same molecules deposited at various temperatures. @FootnoteText@ @footnote 1@See for example L. Sanche, IEEE Trans. Dielec. Elec. Insulat. 4, 507 (1997) @footnote 2@ W.C. Simpson M.T. Sieger, T.M. Orlando, L. Parenteau, K. Nagesha and l. Sanche, J. Chem. Phys. 107 8668 (1997) @footnote 3@K.P. Stevenson, G.A. Kimmel, Z. Dohnalek, R.S. Smith and B.D. Kay, Science 283 1505 (1999).

TF-MoP4 Oxidation Studies and Chemical State Analysis of Polycrystalline Magnetron Sputtered (Ti,Al)N Films, ***A. Kale,*** *S. Seal, S. Sundaram,* University of Central Florida

In order to improve the functional properties of hard coatings, recent investigations have been directed to Ti-N based multicomponent materials. In particular the nitride (Ti,Al)N with a Ti:Al ratio of 1:1 seems to be a promising alternative to the widely used TiN. A disadvantage of TiN in high-temperature applications is that it oxidizes rapidly at temperatures above 500 C. In contrast, (Ti,Al)N coatings are characterized not only by high microhardness and dense microstructure, but also by much higher thermal stability. They exhibit better oxidation resistance and hence improved performance over that of TiN. Because of their outstanding properties with respect to hardness, wear resistance, oxidation resistance and corrosion resistance, it seems to be desirable to study the crystal structure and mechanical and chemical properties in detail. The (Ti,Al)N coatings were dc sputter deposited onto 316SS substrates under ambient as well as liquid nitrogen temperatures. The as formed films were oxidized in a vertical fused-silica tube furnace in a pure O2 flowing atmosphere at varying temperatures (700-900C). Both types of films were compared to each other with respect to their mechanical as well as chemical properties. The characterization work involved x-ray diffraction (XRD) to study the amorphous or crystalline nature of the films thus predicting their crystal structure. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images will provide information about the particle size and film thickness. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) will provide rapid information of elements in the top few atomic layers in addition to the compositional analysis and detailed chemical bonding information. The difference in film stoichiometry will be compared at the two different deposition conditions and will thus reflect their behavior under oxidizing conditions.

TF-MoP5 Characterization of VO@sub 2@ Epitaxial Films with Different Orientations Grown on Sapphire (110) by Sputtering, ***P. Jin,*** *S. Tanemura,* National Industrial Research Institute of Nagoya, Japan*; K. Macak, U. Helmersson,* Linkoping University, Sweden

Vanadium dioxide is one of the most important compounds in the V-O system. It exhibits a semiconductor-to-metal phase transition at 68°C, accompanied by large changes in electrical resistivity (up to 10@super 5@) and optical properties (from transmitting to reflecting in the infrared). Thin films of vanadium dioxide have been studied for electrical and optical switching devices. It is known that an epitaxial film, which can be grown on sapphire substrate, exhibits properties comparable to single crystal. However, there is little information on the deliberate control of orientation of an epitaxial film and the effect on film property. In this study, thin films vanadium dioxide were grown using DC reactive magnetron sputtering on single crystal 110-oriented sapphire substrates held at 400-600°C. The magnetron source was of the unbalanced type giving rise to more intense bombardment as compared to conventional sources. Different film orientations was achieved with different sputtering geometry, most likely due to varying energetic particle bombardment and growth rate, i.e., an on-axis deposition (substrate facing target) and an off-axis deposition resulted in well-defined (100)- and (001)- oriented epitaxial films, respectively. The epitaxial films were examined by x-ray diffraction using conventional @theta@-2@theta@ scans, rocking curves, and pole figure plots. The compositions were determined from Rutherford backscattering spectroscopy (RBS) and the surface morphologies were studied with atomic force microscopy (AFM). The different film orientations resulted in significant difference in film properties such as the temperature and sharpness of the phase transition, as confirmed from the measurement of electrical resistance vs temperature.

TF-MoP6 Towards a Fully Monitored Fourier Transform Infrared Spectroscopic Ellipsometer, ***J.C. Cigal,*** *G.M.W. Kroesen,* Eindhoven University of Technology, The Netherlands

Infrared ellipsometry emerged few years ago as a powerful sensitive and non-intrusive optical technique for characterizing of surfaces, interfaces and thin films. The recent improvements in Fourier transform analysis and of polarizers helped to overcome problems formerly restricting the applications of such a technique. Among the different ellipsometer configurations in use, we opted for a rotating compensator ellipsometer running in the middle infrared. This technique offers several advantages compared to other ellipsometric methods, such as the non-ambiguous

determination of ellipsometric parameters and the insensivity to source and detector polarization. However, the principal fact preventing a widespread application of rotating compensator for spectroscopic purposes was the absence of a good spectroscopic retarder. We are currently developing one available in the 1000-4000 cm@super -1@ spectral range. The principle is based on internal reflection inside a Zinc Selenide crystal. Moreover, measurement speed can significantly be improved by an accurate synchronization between the scanner of the spectrometer and the stepping motors used to rotate the polarizers and the compensator. This will allow us, as a next stage, to perform in-situ and real time measurements.

TF-MoP7 Improved Light Stability of Colored SiO@sub 2@ Coatings Containing Organic and Metalorganic Dye Molecules, *L.L. Diaz-Flores,* Inst. Tecnologico de Saltillo, Mexico*; J.J. Perez-Bueno,* Univ. Autonoma de Queretaro, Mexico*; F.J. Espinoza-Beltran, R. Ramirez-Bon,* ***Y.V. Vorobiev****, J. Gonzalez-Hernandez,* CINVESTAV-IPN, Mexico

The sol-gel method has been used to prepare SiO@sub 2@coatings containing various amounts of organic and metalorganic dyes, introduced in the starting solutions. The starting solutions were mixed of tetraethylorthosilicate, water and ethanol. In order to have a better dispersion of the molecular dye into the glass matrix, the starting solutions were subjected to a milling process at various times using an appropriated ball mill. It is observed that in the coatings prepared from solutions without the milling process, the dye is agglomerated into small particles and those prepared from solutions subjected to the milling process show much better dye dispersion. A good dispersion is achieved after about 4 hr of milling, this is reflected in an increase in the optical absorption and makes the samples stable to light exposure. Both results are explained using a model which predicts the degree of dye dispersion. Using this model, an estimation of the size of the dye aggregates is made.

TF-MoP8 Diamond Formation Using a Low-Pressure Inductively Coupled Plasma*, **H. Ito,*** Nagoya Municipal Industrial Research Institute, Japan*; K. Teii,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan*; M. Hori,* Nagoya University, Japan*; T. Takeo,* Nagoya Municipal Industrial Research Institute, Japan*; T. Goto,* Nagoya University, Japan

Diamond was successfully synthesized by using a H@sub 2@-rich CH@sub 4@/CO/H@sub 2@ and H@sub 2@-rich CH@sub 4@/H@sub 2@ inductively coupled plasma at a low pressure of 11 Pa. The ratio of particle size to deposition time, which is a criterion of the diamond growth rate, in H@sub 2@-rich CH@sub 4@/CO/H@sub 2@ mixture gas plasmas was larger than that in H@sub 2@-rich CH@sub 4@/H@sub 2@ mixture gas plasmas. The nondiamond phases in the deposits increased as CO gas was added to H@sub 2@-rich CH@sub 4@/H@sub 2@ mixture gas as observed by the Raman spectra. In order to investigate the mechanism for the diamond formation, C-atom densities in the plasmas were measured by using a vacuum ultraviolet absorption spectroscopy. In addition CH, OH, H-atom emission intensities were measured by optical emission spectroscopy. As a result, the C-atom densities and OH emission intensity increased with increasing the mixture ratio of CO to CH@sub 4@, while CH and H-atom emission intensities were almost constant. The generation of C-atoms from CO gases was much larger than that from CH@sub 4@. On the basis of the correlation between the quality of deposits and the C-atom densities in the plasma, C-atoms were found to contribute to form amorphous carbon phases rather than diamond phase. Moreover, using the low-pressure inductively coupled diamond formation plasmas, the importance of the abstraction of diamond surface-bonded H-atoms by OH radicals was suggested.

TF-MoP9 Microstructure of Ti:D Films Prepared by Reactively rf Sputtering*, **S. Nakao,*** *P. Jin, K Saitoh, Y. Miyagawa, S. Miyagawa,* National Industrial Research Institute of Nagoya, Japan

Metal deuteride films have attracted much attention because of potential application for neutron source in ion beam technology. Especially, titanium deuteride (Ti:D) films are much stable at relatively high temperature up to about 400 @super o@C. In this study, Ti:D films were prepared by reactively rf sputtering and the microstructure was examined. Ti:D films were deposited mainly on Si substrates under the various conditions of the rf power and the ratio of Ar and D@sub 2@ gases. Thin film x-ray diffraction (XRD) measurements were carried out to examine the crystal structure of the films. Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) were performed with a 1.7 MV tandem-type ion accelerator to analyze the composition of the films. From the results of the XRD measurements, it was found that the Ti:D films have a delta-phase (fluorite) crystal structure at low rf power of 100 W. However, the results of RBS and ERDA measurements revealed that the Ti:D films contained the impurity elements such as hydrogen and oxygen. It was inferred from the quantitative analysis that the films were composed of delta-phase titanium deuterides (or hydrides) and amorphous titanium oxides.

TF-MoP10 Growth of Si Thin Films on CeO@sub 2@/Si(111) Substrate Prepared by Electron Beam Evaporation*, **C.G. Kim,*** *J.H. Yang, B.S. Moon, C.Y. Park,* Sung Kyun Kwan University, Korea

The Si/CeO@sub 2@/Si structure is one of the silicon-on-insulator (SOI) and was prepared by a hetero-epitaxially growing method. Cerium dioxide(CeO@sub 2@) is an insulating material with a lattice mismatch of 0.35% to silicon. Si film was grown on CeO@sub 2@(111)/Si(111) substrate by using high-vacuum evaporation. We have studied on the growth mechanism of Si for the various deposition conditions and analyzed by X-ray diffraction, double crystal XRD, TEM, AFM and the mobility measurement. For homo-epitaxial growth of Si, a better epitaxial Si film had been formed 800@super o@C. But, for the Si epitaxial growth on the CeO@sub 2@(111)/Si(111) the substrate temperature was limited to about 620@super o@, because a dissociated oxygen from CeO@sub 2@ and an out-diffused carbon. The Si film was epitaxially growth along (111) direction of the CeO@sub 2@ at 620@super o@C and consisted of domains oriented along (111) direction. The mobility was 56.4cm@super 2@/(Vs) at carrier density of 5.87x10@super 19@/cm@super 3@.

TF-MoP11 Origin of Electrical Property Distribution on Surface of ZnO:Al Films Prepared by Magnetron Sputtering*, **T. Minami,*** *T. Miyata, T. Yamamoto, T. Nishitani,* Kanazawa Institute of Technology, Japan

This paper investigates the origin of electrical property distribution on the substrate surface of ZnO:Al films prepared by magnetron sputtering on substrates placed parallel to the target surface. The films were prepared using a magnetron sputtering apparatus with a sintered or powder target (diameter of 140mm) and either a dc or rf plasma power source. When the films were prepared on substrates at the same temperature with the same deposition rate under optimized sputter deposition and target preparation conditions, the lowest obtained resistivity found in ZnO:Al films prepared by either dc or rf magnetron sputtering was roughly the same. However, the ZnO:Al films prepared by dc sputtering exhibited a larger increase of resistivity at locations on the substrate corresponding to the target erosion area than found in films prepared by rf sputtering. In contrast, the resistivity distribution of ZnO:Al films prepared by rf magnetron sputtering with an applied external magnetic field which focused the rf plasma was similar to that of films prepared by dc magnetron sputtering. Thus, the difference in electrical property distribution obtained between rf and dc magnetron sputtering is mainly related to the activity and amount of oxygen reaching the substrate surface as well as its spatial distribution.

TF-MoP12 Effect of C@sub 2@ Radicals on Diamond Growth Using Low-Pressure, Radio Frequency, CH@sub 3@OH/H@sub 2@/H@sub 2@O Inductively Coupled Plasma*, **T. Shiomi,*** *H. Nagai, M. Hiramatsu, M. Nawata,* Meijo University, Japan

Previously we demonstrated the successful formation of diamond crystals using a low-pressure, radio frequency (rf, 13.56 MHz), inductively coupled plasma (ICP) in the total pressure range of 9.3-18.6 Pa.@footnote 1@ In contrast with conventional methods of diamond chemical vapor deposition (CVD) employing high-pressure plasma (@>=@100 Pa), in the case of low-pressure, high-density, and highly dissociated plasmas, carbon dimer (C@sub 2@) radicals or carbon atoms instead of methyl radicals might be major species for film formation. C@sub 2@ radical is considered to be one of important radicals for the nanocrystalline diamond deposition using plasma-enhanced CVD.@footnote 2@ In this work, C@sub 2@ radical density in a low-pressure (@<=@13 Pa), rf-ICP employing CH@sub 3@OH/H@sub 2@/H@sub 2@O source for diamond CVD was measured using absorption spectroscopy with Xe lamp emitting a continuous spectrum as a light source. The correlation between the absolute C@sub 2@ radical density and the quality of diamond films was investigated. In the Raman spectra of diamond formed using a low-pressure rf-ICP, a broad peak around 1140 cm@super -1@ arising from nanocrystalline diamond was observed together with the strong 1332 cm@super -1@ diamond Raman peak. C@sub 2@ radical density increased almost linearly with increasing rf input power or CH@sub 3@OH partial pressure. On the other hand, C@sub 2@ radical density decreased with increasing H@sub 2@O partial pressure, while the intensity of 1332 cm@super -1@ diamond Raman peak increased with increase of the H@sub 2@O partial pressure up to 5.3 Pa. @FootnoteText@@footnote 1@H. Noda, H. Nagai, M. Shimakura, M. Hiramatsu, and M. Nawata, J. Vac. Sci. Technol. A 16, 3170

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TF-MoP13 Properties of Indium Oxide Thin Films Prepared by Reactive Electron Beam Evaporation Technique for EMI Control, ***J. Asbalter***, *A. Subrahmanyam,* Indian Institute of Technology, India

It is well known that transparent conductors like Indium oxide (IO) are good Electro Magnetic Interference (EMI) shields. In the present investigation, the EMI shielding property of indium oxide thin films has been studied as a function of growth temperature. All the IO films are grown on glass substrates by reactive electron beam evaporation technique at a chamber pressure (with the reactive gas, oxygen) of 2.5 x 10@super -4@ milli bar. The substrate temperature is varied between 160@super o@C - 200@super o@C. All the films show metallic properties (carrier concentration, N = 10@super 19@/cc, Hall Mobility =20-30 cm@super 2@ V@super -1@ sec@super -1@) with an optical transmission above 85% (at 500 nm wavelength). It is found that the EMI shielding efficiency (SE) of IO films (of 100 nm thickness) is very much comparable to that of the silver coated metal sheet in the measured frequency range 1 MHz till 100 MHz . As is well known that high frequecny shielding is related to the plasma frequency and the low frequency shielding is dependant on the magnetic properties. The AC (magnetic) susceptibility of the films measured in the temperature range 300 K till 6 K show very interesting magnetic properties. All the films show diamagnetic behavior at room temperature (300 K). For the films prepared at 200@super o@C, there is a clear paramagnetic behavior below 250 K. Present work analyses the reasons for the paramagnetic nature and its consequence on the low frequency (< 10 MHz) shielding efficiency.

TF-MoP14 Diffusion of Cu from PVD Al-Cu Alloy and CVD Cu Thin Films into CVD Al Thin Films Inside Submicron Via Holes, ***B. Rogers***, Vanderbilt University

Solid state diffusion of Cu from copper containing films into a chemical vapor deposited (CVD) Al film was evaluated as a method to dope the CVD Al with Cu atoms to enhance its electromigration resistance. CVD Cu and PVD Al-1.5 wt% Cu thin films were used as the copper sources. Thin film stacks consisting of CVD Al/CVD Cu and PVD Al-Cu/CVD Al were deposited onto unpatterned silicon dioxide films as well as silicon dioxide films patterned with 0.6-micron diameter by 1.2-micron deep via holes. Samples were annealed for 0, 5, 15, or 60 minutes at 360, 390, or 420 degrees Celsius. Backscatter electron microscopy was used to image theta phase (Al@sub 2@Cu) precipitates inside vias. The number of precipitates and fraction of via cross-sectional area covered by the precipitates were used to estimate the amount of Cu present in the vias. These results are compared to Rutherford backscatter spectrometry and Auger electron depth profiling analyses of samples with films deposited onto unpatterned substrates.

TF-MoP15 Process Control and Properties of Aluminum Doped Zinc Oxide Films Deposited by High Rate Mid-frequency Reactive Magnetron Sputtering, ***N. Malkomes***, *M. Vergöhl, B. Szyszka, T. Matthée,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany

Aluminum doped Zinc oxide films are promising candidates for economic TCO applications. To reach high deposition rates (about 7 nm/s at 4.5 W/cm2) in combination with optimum TCO properties by reactive mid-frequency (MF) sputter technique, the process window has to be precisely controlled. In order to overcome the typical hysteresis problem the process stabilization was done by plasma impedance control for ease of use, enabling to stabilize the deposition process in any working point on the s-curve of the corresponding hysteresis loop. In addition the setpoints were characterized by partial pressure measurements, optical emission spectroscopy (OES), and with in-situ spectroscopic ellipsometry. The influence of deposition parameters (working point, pressure, temperature) on the electrical and optical properties as well as film growth and morphology were studied by photometry, Hall-measurements and in-situ and ex-situ spectroellipsometry, respectively. Due to the bandgap widening the optimum films show neutral color. The ellipsometric spectra could be well modelled without using interface layers indicating the dense structure of the films. Electrical measurement yield that the optimum resistivity of ZnO:Al films deposited on unheated substrates is about 2.5 times higher than at 200Â°C substrate temperature. In the latter case, a value of 290ÂµOhm cm could be reached. In addition the process window of stoichiometric films is widened due to oxygen partial pressure limited forming of the film on the heated substrate. .

TF-MoP16 Low-temperature Growth of Ti(C,N) Thin Films on D2 Steel and Si(100) Substrates by PEMOCVD, *B.-C. Kang, J.-H. Boo, Y.K. Cho, J.-G. Han,* ***C.H. Heo***, SungKyunKwan University, Korea

We have deposited Ti(C,N) thin films on Si(100) and D2 steel substrates in the temperature range of 150 - 300 @super o@C using tetrakis diethylamido titanium (TDEAT) and titanium isopropoxide (TIP) by pulsed DC plasma enhanced metal-organic chemical vapor deposition (PEMOCVD) method. Polycrystalline Ti(C,N) thin films were successfully grown on either D2 steel or Si(100) surfaces at temperature as low as 150 @super o@C. Compositions of the as-grown films were determined with XPS and RBS. From XPS analysis, thin films of Ti(C,N) with low oxygen concentration were obtained. RBS data were also confirmed the changes of stoichiometry and microhardness of our films. Radical formation and ionization behaviors in plasma are analyzed by optical emission spectroscopy (OES) at various pulsed bias and gases conditions. H@sub 2@ and He+H@sub 2@ gases are used as carrier gases to compare plasma parameter and the effect of N@sub 2@ and NH@sub 3@ gases as reactive gas is also evaluated in reduction of C content of the films. In this study, we found that He and H@sub 2@ mixture gas is very effective in enhancing ionization of radicals, especially N@sub 2@ resulting is high hardness. The higher hardness of film is obtained to be ca. 1700 HK 0.01 but it depends on gas species and bias voltage. The proper process is evident for H@sub 2@ and N@sub 2@ gas atmosphere and bias voltage of 600 V. However, NH@sub 3@ gas highly reduces formation of CN radical, thereby decreasing C content of Ti(C,N) thin films in a great deal. Compared to PVD TiN films, the Ti(C,N) film grown by PEMOCVD has very good conformability; the step coverage exceeds 85% with an aspect ratio of more than 3.

TF-MoP17 A Study on the Characteristics of TiN Thin Film Deposited by Atomic Layer Chemical Vapor Deposition Method, ***H. Jeon***, *J.W. Lee, J.H. Koo, Y.S. Kim, Y.D. Kim, D.S. Kim,* Hanyang University, Korea

A TiN film which exhibits a NaCl structure is now used as a diffusion barrier in ULSI device because it shows a very low resistivity, good adhesion characteristics and thermal stability.@footnote 1@ In this study, we deposited TiN film on Si substrate by using atomic layer chemical vapor deposition system.@footnote 2@ The TiN film deposited by this method is expected to have excellent physical and electrical properties.@footnote 3@ In this system, the TiCl@sub 4@ and NH@sub 3@ gases as Ti source and an reactant were supplied, separately and Ar purge gas was added between each source and reactant supply to suppress the direct reaction between source and reactant. The process parameters to grow TiN were process temperature, number of cycle to supply the reactant and source gases, source supplying time, and purging time. After growing this TiN film, the physical and electrical properties were measured by XRD, AFM, SEM, AES, TEM, RBS and a four point probe. The crystallinity and the surface and interface were analyzed by XRD, SEM and TEM. The root mean square toughness of TiN surface was measured by AFM and its value was about 15Å. The chemical analysis was done by AES and the Cl content in TiN film was below the detection limit of Auger Electron Spectroscopy which was below 1%. We will compare these TiN thin film data with other deposition method, such as PECVD and MOCVD and will discuss the TiN film growing method based on the thermodynamic consideration and atomic size computer modeling. @FootnoteText@ @footnote 1@J. E. Sundgren, Thin Solid Films, 128, 21-44 (1985) @footnote 2@S. Yokoyama, H. Goto, T. Miyamoto, N. Ikeda, K. Shibahara, Applied Surface Science, 112, 75-81 (1997) @footnote 3@T. Suntola, Thin Solid Films, 216, 84-89 (1992).

TF-MoP18 Non-Stoichiometric PMN-PT Films Grown by Laser Ablation, *A. Fundora,* Universidad de la Habana, Cuba; ***J.M. Siqueiros***, UNAM, Mexico; *J. Portelles,* Universidad de la Habana, Cuba

Films of Pb(Mg@sub 1/3@Nb@sub2/3@)@sub2.1@ Ti@sub0.3O3@ (PMN-PT) have been grown on Pt/SiO@sub2@/Si substrates by pulsed laser ablation. The dielectric and microstructural properties of the non stoichiometric thin films of the type: 2.1PMN-0.3PT are studied in this work. The nature of the ferroelectric layer-electrode interface is analyzed by transmission electron microscopy (TEM) as well as the effect of its characteristics in the performance of the multilayer system. Surface structure and cross section studies were performed by scanning electron microscopy (SEM). Curves of dielectric permittivity as a function of temperature and hysteresis loops are reported.

TF-MoP19 The Advancing Techniques and Sputtering Effects of Oxide Films Fabricated by Stationary Plasma Thruster with Argon and Oxygen Gases, ***J. Cho,*** KIST, Korea*; Y. Ermakov,* Mirea, Russia*; K.H. Yoon,* Yonsei University, Korea*; S.K. Koh,* KIST, Korea

The using of stationary plasma thruster (SPT) ion source, invented previously for space application in Russia , in experiments with surface modifications and film deposition systems is reported here. Plasma in the SPT is formed and accelerated in electric discharge taking place in the crossed axial electric and radial magnetic fields. Brief description of the construction of specific model of SPT used in the experiments is presented. With gas flow rate 39 ml/min, ion current distributions at several distances from the source are obtained. These was equal 1-3 mA/cm2 within an ion-beam ejection angle of ï‚± 20o with discharge voltage 160 V, for Ar as a working gas. Such an extremely high ion current density allows us to obtain the â€¦ films with deposition rate â€¦ by sputtering â€¦ target. It is shown a possibility of using of reactive gases in SPT (O2 and N2) along with high purity inert gases used for cathode to prevent the latter contamination. It is shown the SPT can be operated at the discharge and accelerating voltages up to 600 V. The results of presented experiments show high promises of the SPT in sputtering and surface modification systems for deposition of oxide thin films on Si or polymer substrates for semiconductor devices, optical coatings and metal corrosion barrier layers. Also, we have been tried to establish in application of the modeling expertise gained in electric and ionic propulsion to permit numerical simulation of additional processing systems. In this mechanism, it will be compared with conventional DC sputtering for film microstructure, chemical composition and crystallographic considerations.

TF-MoP20 An Alternative Procedure for the Deposition of Close-Spaced Sublimation CdTe/CdS Solar Cells, ***H.R. Moutinho,*** *R.G. Dhere, M.M. Al-Jassim, C. Ballif, L.L. Kazmerski,* National Renewable Energy Laboratory

In previous work (JVST 1998 and 1999), we demonstrated that a recrystallization process causes the changes in physical properties of CdTe films heat-treated with CdCl@sub 2@. Using this information, we were able to induce recrystallization in close-spaced sublimation (CSS) CdTe films, depositing these films at temperatures about 200°C lower than usually used in this process. This lower-temperature deposition process is very attractive in the fabrication of solar cells because it implies in energy economy, and also avoids or minimizes the problem with diffusion of impurities from the glass substrate to the active elements in the cell. In the present work, we deposited CSS CdTe films on solar-cell substrate structures using relatively low temperatures and varied deposition parameters, (e.g., deposition temperature and growth rate). We also subjected the films to two different treatments (dipping in CdCl@sub 2@/methanol solution and exposure to CdCl@sub 2@ vapor), and varied many parameters, such as treatment temperature and time, and saturation of the solution. The objective was to optimize the deposition and heat-treatment parameters to obtain high efficiency cells. The structure of the CdTe films was studied using atomic force microscopy, to obtain information on average grain size and surface topography; X-rays diffraction, to obtain information on lattice parameter and phase formation; and X-ray Photoelectron Spectroscopy, to study film composition. We correlated the various deposition and treatment parameters with the performance parameters (quantum efficiency, open-circuit voltage, short-circuit current, fill factor, and efficiency) of completed devices. We showed that, although the solar cells fabricated at higher temperatures still provide the best efficiencies, the low temperature method can produce solar cells with intermediate efficiencies (>10%), which will be more attractive for industrial application, because of the manufacturing and economic advantages.

TF-MoP21 CdS/CdTe Interface Analysis by Transmission Electron Microscopy, ***R.G. Dhere,*** *M.M. Al-Jassim, K.M. Jones, H.R. Moutinho, T.A. Gessert, L.L. Kazmerski,* National Renewable Energy Laboratory

CdTe-based polycrystalline solar cells are leading candidates for terrestrial photovoltaic applications. High efficiency devices have been obtained despite large lattice mismatch between hexagonal CdS and cubic CdTe. Best CdTe based devices have been made with CdS/CdTe structure. Knowledge of the properties of the CdS/CdTe interface is critical to improve the understanding of the device as this interface lies close to the active junction in the device. In the present work, CdS was deposited by chemical bath deposition on Si substrates and CdTe was deposited by close spaced sublimation. Si substrates were used to facilitate the preparation of thin cross-sectional specimens for TEM analysis. The chemical nature of the CdS/CdTe interface, structural properties, and their dependence on the fabrication parameters e.g. substrate temperature (475-600°C) and post-deposition CdCl@sub 2@ heat treatment were analyzed. In addition, the effects of the interface structural defects on the crystallinity of CdS, prior to CdTe deposition, were examined. Small spot energy dispersive spectroscopy (EDS) of the interface revealed a considerable amount of sulfur in CdTe. The concentration of sulfur, in general, was higher in the grains with higher density of structural defects and at the grain boundaries. Planar defect density in CdTe films increased with substrate temperature while the threading dislocation density decreased. Interface analysis showed that the majority of the crystalline defects in the CdTe films, deposited on CdS, were generated at the interface. The crystallinity of CdS did not have major influence on the interface defect generation.

TF-MoP22 In-Plane Texturing in Evaporated Cr Films, ***J.F. Whitacre,*** University of Michigan*; Z.U. Rek,* Stanford Synchrotron Radiation Laboratory*; J.C. Bilello, S.M. Yalisove,* University of Michigan

The evolution of crystallographic texture in Cr films thermally evaporated using no energetic assistance was examined. In particular, the existence of an in-plane texture in films deposited onto obliquely oriented substrates was studied. All films were grown using electron-beam evaporation in a UHV chamber on (100) test-grade Si wafers with native oxide. The substrates were positioned such that their surface normals were oriented either 0° or 60° with respect to the adatom flux vector. Texturing, grain development, and surface morphology were studied using x-ray and electron diffraction, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The films grown on substrates oriented perpendicular to the flux vector developed a strong (110) out-of-plane texture, but showed no signs of in-plane texturing. These films had well-defined crystalline columnar grain structures and faceted surface morphologies. Those films grown on obliquely oriented substrates also displayed columnar grain structures and surface facets, though they were inclined ~35° with respect to the substrate surface normal. Despite this tilt, the out-of-plane texture was still (110). A heuristic model is proposed which describes the evolution of in-plane texture in evaporated films and accounts for the morphology and grain development observed. The combination of obliquely arriving adatoms and anisotropic surface facets creates an in-plane shadowing phenomena. If surface diffusion lengths are limited to grain dimensions, the model shows how grains with particular in-plane crystallographic orientations will grow at the expense of others. This process is modeled numerically and compared with experimental results. Work supported under ARO Army contracts DAAH 04-95-1-0120 and DAAG 55-98-1-0382. Some data collected at SSRL, funded by the US DoE.

TF-MoP23 Sputter Deposition of Ni Thin Films For Nickel Silicide Metallization, ***H. Zhang,*** Tosoh SMD, Inc.

NiSi is considered as one of the candidates to replace TiSi@sub 2@ contact in deep sub-miron metallization due to its low resistivity and lower formation temperature. Sputter deposition of Ni thin film is one of the crucial steps in nickel salicide (self-aligned silicide) process. One problem associated with sputter deposition of Ni is that Ni is a ferromagnetic material and is difficult to sputter. A Ni sputtering target results in low magnetic flux intensity in front of the target because the target shunts a considerable percentage of magnetic flux from system magnets. High magnetic flux density can be obtained by using a high pass-through flux (PTF) Ni target that allows maximum magnetic flux permeate through a target. In this study, the effects of target PTF and sputtering process parameters such as Ar pressure, sputtering power and substrate temperature on sputter process were studied. Ni targets with the PTF% of 40% (high PTF) and 30% (low PTF) were tested. Ni thin films were deposited on 200 mm (100) Si wafers. Sputter deposition rate, I-V characteristics, film sheet resistance and film uniformity were measured under various sputter conditions. The high PTF target resulted in low sputtering impedance and better Rs film uniformity. Rapid thermal processing (RTP) was carried out to form nickel silicides at temperatures between 300C to 900C for various times. Phases and microstructure of the films were characterized. The sheet resistance decreased significantly after annealing at 400C to 600C due to formation of NiSi. The significant increase in sheet resistance after annealing above 700C was attributed to formation of NiSi@sub 2@ phase.

TF-MoP24 Synthesis of Highly Oriented Piezoelectric AlN Films by Reactive Sputter Deposition, ***F. Engelmark,*** *G. Fuentes, I.V. Katardjiev, A. Harsta, U. Smith, S. Berg,* Uppsala University, Sweden

Nucleation and growth of polycrystalline AlN films on thermal and CVD oxide have been studied during RF reactive sputter deposition. The influence of the growth conditions, namely deposition pressure, RF power, Ar/N@sub 2@ ratio, substrate temperature, on film properties has been systematically studied. The properties of interest are crystallinity, degree of

orientation, crystallite size, surface roughness, stress, piezoelectric coupling, acoustic velocity and others. The films have been analyzed with RBS, ESCA, XRD, ellipsometry, SEM, AFM, stress measurements, etc. It is found that these properties are sensitive functions of all deposition parameters and that there exist optimal deposition conditions under which films of high quality are obtained. The films at optimal conditions were analyzed with the following results: FWHM XRD 0.216 deg, FWHM rocking curve 1.62 deg, crystallite size 38 nm, optical index 2.15, surface roughness 31 Angstroms, stress 400 MPa. Further, to study the electro-acoustic properties of the films surface acoustic wave (SAW) filters were fabricated operating at 534 MHz. The thin film structure consists of AlN/SiO@sub 2@/Si. The electrodes of the interdigital transducers were made of Al. Examination of the frequency response indicated an acoustic velocity of 4900 m/s and a moderate coupling coefficient.

TF-MoP25 Surface Morphology Analysis in Correlation with Crystallinity of CeO@sub 2@(110) Layers on Si(100) Substrates, ***T. Inoue***, *T. Nakamura, S. Nihei,* Iwaki Meisei University, Japan*; Y. Yamamoto,* Hosei University, Japan

In the course of the study on epitaxial growth of CeO@sub 2@ layers on Si(100) substrates, it is found that the layer has (110) orientation and requires substrate temperature above 820°C. Recently, we have succeeded in lowering growth temperature by more than 100°C by using newly developed "electron beam assisted evaporation". In general, epitaxial growth needs enough migration energy for adsorbed atoms and/or molecules. In the vicinity of the critical condition for epitaxial growth, CeO@sub 2@ layers having various crystallinity are obtained depending on growth conditions such as growth temperature, pre-treatment of the Si surface, contents of residual gas in the vacuum atmosphere and so on. It is very important to understand the growth mechanism, which rules crystallinity of the layer. We will present surface morphology analysis by atomic force microscopy (AFM) in correlation with crystallinity of the layers determined by reflection high energy electron diffraction (RHEED). It is clearly observed that surface morphology changes with crystallinity of the CeO@sub 2@ layers. Single crystal samples show a nanometer-scale-periodically corrugated sturcture, which consists of (111)-facets. On the other hand, the surface of poly-crystalline samples with a strong tendency of orientation consists of tetrahedral hillocks with irregular-rotational-orientations within the horizontal plane. Samples with a ring RHHED pattern show a very finely grained surface. These features clearly reflect the difference in the growth mechanism, especially at the early stage of the growth. Results on quantitative analysis of AFM data will be given.

TF-MoP26 Oxide Thin Films for Electroluminescent Phosphors, ***J.S. Lewis***, *P.H. Holloway,* University of Florida

The use of oxide phosphors for thin-film electroluminescent (TFEL) displays has been investigated. Thin films of Zn@sub 2@GeO@sub 4@:Mn were deposited by RF magnetron sputtering from powder targets. The devices exhibited a brightness value of 85 cd/m@super 2@ versus 100 cd/m@super 2@ for the traditional ZnS:TbOF, another green emitting phosphor. The Zn@sub 2@GeO@sub 4@:Mn devices emit in the green with CIE color coordinates x = 0.30 and y = 0.66, which is a more saturated green than ZnS:TbOF. These data show that the performance of oxide phosphors rival that of the traditional sulfide based phosphors. Introduction of surface roughness and further optimization of processing should improve the values even further. Data from blue-emitting oxides will also be presented, as will injection layer schemes which should improve charge injection and lead to lower threshold voltages.

TF-MoP27 XPS and AES Investigation on the Oxidation Resistance of Plasma-treated Copper Leadframe, *A. Wong,* Nanyang Technological University, Singapore*;* ***R.G. Krishnan***, Institute of Microelectronics, Singapore*; G. Sarkar,* Nanyang Technological University, Singapore

Copper is widely used as a material in the microelectronic plastic packaging and IC interconnect applications. The oxidation of copper to form oxide due to microelectronic processing can result in poor copper metal to epoxy mold compound (Cu/EMC) bonding causing package delamination which compromises package reliability. Besides, metallization material problems such as increment in signal transmission delays, decrease power dissipation and decrease reliability to electrical and thermal stress migration failures can occur. Plasma treatment of copper is believed to be able to enhance its oxidation resistance. Based on the x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) results, it was possible to confirm firstly, the successful incorporation of C and N into a copper film above the copper substrate using plasma treatment and secondly, the change in oxidation resistance of this film as a result of the treatment. Thickness measurements from AES depth profiles also confirmed the dominant influence the film thickness have on the enhancement of oxidation resistance in the film as compared to a small change in film stoichiometry. XPS and AES analyses show that once the film was heated at 250@super o@C, the N/Cu (atomic concentration) ratio of the film decreased from 1.074 to 0.635. Heating at 300@super o@C cause further decaying of the N/Cu ratio to to 0 which is confirmed by the disappearance of the XPS N 1s signal. There is no difference in the binding energy of the XPS Cu 2p3/2 signal of the pristine copper and the treated copper. The oxidation of pristine copper at 250 °C can be seen from the shift of the XPS Cu 2p3/2 binding energy at 932.70 eV to 933.60 eV and an increasing Full-width-half-maxima (FWHM) from 1.00 eV to 3.00 eV. However, these are not observed for the oxidation-resistant film at 250 °C as there is a delay in the oxidation onset temperature (shown by the shift in binding energy and increase in FWHM of the XPS Cu 2p3/2 spectra) by at least 50 °C, which depends on the film thickness. The surface analysis data and the oxidation resistance of the film are finally correlated and discussed.

TF-MoP29 Optimization of the Reflectivity of Magnetron Sputter Deposited Silver Films, ***M. Vergöhl***, *N. Malkomes, B. Szyszka, F. Neumann, T. Matthée,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany*; G. Bräuer,* Leybold Systems GmbH, Germany

Silver films were deposited by means of dc and mid-frequency (MF) magnetron sputter deposition on floatglass in order to achieve a maximum reflectivity over the entire visual and infrared spectral range. The films were investigated by means of ex-situ and in-situ spectroscopic ellipsometry, reflectivity, conductivity measurements, and atomic force microscopy (AFM). The following deposition parameters were varied: mid-frequency and dc-technique, power density, sputtering pressure, substrate temperature, sputtering gas (Ar, Kr, Ne), nitrogen and oxygen residual gas, and film thickness. With the aid of in-situ spectroscopic ellipsometry, it can be shown that for certain process parameters an optimum layer thickness exists for achieving a maximum reflectivity in the visual spectral range. With increasing thickness, optical losses come into play which are due to the formation of larger grains. This optimum layer thickness is smaller in the films deposited in the MF mode, indicating a smoother surface and smaller grain size compared to the DC mode. As an optimum value, a reflectivity of R=99.3% is achieved. The resistivity of this film was found to be @rho@=2.4 µ@Omega@ cm. The measured reflectivity is close to the theoretical value, which was determined from the Drude-Lorentz fit parameters with respect to the resistivity. The measured reflectivity of the sputter deposited films will be compared to thin films which are prepared by e-beam evaporation.

TF-MoP30 Preparation and Characterization of RF-sputtered SrTiO@sub 3@ Thin Films, ***K. Radhakrishnan***, *C.L. Tan, H.Q. Zheng, G.I. Ng,* Nanyang Technological University, Singapore

Strontium titanate, SrTiO@sub 3@ (STO) material has found wide applications ranging from capacitor dielectrics in ICs to semiconductor memories and submicron ICs. This paper focuses on synthesis of STO thin films on Si and GaAs substrates under various growth conditions such as oxygen partial pressure and substrate temperature, and post annealing conditions. STO films were deposited by RF-magnetron sputtering in Ar/O@sub 2@ plasma. The substrate temperature was 200 to 300°C. Platinum was used as electrodes. The dielectric constant increased with increase in O@sub 2@ partial pressure during sputtering. However, it showed a decreasing trend when the partial pressure ratio, O@sub 2@/Ar was >1. The dielectric constant measured for these samples is low (14 to 22). X-ray diffraction measurements (XRD) showed peaks mainly due to substrate with weaker peaks corresponding to STO phase. The STO samples were annealed to study the effect of annealing on dielectric constant. The films were annealed for 1 hr under O@sub 2@ flow. It was observed that the dielectric constant was around 20 when the films were annealed below 500°C. However, when the temperature was above 500°C the dielectric constant value increased five times. A high value of 125 was measured for the film annealed at 600oC. The increase in the dielectric constant was due to the development of stable STO phase when annealed under O@sub 2@. Films annealed above 500°C showed intense XRD peaks corresponding to STO phase for (110), (200) and (211). The effect of film thickness on the dielectric constant was determined using 100 to 425nm thick samples. The dielectric constant increased from 117 to a high value of 145 when the thickness was 425nm. The average breakdown voltage measured capacitors with STO film thickness of 110nm was found to be 855kV/cm.

Thin Films Division
Room 615 - Session TF-TuM

Advanced Thin Film Formation Chemistry

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

8:20am **TF-TuM1 Coatings from Liquid and Supercritical Carbon Dioxide**, *B.J. Novick, E.N. Hoggan,* North Carolina State University*; D. Flowers,* University of North Carolina*; Y. Chernyak,* North Carolina State University*; J.M. DeSimone,* North Carolina State University and University of North Carolina*;* ***R.G. Carbonell,*** North Carolina State University **INVITED**

Carbon dioxide offers several environmental as well as performance advantages over conventional solvents. The recent development of CO@sub 2@-soluble polymers and surfactants has broadened significantly the number of potential applications for supercritical and liquid carbon dioxide as a solvent for the formation of thin films and coatings. This paper discusses recent work on coatings of polymeric materials from both supercritical as well as liquid carbon dioxide. The rapid expansion of supercritical solution (RESS) process using CO@sub 2@ can produce thin films and sub-micron powders of a wide variety of inorganic and polymeric materials. The process involves the expansion of a solution through a nozzle to an ambient downstream pressure. The present work is aimed at gaining an understanding of the relationship between the morphology and dimensions of the precipitates and RESS operating conditions. A computational fluid dynamic analysis of the process path can help relate the rates of change of pressure and temperature in the nozzle to the thermodynamics of binodal and spinodal decomposition. These relationships govern deposition rates and the rates of droplet nucleation and growth. Liquid carbon dioxide also offers some advantages over conventional solvents for spin coating and free meniscus (dip coating) applications. Because of its low viscosity and low surface tension, it has the potential of forming thinner films and of penetrating into narrower features on the surfaces being coated. As examples, results are shown on the spin coating and development of CO@sub 2@-soluble polymers for photolithography, and the deposition of polymeric lubricants on the surface of hard disk drive materials by dip coating.

9:00am **TF-TuM3 Organic Films Prepared by Polymer Sputtering**, ***H. Biederman,*** Charles University at Prague, The Czech Republic, Czech Republic **INVITED**

Deposition of organic films by means of radio frequency (rf) sputtering of conventional polymers became the center of attention in the seventies. The interest was particularly in polytetrafluoroethylene (PTFE)@footnote 1@ because of the prospect to prepare useful dielectric films and low friction coatings. Recently the interest in polymer sputtering was renewed and in addition to PTFE polyimide (PI) and polyethylene (PE) etc. were examined.Findings from these studies are concisely reviewed. Recent results are presented from our laboratory, obtained using balanced and unbalanced rf magnetron sputtering of PTFE and PE. The results of the kinetics of rf magnetron sputtering of PTFE by energy resolved mass spectrometry are shown. Various C@sub X@F@sub Y@ species were detected in the discharge, with the composition affected by the discharge parameters. It is assumed that CF, CF@sub 2@ and CF@sub 3@ fragments from the sputter process are the most important for film growth.@footnote 2@ The process was also monitored in situ by OES (Optical emission spectroscopy). The morphology of fluorocarbon plasma polymer films deposited on Si substrates at various temperature was observed by means of scanning electron microscopy. It was concluded that below +23 °C a columnar structure appears. The structure and basic properties of hydrocarbon plasma polymer films prepared by rf sputtering of PE are presented. @FootnoteText@ @footnote 1@ Biederman, H , Ojha, S M, and Holland, L:Thin Solid Films, Vol 41, pp 329- 339, 1977 @footnote 2@ Zeuner, M, Hirsch, D, Neumann, H, Zalman, J and Biederman, H, to be published in Proc. of ISPC 14, Prague August 2-6,1999 .

9:40am **TF-TuM5 Plasma Enhanced Atomic Layer Deposition of Ta for Diffusion Barrier Applications**, *A. Sherman,* Sherman and Associates, Inc.*; S. Malhotra,* ***S.M. Rossnagel,*** IBM Research Division

Atomic Layer Deposition (ALD) is a variation of conventional CVD that uses sequential steps for the adsorption of a monolayer of one reactant and the subsequent exposure of this monolayer to a second reactant, which results in the deposition of roughly a monolayer of the desired elemental or molecular species. This paper describes the use of a free radical second reactant which is produced by a remote plasma source. Because of the high reactivity, it is possible to form films at moderate temperatures rather than the high temperatures of conventional CVD. In this paper, we describe the ALD of Ta, which is used in semiconductor interconect structures for diffusion, adhesion, or nucleation layers in high aspect ratio features which are subsequently filed with Cu. The ALD process is self-limiting in that each 2-step process results in approximately a single atomic layer and film thickness is built up in a controlled manner with a specific number of steps. This is unlike conventional CVD or PVD which are generally timed and require rate calibration. The Ta system uses moderate temperature adsorption of TaCl5 vapor followed by a reaction step using atomic hydrogen from an inductively-coupled rf plasma. The system has been extended to 200mm wafers using a modified Applied Materials Endura (PVD) system, compatible with existing manufacturing tools. Conformal Ta films with uniform thickness have been measured in high aspect ratio features and XRD, AES and RBS data sugget films of high purity adequate for interconnect applications.

10:00am **TF-TuM6 Atomic Layer Deposition of Tungsten and Tungsten Nitride Using Sequential Surface Reactions**, ***J.W. Klaus****, S.J. Ferro, S.M. George,* University of Colorado, Boulder

The deposition of ultrathin and conformal films on high aspect ratio structures is important for forming conducting layers and diffusion barriers. Thin films of tungsten (W) and tungsten nitride (W@sub 2@N) were deposited with atomic layer control using sequential surface reactions. The tungsten growth was accomplished by separating the binary reaction WF@sub 6@ + Si@sub 2@H@sub 6@ --> W + 2SiHF@sub 3@ + 2H@sub 2@ into two half-reactions. The tungsten nitride growth was performed by dividing the binary reaction 2WF@sub 6@ + NH@sub 3@ --> W@sub 2@N + 3HF + 9/2F@sub 2@ into two half-reactions. Successive exposure to WF@sub 6@ and Si@sub 2@H@sub 6@ (NH@sub 3@) in an ABAB... binary reaction sequence produced W (W@sub 2@N) deposition at substrate temperatures between 425-600 K (600-800K). The W deposition rate was 2.49 Å/AB cycle for WF@sub 6@ and Si@sub 2@H@sub 6@ reactant exposures > 800 L and 1600 L, respectively. The WN deposition rate was 2.55 Å/AB cycle for WF@sub 6@ and NH@sub 3@ reactant exposures > 3000 L and 10,000 L, respectively. Atomic force micrographs of the deposited films on Si(100) were remarkably flat indicating smooth and conformal deposition. These results for W represent the first demonstration of atomic layer deposition of conformal single-element films using sequential surface reactions. Similar surface chemical strategies may facilitate the atomic layer growth of other metals besides tungsten.

10:20am **TF-TuM7 Relating Phase Content to Deposition Kinetics in Ultra-Thin Sputtered Tantalum Films**, ***J.F. Whitacre****,* University of Michigan*; Z.U. Rek,* Stanford Synchrotron Radiation Laboratory*; S.M. Yalisove, J.C. Bilello,* University of Michigan

How phase and stress formation relate to adatom kinetics in extremely thin sputtered Ta films was examined. This was accomplished by controlling the adatom kinetic energy distribution at the substrate during growth. If low sputter gas (Ar) pressures are used (less than 5 mTorr), arriving adatoms have kinetic energies on the order of 10 eV as they impinge upon the substrate. At pressures above 15 mTorr, the energy distribution shifts to the thermal regime, where all atoms have energies less than 1 eV. For this experiment, Ta films 25 to 500 Å in thickness were DC magnetron sputter deposited using Ar pressures ranging from 2 to 20 mTorr. The films were analyzed using a synchrotron x-ray source (SSRL beamline 7-2) in conjunction with a four-circle diffractometer aligned in the grazing incidence x-ray scattering (GIXS) geometry. The stress in these films was calculated using double crystal diffraction topography (DCDT, a wafer curvature method) data. Film nanostructure was examined using TEM analysis. Phase content was determined by modeling ideal polycrystalline x-ray diffraction patterns and comparing them with corrected (for air scattering) diffraction data. It was found that films grown at progressively higher pressures displayed a systematic increase in amorphous content. Film grown using 20 mTorr of Ar were 100% amorphous to thicknesses as great as ~150Å. Residual stress analysis showed that all films less than 100 Å thick had compressive stresses on the order of -2 GPa. These results are discussed in context of a model that relates adatom kinetics, surface diffusion, and grain development during the early stages of film growth. Work supported by ARPA under contract No. DAAH-04-95-1-0120. Work done (partially) at SSRL, which is operated by the Department of Energy, Office of Basic Energy Sciences.

10:40am **TF-TuM8 Atomic Layer Controlled Growth of SiO@sub 2@ and Al@sub 2@O@sub 3@ on BN Particles Using Sequential Surface Chemistry**, ***J.D. Ferguson***, *A.W. Weimer, S.M. George,* University of Colorado, Boulder

BN particles have a high thermal conductivity and are relatively inert. To improve BN particle coupling in polymer composites for thermal management applications, ultrathin coatings can be deposited that are more reactive and do not degrade the BN thermal properties. SiO@sub 2@ and Al@sub 2@O@sub 3@ were grown on BN particles with atomic layer control using sequential surface reactions of SiCl@sub 4@/H@sub 2@O@footnote 1@ and Al(CH@sub 3@)@sub 3@/H@sub 2@O,@footnote 2@ respectively. The sequential surface chemistry was monitored in vacuum using transmission Fourier transform infrared vibrational spectroscopy. The initial BN particles displayed B-OH and B-NH@sub 2@ surface species. These groups reacted with SiCl@sub 4@ or Al(CH@sub 3@)@sub 3@ and converted the surface species to Si-Cl or Al-CH@sub 3@. The subsequent reaction with H@sub 2@O converted the surface species to Si-OH or Al-OH. By repeating the sequential surface reactions, SiO@sub 2@ and Al@sub 2@O@sub 3@ bulk vibrational modes increased with number of reaction cycles. Transmission electron microscopy studies revealed conformal coatings on the BN particles. X-ray photoelectron spectroscopy analysis was also consistent with uniform and conformal deposition. These results illustrate the potential of sequential surface reactions to deposit conformal and atomic layer controlled coatings on particles. @FootnoteText@ @footnote 1@ J.W. Klaus, A.W. Ott and S.M. George, Appl. Phys. Lett. 70, 1092 (1997). @footnote 2@ A.W. Ott, J.W. Klaus and S.M. George, Thin Solid Films 292, 135 (1997).

Vacuum Metallurgy Division
Room 620 - Session VM+TF-TuM
Ionized Plasma and Chemical Vapor Deposition

Moderator: B. Sartwell, Naval Research Laboratory

9:00am **VM+TF-TuM3 New Plasma Sources for Ionized PVD**, ***D.N. Ruzic***, University of Illinois, Urbana*; D.B. Hayden,* Novellus Systems Inc.*; D.R. Juliano, M.M.C. Allain,* University of Illinois, Urbana **INVITED**

Three plasma sources have been investigated on a commercial magnetron sputtering system: an inductively coupled plasma (ICP) coil, a helical resonator, and an external helicon antenna.@footnote 1@ The main variables presented are the ionization fraction to the substrate, the deposition rates, the electron density and temperature. The ICP coil with an Al target achieved ionization fractions to the substrate in excess of 80%. The deposition rates are around 1500 Å/min. Electron densities are found as high as 2.6±0.3 X 10@super 11@ cm@super -3@. The main drawback to the ICP approach is that the coil is too intrusive, leaving visible shadowing effects which destroy uniformity. The coil sputters some, and also flakes off built-up deposited metal, which can contaminate the system. The helical resonator coil has a much larger diameter and avoids the shadowing effects. Ionization fractions are found with a Cu target at 73±15% under conditions with deposition rates of 1000 Å/min. The electron densities approach 2. X 10@super 12@ cm@super -3@. A ground at the center of the coil eliminates the sputtering problem by maintaining a DC bias of 0~V. There is still metal flaking off the coil as metal builds up on it. The helicon antenna sits remotely outside the vacuum system, so all shadowing and contamination problems are eliminated. Cu ionization fractions to the substrate of 51±10 % with a deposition rate of 850 Å/min. are found using one remote source. The plasma density was only 2. X 10@super 11@ cm@super -3@, but the temperature of that plasma was significantly higher than without the remote helicon present. Six or more remote sources are envisioned to sit around a sputtering chamber, which can help control uniformity while increasing the ionization further. Since there is no threat of contamination inside the vacuum chamber and the substrate to target distance can remain small, the helicon source may have the highest potential of these three secondary sources in industrial IPVD applications. @FootnoteText@ @footnote 1@ D.B. Hayden, D.R. Juliano, M.N. Neumann, M.M.C. Allain, D.N. Ruzic, "Helicon Plasma Source for Ionized PVD," Surf. Coating Tech., to be published (1999).

9:40am **VM+TF-TuM5 Simulations and Experimental Measurements of a Hollow Cathode Magnetron Ionized Metal Plasma Deposition System**, ***G.I. Font***, *K.F. Lai, Q. Lu,* Novellus Systems, Inc.*; M.J. Kushner,* University of Illinois, Urbana

The hollow cathode magnetron (HCM) is a novel new plasma source used for ionized metal deposition. The HCM employs geometric, electrostatic, and magnetic confinement to produce a high density plasma (>1e+12 #/cm3). This plasma serves as a source of ions for sputtering the target and metal ions for deposition on a wafer. In the results reported here, numerical simulations of the HCM using a copper target were performed using the Hybrid Plasma Equipment Model (HPEM) developed at the University of Illinois. The HPEM iteratively combines particle and fluid transport models for ions, electrons, and neutrals to simulate HCM performance. The model includes sputtering of the target by metal and argon ions, secondary electron emission, magnetic confinement of electrons, and thermalization and ionization of sputtered neutrals. The numerical results are compared with experimental Langmuir probe and wafer deposition profile measurements. The numerical results are found to systematically track the experimental measurements. In both experiments and modeling of an HCM, the magnetic field configuration resulted in a confined 'beam' of plasma emanating from the HCM. The physics of the operation of the HCM is described as supported by numerical and experimental results.

10:00am **VM+TF-TuM6 Low Temperature Polysilicon Deposition by Ionized Magnetron Sputtering**, ***J. Joo***, Kunsan National University, Korea

Ionized PVD has deep potential for wide range of applications in thin film deposition. Poly Si deposition on glass should be one of them. A-Si based TFT technology has a limit of electron mobility less than 1 cm@super 2@ V/sec. Excimer laser annealing would be one solution for recrystallization but too expensive and slow process in economic point of view. As Si has very high melting temperature, the required substrate temperature for crystallization is well over the softening temperature of conventional glass in flat panel industry. RF ICP based ionized magnetron sputtering was applied to deposit polysilicon on glass substrate while keeping substrate temperature less than 400C. From X-ray diffraction analysis, small evidence for microcrystalline Si was confirmed at 250C of substrate temperature and floating substrate potential. The effects of pulsed dc sputtering power, substrate biasing frequency and ICP driving frequency will be addressed in detail.

10:20am **VM+TF-TuM7 A Study of the Mechanical Behaviour of Plasma Deposited Silica Films on Polycarbonate and Steel**, *A. Hofrichter, A. Constantinescu,* CNRS, Ecole Polytechnique, France*; S. Benayoun,* E.N.S.A.M, France*; P. Bulkin,* ***B. Drévillon***, CNRS, Ecole Polytechnique, France

The deposition of silica for protective coatings on polymers is of increasing interest for various applications. Key issues in the mechanical behaviour of the film are the properties of the film-substrate interface that can be modified by different pretreatments. The objective of this work is to estimate the constitutive behaviour of the film and the interface by a serie of mechanical experiments and computer simulations. In order to gain a better understanding of the involved phenomena a comparison between depositions on polycarbonate and stainless steel have been performed. The films are deposited in a low pressure (1 mTorr), scaleable integrated distributed microwave 2.45 GHz electron cyclotron resonance (IDECR) reactor, which allows fast deposition at room temperature of dense, stoechiometric silica. The internal stress of the films was evaluated with profilometry and their Young modulus measured by the vibrating slab technique. Microscratch as well as nano-, micro- and Vickers indentation tests were performed on polycarbonate and steel samples for different thickness and processing powers. As indentation measurements can not be interpreted directly, the tests have been simulated by finite elements using the Castem2000 code (CEA-France). The simulated indentation curves and the final shape of the indent were compared to the measurements. The obtained stress and strain distribution in the film conducts to a reasonable explanation of the crack system observed on the indented surfaces. Finally a parametric study of the influence of the material parameters of the interlayer on the global mechanical behaviour will also be presented.

10:40am **VM+TF-TuM8 Carburizing of Tantalum by Radio-Frequency Plasma Assisted CVD**, *A. Rubinshtein,* Ben-Gurion University*;* ***A. Raveh***, NRC-Negev, Israel*; J.E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique, Canada

Tantalum carbide has a great potential as an alternative to tantalum and tantalum oxide for applications requiring thermal stability and corrosion resistance. In the present work we are studying hard TaC layers prepared by inductive rf plasma-assisted CVD (IPACVD) in different gas mixtures containing argon, methane, and hydrogen. The IPACVD approach combines plasma-induced diffusion with chemical vapor deposition. Maximum temperature of the tantalum substrate measured during 6 hours of processing time was 900 degC. Microstructure of the TaC layers was

characterized by XRD, AFM, AES, and XPS, and the mechanical properties were studied by micro- and nanoindentation techniques. Close correlation between carburizing parameters, microstructure and mechanical properties of the layers has been established. The best mechanical performance in terms of elasto-plastic properties (microhardness of about 25 GPa) were obtained for several micrometers thick TaC films prepared at rf power levels between 1.6-2.0 kW and pressures between 40 and 60 mTorr. The effect of gas composition, rf power and substrate temperature on the layer composition (TaC/Ta@sub 2@C phase ratio), and the mechanical behavior will be presented and discussed.

11:00am **VM+TF-TuM9 Electrical and Pressure Probe Measurements of a Hollow Cathode Magnetron Plasma***, **K.F. Lai**, Q. Lu, J. Chau, G.I. Font,* Novellus Systems

The hollow cathode magnetron (HCM) is a new type of high-density plasma device developed for ionized physical vapor deposition (I-PVD). While I-PVD using RF inductively coupled plasma has a plasma density of 10@super 11@ to 10@super 12@ cm@super -3@ and operates best above tens of mTorr, the HCM achieves high levels of ionization at only a few mTorr, primarily due to its extremely high plasma density (~10 @super 13@ cm@super -3@). The plasma profiles of a HCM were measured using Langmuir probes and a novel pressure probe under various operating conditions for two different target materials (Cu and Ti). With the exception of the plasma edge where the presence of an energetic electron tail was clearly evident, the electron energy distribution function (EEDF) was approximately Maxwellian. The measured plasma density was found to increase linearly with the magnetron power whereas the electron temperature only has a weak dependence. Under similar operating conditions, the Ti HCM has a plasma density ~30% higher than that of Cu. A novel pressure probe was used to measure both the argon neutral and ion density profiles. Argon neutrals were measured when the probe was biased slightly above the plasma potential whereas both the argon neutrals and ions were collected when the probe was negatively biased. The percentage of gas rarefaction was found to increase with sputtering power but was only weakly dependent on argon density. The argon ion density profile (deduced by alternating the pressure probe bias) has similar shape as the electron density (measured by the Langmuir probe) indicating that argon is the dominant ion species. The experimental results are in good agreement with simulation using the hybrid plasma equipment model (HPEM) code.

Thin Films Division
Room 615 - Session TF-TuA

Fundamentals of Si and Dielectric PVD

Moderator: S. Zarrabian, Optical Coating Labs

2:00pm **TF-TuA1 Preparation of Co and CoN@sub x@ Thin Films by Unbalanced r.f. Magnetron Sputtering**, ***T. Tanaka,*** Hiroshima Institute of Technology, Japan; *A. Kitabatake,* Sanyo Shinku Kogyo, Japan; *K. Kawabata,* Hiroshima Institute of Technology, Japan

It has been difficult to deposit ferromagnetic thin films by using a conventional planar magnetron sputtering at low pressure. We have developed a modified process based on an unbalanced magnetron sputtering of a magnetic Co target (100 mm, 5mm thick) to deposit Co and CoN@sub x@ films where an external magnet is added to a conventional planar magnetron to confine the efficient plasma near the magnetron target. The plasma confinement can be controlled by the shape of the magnetic field in the sputter deposition device with a multipolar magnetic-field plasma confinement. Cobalt films were prepared by this sputtering system at the r.f. powers of 100 to 200 W and argon pressure less than 5x10@super -3@ Torr. It is shown that the deposition rate of Co films significantly increases from 8.7 to 25 nm/min whose values are two times that of a conventional magnetron sputtering. Co film with the preferred orientation of (111) plane is formed and the value of the grain size estimated from the plane is about 30 nm. Cobalt nitride (CoN@sub x@) films were also prepared by the unbalanced magnetron sputtering in mixtured argon and nitrogen plasma. It is also found from the results of electron probe microanalysis that the content of nitrogen in CoN@sub x@ films increases with the increasing gas flow ratio of N@sub 2@ . The electrical resistivity for reactively sputtered films is less than 80x10@super -6@ @ohm@ cm which makes this compound a relatively good conductor.

2:20pm **TF-TuA2 Microstructural Control of Thin Silicon Films Grown by Reactive Magnetron Sputtering Utilizing Low Energy Ion Bombardment**, ***J. Gerbi***, *J.R. Abelson,* University of Illinois, Urbana-Champaign

We use spectroscopic ellipsometry, Raman scattering, TEM, SIMS, and photoluminescence to analyze the optical properties and microstructure of hydrogenated or deuterated Si thin films of various crystallinities. Bulk mc-Si films are of current interest for solar cell, hybrid solar cell, and thin film transistor applications; low temperature deposition enables the use of plastic substrates. We have previously demonstrated that RMS can deposit mc-Si films directly on glass with no amorphous boundary layer,@footnote1@ and that substituting D2 for H2 in the growth process enhances crystallinity.@footnote2@ In this work, we deposit 0.5 micron thick hydrogenated or deuterated mc-Si films on glass substrates by RMS of a Si target using 1.6 mT Ar plus H2 or D2 at partial pressures from 0 mT (producing amorphous films) to 5.5 mT (producing fully microcrystalline films) at substrate temperatures of 120 and 230 C. In our system, the ion flux and energy are decoupled parameters. The ion flux is controlled by the application of a cylindrical magnetic field created by external coils. This field directs a weak plasma toward or away from the substrate, controlling the ion flux such that the ratio of arriving ions to depositing Si atoms can be varied from < 1 to > 30. The ion energy is also externally controlled by biasing the substrate. We find marked differences in microstructure using high ions fluxes at energies <~ 30 eV, and we will report both the microstructural and optical properties of the films. We also show that biasing of the substrate to produce ion energies >= 50 eV (as often done in conventional diode sputtering systems at higher pressures) produces damage which degrades the mc-Si microstructure. @FootnoteText@ @footnote 1@Y. H. Yang and John R. Abelson, Appl. Phys. Lett. 67, 3623 (1995). @footnote 2@ J. E. Gerbi and John R. Abelson, "Enhanced Crystallinity of Microcrystalline Silicon using Deuterium in Low Temperature Reactive Magnetron Sputter Deposition," MRS Proc. 507, 429 (1998).

2:40pm **TF-TuA3 PVD of Thin Film Silicon: How Fast Light Atom and Slow Heavy Ion Bombardment During Growth Promote Low-Temperature Crystallinity**, ***J.R. Abelson,*** University of Illinois, Urbana **INVITED**

Macro-electronic devices such as photovoltaic cells and active matrix displays are based on the deposition of thin semiconductor films onto large area substrates at low temperatures. Silicon presents an interesting case because the microstructure can range from amorphous to nanocrystalline to polycrystalline. These different microstructures can be produced by manipulating the concurrent particle bombardment during PVD growth by dc reactive magnetron sputtering of a Si target in Ar + H2. Three types of particles impinge on the film: (i) sputtered Si atoms of a few eV; (ii) H atoms with ~ 100 eV, generated by the acceleration and reflection of H2+ ions at the target; and (iii) bulk plasma Ar+ and H2+ ions with ~ 25 eV, whose flux is controlled using an externally-generated magnetic field to unbalance the magnetron. We analyze the growth process using real-time mass spectroscopy, spectroscopic ellipsometry, and reflection IR absorption, including isotopic H2/D2 exchange experiments. We combine these data with binary collision simulations in the gas-phase and substrate to show how each flux modifies the microstructure. The essential results are: (i) Few-eV sputtered Si atoms produce a dense microstructure, as predicted by the Thornton zone diagram, but also lead to the random formation of nanocrystalline Si particles in an amorphous Si matrix. These particles can serve as nuclei for solid-phase crystallization processes. (ii) 100 eV H atoms penetrate ~ 50 A into the growing film, where they drive crystalline nucleation and subsurface transformation through bond-insertion and momentum-transfer events. Fully nanocrystalline films can be deposited on glass substrates using large fluxes of fast H or D atoms. (iii) 25 eV Ar+ ions modify the competitive growth of polycrystalline grains at the film surface, which leads to a coarsening of the grain structure at modest substrate temperatures.

3:20pm **TF-TuA5 Deposition Behavior and Film Characteristics of Aluminum Oxide Deposited using High Frequency Pulsed-DC Magnetron Reactive Sputtering**, ***D.C. Carter***, *G.W. McDonough, L.J. Mahoney, G.A. Roche, H.V. Walde,* Advanced Energy Industries

The affects of pulsed-DC power application in reactive magnetron sputtering of insulating films has been the subject of much study in recent years. Improved process stability with decreased arcing incidence and cleaner films have resulted by applying bi-polar pulsed power at frequencies from 10 to 200 kHz to otherwise traditional DC magnetron reactive sputtering processes. Recent advances in power supply design, however have extended the usable range of DC pulsing to 300 kHz and above. At these extended frequencies it is observed that transient behavior in the magnetron discharge becomes increasingly dominant on the measured waveforms of the applied power. Little is known of how this behavior affects the dynamics in a reactive sputtering environment or how these high pulsing frequencies can act to influence the character of films reactively deposited. This study looks specifically at the affect high frequency DC pulsing has on reactively sputtered aluminum oxide. Target voltage and partial pressure hysteresis behavior are reviewed from 0 to 350 kHz to ascertain the affect pulsing frequency has on sputter target condition. Deposition rate and film properties of hardness and optical transmission are reviewed to better understand the impact high frequency pulsing has on the deposited material itself.

3:40pm **TF-TuA6 AC Reactive Sputtering of Dielectric Films using a Dual Magnetron**, ***A. Belkind***, *J. Cai,* Stevens Institute of Technology; *R. Scholl,* Advanced Energy Industries, Inc.

DC reactive sputtering to produce dielectric films suffers from two problems: Arcing on the target surface and covering the anode (the 'disappearing anode problem'). Both problems have received serious attention in recent times. One way to solve both simultaneously is to apply ac power between two magnetrons. Although this approach was first suggested more than ten years ago, and has been widely implemented, a detail investigation of it is remains lacking. In this work, ac reactive sputtering from a dual magnetron system is studied. The effects of ac frequency and discharge current on reactive sputtering of aluminum oxide using both balanced and unbalanced magnetrons are investigated. Special attention is given to ion bombardment of a substrate, both electrically floating and connected to the power supply system.

4:00pm **TF-TuA7 Characterization Studies of Reactively Pulsed Magnetron Sputtered Alumina Films**, ***P.J. Kelly***, *P.S. Henderson, R.D. Arnell,* University of Salford, UK

It is well-established that pulsing the magnetron discharge during the reactive sputtering of insulating films, particularly alumina, can significantly reduce arc events at the target. The suppresion of arc events stabilises the reactive depositon process and, thus allows control over the coating composition, structure and properties. Fully dense, defect-free ceramic films can now be routinely produced at high depositon rates using the pulsed magnetron sputtering process. However, despite the success of this process, optimum deposition conditions and the relationships between deposition conditions and film properties are not well reported. In this investigation, alumina films have, therefore, been deposited by reactive magnetron sputtering using various combinations of DC and pulsed DC

power. The deposition conditions, including pulse frequency, reverse voltage and reverse time, were systematically varied, and the coatings were characterised in terms of their structures and properties. Properties measured include nanohardness, resistivity and scratch adhesion. The optical properties of the coatings have also been investigated. In addition, the power supplies and pulse units were characterised in terms of their effectiveness at arc suppression and their suitability for particular deposition processes. A range of operating conditions have been identified over which hard arcs are fully suppressed and coatings with consistent properties are produced.

4:20pm **TF-TuA8 Change in Surface Roughness with the Thickness of TiO@sub2@ Film Grown on MgO(001) by Ar-ion Beam Sputtering**, *T. Uchitani,* ***K. Maki,*** Yokohama City University, Japan

Thin film growth mode is closely correlated with the surface roughness as predicted from some simulation by Kim and Kosterlitz (Phys. Rev.Lett., vol. 62, 2289(1989)). According to their study, the surface roughness, R@sub a@, is proportional to d@super L@ with L = 1/(D+1), where d and L represent the film thickness and the dimension, respectively. The rutile-type TiO@sub 2@ film was deposited on air-cleaved MgO(001) held at 630 °C at 3.1 x 10@super -3@ Pa in the partial pressure of O@sub 2@ and at 7.9 x 10@super -3@ Pa in the pressure of Ar by sputtering the Ti target by Ar-ion beams accelerated at 1.2 kV. The R@sub a@ versus d relationship at d > 10 nm was determined with an AFM observation, and the film crystallinity was evaluated by determining the relationship between the intensity ratio of (110) peak of TiO@sub 2@ to (004) peak of MgO in X-rays diffraction pattern and d@super 2@. By determining the former relationship, the amount of L is estimated to be 1/2 and so D is one. In other words, the growth of TiO@sub 2@ film at d > 10 nm in the present study progresses by atom by atom process which is not accompanied with the surface diffusion for the adatoms and some atomic rearrangement in the condensed phase during the film deposition. This means that the film crystallinity is independent of d which is supported from the linear relationship between X-rays diffraction intensity peak ratio and d@super 2@.

4:40pm **TF-TuA9 Chemical Vapor Deposition of Alpha Aluminum Oxide for High Temperature Aerospace Sensors**, ***R.H. Niska,*** AlliedSignal Aerospace Co.*; A.P. Constant, T. Witt,* Iowa State University*; O.J. Gregory,* University of Rhode Island

Thin film thermocouples and strain gages are being developed for high temperature application on aerospace propulsion hardware for both development test purposes and as active control sensors. The critical technology necessary in the fabrication of the sensor is an adherent, dense, and homogeneous dielectric to provide electrical isolation at engine operating temperatures. Techniques are being developed to create a crystalline aluminum oxide dielectric formed by a combination of a thermally grown oxide [TGO] from a NiCoCrAlY hardcoating which is then enhanced with the addition of a chemical vapor deposited [CVD] crystalline aluminum oxide layer. This paper will focus on the process development used to deposit the alpha alumina layer on the TGO using CVD in a coldwall reactor at 1100C. The chemistry employed in this process is the pyrolitic decomposition of aluminum tri-isopropoxide. The hexagonal [HCP] alpha phase is achieved at deposition temperatures of 1000C-1100C, as confirmed by X-ray diffraction analysis. By eliminating gas phase and hot wall decomposition, this approach minimizes precursor depletion effects, yielding a more dense and uniform film morphology. Conformal coatings up to 10 microns thick with high resistivity and good adhesion and hardness have been observed on complex airfoil geometries. Growth rates up to 10 microns per hour are possible although low growth rates lead to more desirable film properties. The kinetics of the deposition indicate that the reaction proceeds by a mass transport limited mechanism. Uniform temperature control over highly complex geometry is desireable, but not essential for uniform film growth. Results indicate that the gas flow uniformity and the precursor transport rate are the critical variables.

5:00pm **TF-TuA10 Phase Development of Radio Frequency Magnetron Sputter Deposited Pb(Mg@sub 1/3@Nb@sub 2/3@)O@sub 3@-PbTiO@sub 3@ (90/10) Thin Films**, ***J.-K. Lee,*** Korea Institute of Science and Technology, Korea*; D.K. Park, D.-S. Cheong,* Korea Institute of Science and Technology*; J.-W. Park,* Hanyang University, Korea

The electrostrictive properties of relaxors, PMN-PT, have been the focus of intensive studies in view of their application in microactuator. This is because at around the dielectric constant maximum, relaxors exhibit large electrostrictive strain, the strain-field relationship is practically free of hysteresis, and the effective piezoelectric coefficient can be tuned by changing the magnitude of the dc bias field. PMN-PT films were deposited by r.f. magnetron sputter deposition from Pb, Mg enriched ceramic targets. The Perovskite structural analysis was confirmed by X-ray diffraction. Film growth was carried out over a wide range of processing parameters such as substrate temperature, sputtering pressures, and post annealing conditions. We focus on the formation of 100% Perovskite structured PMN-PT film with good electrostrictive properties. Composition and phase development were controlled by observing the sputter physics and the depositon mechanism. In case of the film containing the volatile species such as Pb and Mg, the sputtering pressure must be controlled. We also discuss the role of excessive MgO phase on the nanocomposite characteristics in PMN-PT films.

Thin Films Division
Room 615 - Session TF+MM-WeM

Thin Films in MEMS and MOEMS

Moderator: S. Patton, Air Force Research Laboratory

8:20am **TF+MM-WeM1 Detection of Photons Using Thin Films in Semiconductor MEMS**, ***P.G. Datskos,*** *S. Rajic,* Oak Ridge National Laboratory*; I. Datskou,* Environmental Engineering Group, Inc.

We report on a new method for detecting photons using the stress caused by photoelectrons emitted from a thin metal film surface in contact with a semiconductor microstructure which forms a Schottky barrier. As photoelectrons diffuse from the metal film into the microstructure they produce an electronic stress. The photon detection results from the measurement of the photo-induced bending of the microstructure. Internal photoemission has been used in the past to detect photons, however, in those cases the detection was accomplished by measuring the current due to photoelectrons and not due to electronic stress. Small changes in position (displacement) of microstructures are routinely measured in atomic force microscopy (AFM) where atomic imaging of surfaces relies on the measurement of small changes (< 10@sup -9@ m) in the bending of microcantilevers. In this work we studied the photon response of Si microcantilevers coated with a thin film of Pt. The Si microcantilevers were 500 nm thick and had a 30 nm layer of Pt. Photons with sufficient energies produce electrons from the platinum-silicon interface which diffuse into the Si and produce an electronic stress. Since the excess charge carriers cause the Si microcantilever to contract in length but not the Pt layer, the bimaterial microcantilever bends. In our present studies we used the optical detection technique to measure the photometric response of Pt-Si microcantilevers as a function of photon energy. The charge carriers responsible for the photo-induced stress in Si, were produced via internal photoemission using a 1550 nm wavelength diode laser.

8:40am **TF+MM-WeM2 Sputtered Coatings for Microfluidic Applications**, ***D.W. Matson,*** *P.M. Martin, W.D. Bennett, J.W. Johnston, D.C. Stewart, C.C. Bonham,* Pacific Northwest National Laboratory

Magnetron sputter-deposited features and coatings are finding a broad range of uses in microfluidic devices being developed at the Pacific Northwest National Laboratory (PNNL). Such features have routinely been incorporated into multi-layer laminated microfluidic components where specific functionality is required and other methods for producing these features have been deemed unacceptable. Applications include electrochemical sensors, heaters and temperature probes, electrical leads and insulation layers, and chemical modification of surfaces. Small features, such as those required for the production of microsensor electrodes or miniature resistive heaters on microfluidic chips, were patterned using standard lithographic methods or with masks produced by laser micromachining processes. Use of the coating technology and its application in specific microfluidic devices, including a groundwater sensor, a piezoelectrially actuated airflow regulator, and a microchannel flow diagnostic device, will be discussed.

9:00am **TF+MM-WeM3 A Novel Thin-Film Proton Exchange Membrane Fuel Cell for Microscale Energy Conversion**, ***J.D. Morse,*** *A.F. Jankowski, J.P. Hayes, R.T. Graff,* Lawrence Livermore National Laboratory

A novel approach for the fabrication and assembly of a proton exchange membrane (PEM) fuel cell system enables effective scaling of the fuel delivery, manifold , and cell stack components for applications in miniature and microscale energy conversion. Electrode materials for PEM fuel cells are developed using sputter deposition techniques. A thin film anode is formed through the deposition of nickel, followed by the deposition of a platinum catalyst layer. A proton conducting membrane electrolyte is formed over the catalyst using spin cast techniques. Finally, a thin film cathode is formed that incorporates a thin platinum layer, followed by a layer of silver. Scaling towards miniaturization is accomplished by utilizing novel micromachining approaches. Manifold channels and a fuel delivery system are formed within the substrate that the cell stack is fabricated on thereby circumventing the need for bulky manifold components that are not directly scalable. Methods to synthesize a base electrode layer to a thin-film PEM fuel cell from the electrolyte and a conductive material are developed using photolithographic patterning and physical vapor deposition. The microstructure and morphology desired for the anode layer should facilitate generation of a maximum current density from the fuel cell. For these purposes, the parameters of the deposition process and post-deposition patterning are developed to optimize porosity in the anode layer. The fuel cell microstructure is examined using scanning electron microscopy and the power ouput generated is characterized through current-voltage measurement. This work was performed under the auspices of the United States Department of Energy by Lawrence Livermore National Laboratory under contract #W-7405-Eng-48.

9:20am **TF+MM-WeM4 Thin Films in MEMS and MOEMS**, ***W.D. Cowan,*** Air Force Research Laboratory **INVITED**

Micro-Electro-Mechanical Systems (MEMS) and Micro-Optical-Electro-Mechanical Systems (MOEMS) employ batch fabrication processes to construct miniature devices with macroscopic functionality. Surface micromachined MEMS structures are manufactured by the deposition and patterning of thin films. In marked contrast with conventional fabrication processes (and bulk micromachining), the thin film materials used in surface micromachined structures are formed as the device is processed. In general, the material properties of thin films are not controlled during deposition, and are only measured after processing is completed. Characterization methods include wafer curvature measurements and a variety of test structures. None of the thin film characterization techniques currently employed is entirely satisfactory and all methods rely on process repeatability to be useful. The ultimate performance of many MEMS and MOEMS depends directly on the materials properties of the thin films employed. Processing variations induce variations in materials properties that directly impact device performance. For MOEMS, residual material stresses can cause curvature of nominally flat reflecting surfaces that degrades optical performance. Recent work in which MEMS foundry processes were used to fabricate low-cost deformable mirrors (MEM-DMs) for adaptive optics illustrates the impact of residual material stress on system level optical performance. Residual material stress can be exploited in other MEMS devices to produce unique structures. More precise monitoring and control of film stress during deposition remains as a challenge for MEMS and MOEMS.

10:00am **TF+MM-WeM6 Residual Stresses in MEMS Structures**, ***B.S. Majumdar,*** UES, Inc.*; W.D. Cowan,* Air Force Research Laboratories*; S. Rogers,* AFIT*; N.J. Pagano,* Air Force Research Laboratories

Residual stresses impose major restrictions on the performance of MEMS devices. Although different techniques have been developed to measure such stresses, they suffer from a number of limitations. We have focused our attention on square and circular micro-mirrors that are supported by electrically activated arms. Permanent curvature in such mirrors arise from thermal and process-generated residual stresses, and they seriously impair mirror performance. In this work, the residual stresses were estimated from curvature measurements on different sized beams using an interferometric technique, complemented by rigorous elastic analysis of composite beams. It is notable that typical analyses is based on Stoney's equation, which is not believed to be valid for the thin MEMS structures. The composite beams consisted of different grades of poly-silicon with and without gold coating, and the measurements and analysis showed consistent results for the different beams and mirrors. In an effort to de-couple the thermal and process component of the residual stresses, curvature measurements were made at different temperatures. The results and analysis technique will be presented in detail, and possible methods to reduce the residual stresses will be discussed.

10:40am **TF+MM-WeM8 Investigation and Modeling of Electrical Resistance in Polysilicon Thermal Actuators**, ***J.T. Butler,*** *W.D. Cowan,* Air Force Research Laboratory

This paper reports on investigation and modeling of the electrical resistance of micromachined polysilicon thermal actuators. The availability of models compatible with commonly used circuit simulators such as SPICE are extremely useful for design of integrated microsystems which include thermal actuators. The development of a model for thermal actuators necessitated an analysis of the electrical resistance characteristics of the MEMS fabrication process in order to provide an understanding of a key material property. The thermal actuators investigated in this research were fabricated through the DARPA-sponsored Multi-User MEMS Processes (MUMPs). Hence, a TSUPREM model of the MUMPs fabrication process was created to generate polysilicon resistivity parameters which were then fed into the electrothermal SPICE model. Two types of thermally actuated devices were modeled: a lateral thermal actuator and a thermally actuated piston micromirror. The SPICE model exhibits very close agreement with the measured performance of the polysilicon thermal actuators. The MUMPs process used to fabricate the thermal actuators has three structural layers of polysilicon. The resistivity of each of the MUMPs

polysilicon layers varies due to differences in fabrication. Moreover, our resistance measurements of test structures and actuators showed that the resistivity of devices formed from the various MUMPs polysilicon layers also varies based on structure linewidth. A TSUPREM fabrication model of the MUMPs process was generated which validated the empirical resistance measurements and the dependence of resistivity on linewidth. The TSUPREM simulation revealed that the diffusion of phosphorus dopant during the anneal cycles in the MUMPs fabrication process were largely responsible for the variations in resistivity due to linewidth. For small (< 10 (m) linewidth structures, the presence or absence of lateral diffusion of dopant through the sidewall can significantly alter the electrical resistance. The resistivity dependence on linewidth is significant for our thermal actuators because they are designed with elements having linewidths varying from 2 (m to greater than 20 (m. The electrothermal SPICE model augmented with the TSUPREM resistivity data accurately predicted the I-V performance of both the lateral thermal actuator and the thermal piston micromirror. The use of SPICE allows simulation of both the MEMS device and control electronics in the same analysis package and enables the designer to gain insight into the expected performance of the microsystem prior to fabrication. On-going work includes investigation of adding thermal mechanical modeling to our simulation.

Thin Films Division
Room 615 - Session TF-WeA

Transparent Conductive Oxides
Moderator: P. Beauchamp, Optical Coating Labs

2:00pm **TF-WeA1 Recent Progresses on High Quality Tin-doped Indium Oxide (ITO) Films**, ***Y. Shigesato,*** Aoyama Gakuin University, Japan **INVITED**

Considerable efforts have been focused on depositing thin film tin-doped indium oxide (ITO) (thickness of 100-300 nm) with significantly reduced resistivity (lower than 1.0-1.5@Ao@10@super-4@ @ohm@cm) in order to accommodate the increasing technological demand for larger area flat panel displays with higher image quality. In this decade several breakthrough to deposit the low resistivity ITO with high reproducibility had been successfully carried out both for the evaporation-based and sputtering-based deposition processes applying quite different plasma techniques. As for e-beam evaporation (EB) processes, activation of the chemical reaction close to the substrate surface and low energy Ar@super+@ bombardment (10-30 eV) using tungsten electron emitters (EEIP) or an arc plasma generator (HDPE) were found to be effective for the low-resistivity ITO deposition. Whereas for the magnetron sputtering (SP) processes, lowering the sputtering voltage caused by lowering plasma impedance using the stronger magnetic field close to the cathode target or DC+RF technique was confirmed to be effective. Analyses on the crystallinity of the ITO films using XRD, FE-SEM, HREM and on chemical state of doped tin ions using ESCA, Transmission Mossbauer Spectra (TMS) were carried out to investigate how the deposition conditions affected the film structure and properties, and hence the reason for the low resistivity. It was clarified to be the key factors to deposit the very low resistivity ITO films that the doping efficiency of tin should be increased by decreasing the segregation at grain boundaries for the EB films, whereas the crystallinity should be improved by lowering the damages caused by high energy ion bombardments (more than 100 eV) during the SP deposition.

2:40pm **TF-WeA3 Electrical Properties and Surface Morphology of Heteroepitaxial Grown Tin-doped Indium Oxide Films Deposited by Molecular Beam Epitaxy**, ***N. Taga,*** Asahi Glass Co., Ltd., Japan*; Y. Shigesato,* Aoyama Gakuin University, Japan*; M. Kamei,* National Institute for Research in Inorganic Materials, Japan

Heteroepitaxial growth of Sn-doped indium oxide (ITO) and non-doped indium oxide (IO) thin films was carried out on optically polished single-crystal yttria-stabilized zirconia (YSZ) substrates by molecular beam epitaxy. The surface morphology of these epitaxial films was analyzed by scanning electron microscopy and the electrical properties were measured by four-point probe method and Hall-effect measurements. The ITO and non-doped IO films showed quite different surface morphology, suggesting that Sn acted not only as dopant but also as growth modifier for IO films. The surface morphology analysis on IO and ITO films revealed that a growth rate along the direction was enhanced by Sn doping. Resistivity (@rho@) of the epitaxial grown ITO films was 1.7E-4 @ohm@cm which was smaller than the @rho@ of polycrystalline ITO films (2.1E-4 @ohm@cm) deposited on glass substrate under the same deposition conditions. This result was consistent with the report on the heteroepitaxial films deposited by a conventional electron beam evaporation.@footnote 1@ The epitaxial ITO film deposited on YSZ(100) substrate showed higher carrier density N = 8.7E+20 cm@super -3@ and lower resistivity @rho@ = 1.7E-4 @ohm@cm compared with the one deposited on YSZ(111) substrate (N = 8.0E+20 cm@super -3@, @rho@ = 1.9E-4 @ohm@cm) deposited at simultaneously in the same batch. Such a difference between ITO(100)/YSZ(100) and ITO(111)/YSZ(111) implying that the crystal growth orientation should have large effects on the electrical properties. Sn concentration analyzed by X-ray photoelectron spectroscopy showed difference between the ITO(100) and the ITO(111), which was considered to be the one of the dominant factor for electrical properties. @FootnoteText@ @footnote 1@ N. Taga, H. Odaka, Y. Shigesato, I. Yasui, M. Kamei and T. E. Haynes, J. Appl. Phys. 80, 978 (1996).

3:00pm **TF-WeA4 Influence of the Target-Substrate Distance on the Properties of ITO Films Prepared by rf Reactive Magnetron Sputtering**, ***L.-J. Meng,*** Inst. Duperior de Eng. do Porto, Portugal*; M.P. Dos Santos,* Univ. Minho, Portugal

ITO films have been deposited onto glass substrates by rf reactive magnetron sputtering. The distance between the target and the substrate has been changed from 50 mm until 100 mm. The x-ray diffraction shows that the film prepared at large target-substrate distance has a strong orientation along [440] direction, and as the distance decreases, the intensity of the [440] peak decreases and the intensity of [222] peak increases. The electrical resistivity of the ITO films decreases as the target-substrate distance get small. This variation could be related with the change of the orientation of the films, the film, which has strong [222] peak intensity, has low electrical resistivity. The transmittance of the ITO films decreases and the optical band gap move to low energy direction as the target-substrate distance becomes small. In this work, all these phenomena will be discussed.

4:00pm **TF-WeA7 Properties of Fluorine-Doped Tin-Oxide Films**, ***X. Li,*** *S. Asher, R. Ribelin, P. Sheldon, T.A. Gessert,* National Renewable Energy Laboratory

Conductive tin-oxide (SnO@sub 2@) films are used extensively for transparent electrodes in electrochromic devices, flat-panel displays, and thin-film photovoltaic solar cells. SnO@sub 2@ with a tetragonal structure is naturally an n-type semiconductor because of a deviation from stoichiometry. With n-type dopants such as antimony, chlorine, and fluorine (F), very high electrical conductivity can be obtained. In this study, we investigated F doped SnO@sub 2@ films produced by low-pressure metal organic chemical vapor deposition. Tetramethyltin (TMT), oxygen, and bromotrifluoromethane (CBrF @sub 3@) were chosen as precursors. Due to the high volatility of CBrF@sub 3@ precursor, the F doping efficiency is strongly dependent on the substrate temperature and reaction chamber pressure. Secondary ion mass spectrometry (SIMS) analysis has revealed that the F doping level depends logarithmically on the CBrF@sub 3@ partial pressure, and the electronic concentration depends logarithmically on the F doping level. SIMS results also show that the F doping level remains constant through the film thickness, and that F does not diffuse from a doped layer into an undoped layer. Hall measurements show the electron mobility (μ) of the film increases with the doping level, which contrary to what is expected from ionized impurity scattering. For undoped SnO@sub 2@ films, the μ is ~1 cm@super 2@/V-s and electron concentration is low-10@super 18@/cm@super 3@. For F doped SnO@sub 2@ films, the electron concentration increases to mid-10@super 20@/cm@super 3@, and μ increases to 40 cm@super 2@/V-s. The optical and structure properties of doped and undoped SnO@sub 2@ films were also compared. Spectrophotometry demonstrated that the fluorine-doped film had a higher absorption than the undoped film. X-ray diffraction texture analysis revealed that as F is added to the film, the film orientation changes from random to a strong preference toward the (200) direction.

4:20pm **TF-WeA8 P-type Transparent Conducting In@sub 2@O@sub 3@ - Ag@sub 2@O Thin Films Prepared by Reactive Electron Beam Evaporation Technique**, *J. Asbalter,* ***A. Subrahmanyam,*** Indian Institute of Technology, India

The transparent and conducting oxide thin films are all, so far, n - type. In the present investigation we report the results of thin films of silver doped In@sub 2@O@sub 3@ prepared on glass substrates by reactive electron beam evaporation at a substrate temperature of 180@super o@ C (at a chamber pressure of 2.5x10@super -4@ milli bar with oxygen) which have shown p-type conductivity under specific conditions. The evaporation rate is varied by changing the current (30 - 100 mA) to the electron beam. The starting material is the mixture of In@sub 2@O@sub 3@ and Ag@sub 2@O powder (of purity 99.99%). The composition of Ag@sub 2@O in the starting material has been varied from 0 to 100 Weight%. The electrical and optical properties of the films have been studied. The p-type conductivity has been observed in the films prepared at 80:20 composition evaporated at the rate of 65 Å per minute. The mobility and resistivity are 8.2 cm@super 2@volt@Super -1@sec@super -1@ and 22.5 ohm cm respectively. These films show an optical transparency of 38% at 500 nm and have an optical band gap of 3.95 eV. These data are being analyzed to understand the physics of the p-type conduction.

4:40pm **TF-WeA9 Mott-Schottky Analysis of Thin ZnO Films**, ***C.F. Windisch,*** *G.J. Exarhos,* Pacific Northwest National Laboratory

Thin ZnO films have been prepared in our laboratory using both rf-sputtering and solution deposition routes. Processing parameters were found to have a marked effect on film conductivity. In addition, measured conductivity and infrared reflectivity could subsequently be enhanced by either chemical treatment in hydrogen gas at 400°C or cathodic electrochemical treatment in a neutral (pH = 7) phosphate buffer solution. While film conductivity and free carrier content usually are determined by Hall measurements, the present study focused on whether a conventional Mott-Schottky analysis could be used to monitor the change in

concentration of free carriers in these films before and after chemical and electrochemical reduction. The Mott-Schottky approach is particularly promising for electrochemically modified films since the measurements could be made in the same electrolyte used for post-deposition electrochemical processing. Results of studies on sputtered pure ZnO films in ferricyanide solution were encouraging. Mott-Schottky plots were linear and gave free carrier concentrations typical for undoped semiconductors. Film thicknesses estimated from the Mott-Schottky data agreed with values calculated from reflectance measurements and confirmed by spectroscopic ellipsometry. However, studies on solution-deposited films yielded anomalous results. Mott-Schottky plots were nonlinear, apparently due to film porosity. A combination of dc polarization and AFM measurements confirmed this conclusion. The results suggest that Mott-Schottky analysis would be suitable for characterizing the dielectric response of solution-deposited ZnO films only if the effects of film porosity on the characteristics of the space charge region of the semiconductor were included in the analysis. This work was sponsored by the Office of Materials Science of the Office of Basic Energy Science, U. S. Department of Energy, under contract DE-AC06-76RLO 1830.

5:00pm **TF-WeA10 Direct Measurement of Density-of-States Effective Mass and Scattering Mechanisms in Transparent Conducting Oxides Using Second-Order Transport Phenomena**, ***D.L. Young***, *T.J. Coutts,* National Renewable Energy Laboratory*; V.I. Kaydanov,* Colorado School of Mines*; W.P. Mulligan,* Sunpower Inc.

TCOs have relatively low mobilities, which limit the techniques that may be used to explore their band structure via the effective mass, and limit the performance of the materials optically and electrically. The de Haas-van Alphen and other resonance techniques used to characterize the Fermi surface are not appropriate for TCOs that have a rather short relaxation time (i.e., low mobility). We have used transport theory to directly measure the effective mass and other fundamental properties of TCO films.@footnote 1@ The Boltzmann transport equation can be solved to give analytical solutions to the resistivity, Hall, Seebeck, and Nernst coefficients. In turn, these may be solved simultaneously to give the density-of-states effective mass, the Fermi energy relative to either the conduction or valence band, and the scattering parameter, s, which is related to the relaxation time and the Fermi energy. The little-known Nernst-Ettingshausen effect is essential for determining the scattering parameter and, thereby, the effective scattering mechanism(s). We constructed equipment to measure these four transport coefficients simultaneously over a temperature range of 30 - 350 K for thin semiconducting films deposited on insulating substrates. We measured the resistivity, Hall, Seebeck, and Nernst coefficients for rf magnetron-sputtered cadmium stannate (CTO) films@footnote 2@ with carrier concentrations in the range of 2-7x10@super 20@ cm@super -3@. We found that CTO is a highly degenerate semiconductor with a parabolic conduction band in this range of carrier concentration and that the density-of-states effective mass is 0.29±0.04 m@sub e@. This value agrees well with earlier studies of CTO@footnote 3,4@ but is, to our knowledge, the first direct measurement of both m@super *@ and s. Optical modeling of the effective mass agrees well with our directly measured value. Spectrophotometric analysis, resistance as a function of frequency, and mobility as a function of carrier concentration all indicate that grain-boundary scattering plays only a minor role in degenerate CTO. Early results indicate that the mobility reaches a maximum of nearly 80 cm@super 2@ V@super -1@ s@super -1@ for a carrier concentration of about 5x10@super 20@ cm@super -3@ when s approaches zero. The transition in the dominant scattering mechanism is indicated by a change in the sign of the Nernst voltage. @FootnoteText@ @footnote 1@ I.A. Chernik, V.I. Kaydanov, M.I. Vinogradova, and N.V. Kolomoets: Soviet Physics - Semiconductors, Vol. 2, No. 6 (1968) 645. @footnote 2@ X. Wu, W.P. Mulligan, and T.J. Coutts: Thin Solid Films, 286 (1996) 274. @footnote 3@ G. Haacke: Applied Physics Letters, Vol. 28, No. 10 (1976) 622. @footnote 4@ W. Mulligan: Ph.D. Thesis, Colorado School of Mines, Golden, CO (1997).

Thin Films Division
Room 615 - Session TF-ThM

Nanophase Thin Films
Moderator: J.S. Zabinski, Air Force Research Laboratory

8:20am **TF-ThM1 Thin Films from Slow and Energetic Cluster Impact**, ***H. Haberland***, University of Freiburg, Germany **INVITED**

An intense beam of clusters can be produced by first sputtering atoms into an argon atmosphere and then forming the clusters into a beam. Deposition rates of about 5 ML are observed for clusters between 1000 and 12.000 atoms of all metals tried so far (Ag, Al, Cu, Co, Mo, Ti, TiN, Pd) as well as for Si. Up to one third of the beam can be charged, so that an intense beam of cluster ions can be produced. Mass spectroscopy is used to determine the cluster size. Several examples will be discussed; e.g. Co clusters embedded in a Ag matrix for magnetic applications, Ag clusters in a SiC matrix for a two-dimensional conductor, etc. If the clusters impinge on the substrate with high kinetic energy (up to 30.000eV) they are deformed on impact and form a well adhering, smooth thin film. Unusual properties are observed: e.g. golden TiN films produced at room temperaturs, or well adhering metal films on Teflon, etc. Molecular Dynamics simulation are used to explain these unusual properties.

9:00am **TF-ThM3 Spark-Processing - A Novel Technique to Prepare Light-Emitting, Nanocrystalline Silicon Films**, ***R.E. Hummel***, University of Florida **INVITED**

Scientists are constantly searching for new processing techniques which are capable of modifying the properties of materials. This could yield alternative characteristics that may lead eventually to new consumer products or, more importantly, provide a better understanding of nature. Such a new technique is spark-processing, which has been shown to change remarkably the optical properties of silicon (and other materials). Specifically, spark processing (sp) creates a substance which transforms Si into a strongly photo-luminescing and cathodoluminescing material (in contrast to ordinary Si which is not light emitting). The resulting material is extremely stable against high temperature annealings, HF etching, and laser irradiation. The emission wavelengths range from violet to green to red, depending on the processing parameters. Further, sp-Si is ferromagnetic (compared to conventional Si which is diamagnetic). A new photoresitive device has been created from sp-Si which, upon impingement of light, increases or decreases its resistivity depending on geometric variables. Sp-Si is produced by high frequency, high voltage, low current electric pulses which are applied for a short time between a Si substrate and a counter electrode.

9:40am **TF-ThM5 Interesting Properties of Nanophase Films Deposited from a High-rate, Nanoparticle Beam**, ***F.K. Urban III***, *A. Khabari, A. Hosseini-Tehrani, P. Griffiths,* Florida International University

Nanophase thin films have been deposited by sputtering target material into a chamber designed and operated to promote condensation of the sputtered species into nanoparticles. Flowing argon and helium gas are used to sputter and assist condensation. Particle size and numbers depend on the nucleation rate, condensation rate, and time available for these processes. Films have been deposited from copper, cobalt, molybdenum, and composite copper-cobalt targets. The work to be reported here explores soft-landed nanoparticle films using no acceleration. The soft landed films are porous with nanocrystalline structure from about 5 to 10 nm crystallites. Properties of films are different from bulk and film literature values. The change in film structure with acceleration will be reported. SEM, TEM, AES, RBS, and AFM results will be presented.

10:00am **TF-ThM6 Simulation of Fundamental Physical Phenomena in the Deposition of Nanophase Thin Films using a Sputtering Based Source**, *F.K. Urban III,* ***A. Hosseini-Tehrani***, *A. Khabari, P. Griffiths,* Florida International University

Recently, nanophase thin films have been deposited by sputtering target material into a chamber designed and operated to promote condensation of the sputtered species into nanoparticles. Interesting optical and magnetic properties has been reported for these films. It has been recognized that quantum size effects are most consistent with observed data. The structure of the film and the grain size determines the film properties. In this work, the classical nucleation theory has been used to understand the processes involved in the nucleation and condensation of the particles. A detailed analysis of the nanoparticle beam energy has been carried out by deflecting, accelerating the beam and comparing the experimental data with simulations by SIMION computer code. Results of simulations and comparison to measuremnts and to the resulting depositd films will be presented.

10:20am **TF-ThM7 Deposited Porous Silicon on Insulator Substrates**, *A.K. Kalkan, S.H. Bae, H. Li,* ***S.J. Fonash***, The Pennsylvania State University

High porosity crystalline Si thin films have been directly deposited using a high density plasma approach at temperatures as low as 100°C. These films exhibit the same unique properties, such as visible luminescence and gas sensitivity, that are seen in electrochemically etched Si (i.e., porous Si). The ultimate advantage of our low temperature direct deposition approach is that now porous Si films can be obtained on any substrate including plastics. XRD identifies our films, deposited by ECR-PECVD, as crystalline with no preferential orientation. TEM shows our as-deposited porous Si films consist of a periodic array of uniformly sized rodlike columns normal to the substrate surface in a void matrix. A typical rod diameter is 80 Å and a typical rod separation is 30 Å. Unlike other previously obtained columnar films, these rodlike columns are not tapered but have a constant diameter. We have demonstrated this structure is fully controllable and have varied the porosity up to ~80% by varying the deposition conditions. We have also found that the porosity can be further increased by reducing the diameter of the Si columns by hydrogen ECR-plasma etch exposures after deposition. Red and orange photoluminescence has been observed from our high porosity films. Furthermore, a large and fast conductivity response to certain vapor or gas ambients has been found. In particular, in the case of humidity, a weak response was found up to a threshold humidity level. Above this level a steep exponential increase in conductivity of 3-4 orders of magnitude was observed. The onset of this steep increase was found to occur at higher humidity levels as the porosity is increased. A saturation is observed at relative humidity levels above 75%. Sensitivity for acetone and isopropyl alcohol was observed also for films in the higher porosity range. This implies the sensitivity for larger molecules may be enabled by increasing the void size.

10:40am **TF-ThM8 Optical Properties of Chiral Thin Film Nanostructures and Composites**, ***S.R. Kennedy***, *J.C. Sit, M.J. Brett,* University of Alberta, Canada

We have fabricated porous, chiral thin films with distinct helical nanostrucutures of dimension 300nm pitch and 100nm separation. The geometry of these microstructures can be easily controlled by careful substrate motion using the GLancing Angle Deposition (GLAD) technique.@footnote 1@ Because of their nanometer size scale, these helices give rise to optical phenomena, such as the wavelength specific rotation of linearly polarized light, or optical activity. Analysis of films has found that optical properties are functions of film material and thickness as well as helical pitch and radius. All of these characteristics can be accurately controlled during the deposition process to tailor the film's properties to the desired wavelength regime and rotatory power. For example, we have measured a peak rotation of 2.0° at a wavelength of 480nm when polarized light is incident normal to the plane of the film. The porosity of GLAD thin films has also allowed us to fill gaps surrounding the nano-helices with fluids to enhance the film properties. By filling the films with substances of varying indices of refraction, we were able to modify the rotational effect. In addition to filling with non-active fluids, we investigated the effect of combining optically active nematic liquid crystals with our chiral films. @FootnoteText@ @footnote 1@Robbie, K., & Brett, M. J., Nature, v13, 616 (1996).

11:00am **TF-ThM9 Solid State Electrochromic Devices for Thermal Emittance Control**, ***C.L. Trimble***, *E. Franke, M.J. DeVries,* University of Nebraska, Lincoln*; J.S. Hale,* J.A. Woollam Company*; J.A. Woollam,* University of Nebraska, Lincoln

Thin films of crystalline Li@sub x@WO@sub 3@ (0@<=@ x @<=@ 0.5) allow modulation of IR reflectance within the spectral region from 2 to 30µm depending on the amount of inserted Li ions. Weakly crystalline or amorphous NiO thin films maintain a highly IR transparent state upon Li intercalation. By changing the reflectance of the Li@sub x@WO@sub 3@ layer in contrast to the supporting device layers, electrochromic devices with variable IR emittance can be built. We study a solid state electrochromic device consisting of a five layer stack on glass substrates with a layer sequence: electrode/a-Li@sub x@NiO/Ta@sub 2@O@sub 5@/c-Li@sub x@WO@sub 3@/electrode. The layers are deposited by reactive dc and rf magnetron sputtering at various substrate temperatures, total gas pressures, and oxygen partial pressures, in high-vacuum conditions. Lithium is electrochemically inserted into WO@sub 3@ using a

1N LiClO@sub 4@/propylene carbonate solution. WO@sub 3@, NiO, and Ta@sub 2@O@sub 5@ are deposited on glass/ITO, or Si substrates. The structural and optical properties of the as-deposited thin films, as well as the Li intercalated WO@sub 3@ and NiO single layers are investigated by XRD, AFM, and IR ellipsometry, in-situ and ex-situ UV-VIS ellipsometry, and IR reflectance measurements. The WO@sub 3@, NiO, and Ta@sub 2@O@sub 5@ thin film optical constants are obtained in the IR and VIS spectral region. Electrochromic devices are designed with consideration of the single layer thin film properties. To predict the device IR emittance modulation performance IR reflection and transmission of the colored and bleached devices are measured. The device switching and memory behavior are tested. The Li depth distribution within the electrochromic devices is investigated by secondary neutral mass spectroscopy (SNMS).@footnote 1@ @FootnoteText@ @footnote 1@ Research supported by BMDO contract #DSAG60-98-C-0054 and NASA Epscor Research Center contract #NCC5-169.

11:20am **TF-ThM10 Correlation Between Phase Constituency and Near Ultraviolet Optical Absorption in Nanophase Titania Films**, *J.D. DeLoach, G. Scarel,* University of Wisconsin, Milwaukee; ***C.R. Aita,*** University of Wisconsin, Milwaukee, US

Titania forms coexisting nanocrystalline and vitreous structures in films grown at room temperature. This study's goal is to correlate fundamental optical absorption edge characteristics with nanophase constituency of titania films. Films with coexistent rutile, anatase, and vitreous constituents were sputter deposited onto fused silica, and post-deposition air-annealed at 700 and 1000 @super o@C to affect phase changes. X-ray diffraction was used for phase identification, and UV spectrophotometry was used to determine the optical absorption coefficient at the onset of interband transitions. The absorption coefficient was modeled using the coherent potential approximation, with Gaussian site disorder introduced into the valence and conduction bands of a perfect virtual crystal. Two parameters of the disordered crystal were defined: the optical band gap, E@sub x@, and the slope of absorption edge, E@sub o@. The results are discussed in terms of two extreme cases: (1) Films containing a large rutile volume fraction (0.70-1) share a rutile virtual crystal, with E@sub g@=3.22 eV. Data for these films were combined with single crystal data to develop an expression interrelating E@sub g@, E@sub x@, and E@sub o@. This expression is applicable to any structure with a rutile virtual crystal. The relationship between structural disorder (i.e., volume fraction of vitreous material) and electronic disorder (i.e., E@sub o@), is consistent with the CPA model. (2) Films with a small rutile volume fraction (0.02-0.17), and hence a large anatase+vitreous component, share a non-rutile virtual crystal, with E@sub g@=3.41 eV. The effect of increasing the structural disorder (i.e., rutile volume fraction), in these films is to shift E@sub x@ to lower values, which is consistent with the CPA model. Furthermore, anatase and vitreous components were modeled using the same non-rutile virtual crystal, indicating these structures have a common short-range order in these films.

Thin Films Division
Room 615 - Session TF-ThA

Ex-situ Characterization

Moderator: J.J. Nainaparampil, Air Force Research Laboratory

2:00pm **TF-ThA1 Working Smarter with Microanalytical Tools**, ***M.J. Edgell***, Charles Evans & Associates **INVITED**

New materials development and high yield production lines are key to future generations of integrated circuits (ICs). Material and contamination characterization is therefore an integral part of the semiconductor industry. The capabilities of analytical tools are continuously improving to meet the needs of the National Technology Roadmap for Semiconductors (NTRS). The analytical improvements include electron and ion beam resolution, detector technology, and surface sensitivity. This paper reviews several ex-situ analytical tools, such as AES, RBS, SIMS, SEM, SIMS, TXRF, TOF-SIMS, XPS, used in today's high technology industries. The strengths and weaknesses of the techniques and their applications will be discussed.

2:40pm **TF-ThA3 Near Surface Chemical Dependence of Electronic States at Al-Doped TiO@sub 2@(110)Ultrathin Films**, ***S.H. Goss***, *L. Brillson,* Ohio State University*; S.A. Chambers,* Pacific Northwest National Laboratory

Impurity doping of TiO2 has important catalytic and photocatalytic applications.@footnote 1@ Al doping is known to enhance TiO2's chemical properties and is used extensively in surface coatings. We have used electron excited nanoscale luminescence spectroscopy (EENLS) to observe the dependence of electronic states with chemical composition of Al-doped TiO2 ultrathin films. Using incident electron beams of varying energy to probe depths from 150 nm below the free surface, we observe: mid-gap state emission at 1.4 eV due to Al doping, O vacancy emission at 2.5 eV, and near band edge (NBE) transitions at 3.0 eV. The 1.4 eV emission appears specifically within a 20 nm, 6% Al - doped TiO2 layer stacked on 4% and 2% doped layers, all grown epitaxially on TiO2 substrates. No 1.4 eV emission is evident for these deeper layers. Recombination involving this 1.4 eV level increases dramatically with annealing at 600 C under 5-x 10e7 L O2 treatment, while the 2.5 eV peak decreases. As mid-gap recombination increases, NBE emissions decrease strongly, indicating a pronounced decrease in free carrier concentration near the free surface. Auger electron spectroscopy (AES) shows Ti and O in correct proportion and only C contamination at the free surface. Mid-gap emission intensities show no correlation with surface C concentration which range from

3:00pm **TF-ThA4 Microstructure and EL Properties of the ZnS:Mn Luminescence Materials with Co-dopants**, ***Q. Zhai***, *K.E. Waldrip, J. Li, J.S. Lewis, K. Jones, P.H. Holloway,* University of Florida*; M. Puga-Lambers, M. Davidson,* MICROFABRITECH

ZnS:Mn thin films were deposited onto glass substrate with pre-deposited indium tin oxide (ITO) and aluminum titanium oxide (ATO) layers, using magnetron sputter source. Transmission electron microcopy (TEM) indicated that the microstructure of the as-deposited films was heavily faulted with fine columnar grains formed through most of the film and a 100nm layer of equiaxed fine grains at the ATO/ZnS:Mn interface. The electroluminescence (EL) properties of the as-deposited films were poor. Post deposition rapid thermal annealing (RTA) with and without co-dopants was studied. KCl co-doped samples showed remarkable improvement in EL brightness after an RTA of 5 min. at 700@super o@C. The threshold voltage was slightly increased. Grain growth from 80nm as-deposited to 200nm after RTA was observed, and the fine-equiaxed-grain crystal layer was removed. Energy dispersive X-ray (EDX) spectra analysis of plan-view transmission electron microscoy (PTEM) samples detected no segregation of any element. Ga@sub 2@S@sub 3@ co-doped samples had no improvement in EL brightness after 5 min. RTA at 800@super o@C, but the threshold voltage was reduced. Grain growth was less than the samples without Ga@sub 2@S@sub 3@, and the fine-equiaxed-grain layer was still visible. EDX results showed Ga segregation at grain boundaries and triple points. When both KCl and Ga@sub 2@S@sub 3@ were introduced into the films through double thermal evaporation/annealing, the sample co-doped with Ga@sub 2@S@sub 3@ at 800@super o@C followed by KCl at 700@super o@C gave the best EL results, but the properties were still inferior to the samples with only a KCl treatment. EDX on PTEM samples detected both K and Ga segregated to grain boundaries and triple points of these samples. The diffusion of co-dopants was analyzed by dynamic secondary ion mass spectrometry (SIMS). Detailed electrical properties of these samples are being studied. A correlation between EL properties and the microstructure will be presented.

3:20pm **TF-ThA5 Structural Determination of Wear Debris Generated from Sliding Wear Tests on Ceramic Coatings Using Raman Microscopy**, ***C.P. Constable***, *J. Yarwood, P. Hovsepian, L.A. Donohue, W.-D. Münz,* Sheffield Hallam University, UK

During sliding, the high pressure at the point of contact can contribute to high flash temperatures, which are not accurately measurable. The magnitude of these flash temperatures has been quoted as being up to several hundred degrees Celsius for some systems but remains a topic for debate. Tribologists interested in ceramic coatings are realising that the wear debris can bear the signature of the wear process and the composition of the debris can enable an estimate of these contact temperatures. Raman microscopy is utilised here for the identification of compounds, especially oxides, generated during the wear process to endeavour to gain a better understanding of tribochemical reactions. A series of PVD ceramic hard coatings; CrN/NbN, CrN, NbN, TiAlN/VN, TiAlCrYN and TiCN have been deposited on steel substrates using the cathodic arc/unbalanced magnetron deposition technique. Ball-on-Disk sliding wear tests against corundum were performed for all the above coatings. The debris generated were characterised using vibrational spectroscopy; namely Raman microscopy. The high spatial resolution (2μm), in-situ capability, sensitivity to structural changes and non-destructive nature make this technique ideal for the study of such small amounts of wear debris. Previous work has centred on TiN coatings. This paper attempts to broaden the discussion to include other more complex monolithic and multilayered superlattice coatings. Under dry sliding conditions of 5N normal load, 10cms@sup -1@ in ambient air (humidity ~33%) titanium based alloy coatings were found to provide TiO@sub 2@ (rutile) debris. However the addition of fine layers of VN to the TiAlN system provided lower friction coefficient, wear rate and less debris through the possible formation of a lubricious surface oxide. CrN and NbN based coatings were also found to produce debris with Raman bands corresponding to various oxides.

3:40pm **TF-ThA6 Effect of Rapid Thermal Annealing Temperature on the Formation of CoSi Studied by X-ray Photoelectron Spectroscopy and Micro Raman Spectroscopy**, ***J. Zhao***, *L. Ballast, T. Hossain, R. Trostel, B. Bridgman,* Advanced Micro Devices

Silicides are widely used on poly-Si as low resistance gate electrodes and local interconnects. Among all silicides, CoSi@sub 2@ attracts a special interest, not only because of its low resistance and its technical advantages in processing, but also its excellent match with Si. CoSi is the intermediate phase in the conversion sequence of pure Co, CoSi and CoSi@sub 2@. In this paper, we investigated the effect of rapid thermal annealing (RTA) temperature on the formation of CoSi using X-ray photoelectron spectroscopy (XPS) and micro Raman spectroscopy. With pure Co deposited on single crystalline Si wafer and capped by Ti thin film, the wafers were rapid thermal annealed at 450, 460, 470, 480 and 490@super o@C, respectively. These wafers were then stripped with SPM (H@sub 2@SO@sub 4@/H@sub 2@O@sub 2@). XPS was used to determine the chemical composition of the CoSi thin films and Auger parameter was continuously monitored along with ion sputtering to provide chemical state depth profile. XPS depth profile shows that uniform CoSi film was developed with RTA at 470@super o@C. The wafer with RTA at 450@super o@C has a pure Co layer in between the CoSi film and Ti cap. After strip, the thinnest CoSi film was observed with this wafer among the five. On the other hand, the wafer with RTA at 490@super o@C shows significant amount of Ti diffusion into the CoSi film. After strip, XPS depth profile indicates that this wafer has residue Ti on the top of CoSi surface. Micro Raman spectroscopy was used as a non-destructive method to characterize the film thickness and uniformity of the CoSi films on Si wafer. The product, @theta@d (@theta@ - absorption coefficient, d - film thickness) was calculated from both the Si excitation wavelength of 521cm@super -@ and CoSi excitation wavelengths of 206cm@super -@ and 224cm@super -@. The correlation of the measured Raman peak intensity ratio, the calculated product @theta@d and the sheet resistance of CoSi thin film were also elucidated.

4:00pm **TF-ThA7 Optical Metrology for Process Development and Control of Universal Anti-Reflective Layers**, ***J.M. Holden***, Nanometrics, Inc.*; Y. Wang, Z. Karim, K. MacWilliams,* Novellus Systems

A two-layer, inorganic anti-reflective layer (ARL) consisting of a high extinction coefficient SiO@sub x@N@sub y@ bottom layer and a low extinction coefficient SiO@sub x@N@sub y@ top layer is used as a

"Universal" ARL or UARL. The UARL is useful in damascene lithography or anywhere substrate reflectance is unknown or uncontrollable. The optical dispersions of individual films of the structure are characterized by Variable Angle Spectroscopic Ellipsometry (VASE@footnote 1@). Minimal parameter models are used to describe refractive index, n(@lambda@), and extinction coefficient, k(@lambda@), dispersions for top and bottom films. The dispersion models are implemented on a metrology tool that uses combined reflectance and spectroscopic ellipsometry (R+SE). Quantities relevant to DUV lithography, n(248 nm), k(248 nm), and thickness, t, are measured identically by VASE and R+SE methods. The metrology tool was used for process development and is applicable to process monitoring in a fab environment. Individual films are deposited as either a single film deposited on a single deposition station (static) or deposited in a multi-station, sequential deposition. The effect of interface layers in the sequentially deposited films can be detected weakly from ellipsometric data but not from reflectance. Normal incidence reflectance measurements and lithography simulations for typical DUV exposure tools indicate no significant differences between static and sequentially deposited films. @FootnoteText@ @footnote 1@VASE is a trademark of the J. A Woollum Company.

4:20pm **TF-ThA8 Temperature Dependence of Structure and Electrical Properties of Germanium-Antimony-Tellurium Thin Films**, *J. González-Hernández,* ***E. Prokhorov,*** *Y.V. Vorobiev,* Centro de Investigacion y de Estudios Avanzados del IPN, Mexico

The interest in the study of Ge:Sb:Te thin films is due to their use as optical and electrical devices materials. Both of these applications are based on structure change from amorphous to crystalline. Thus, understanding of the mechanism of crystallization in this material is important from the basic technological point of veiw. In this work we have studied the kinetics of the crystallization of Ge:Sb:Te films prepared by thermal evaporation. For that, in situ resistance and capacitance measurements during heating were used. The transformation kinetics from amorphous to crystalline phase was analyzed on the basis of the annealing behavior. The results were interpreted using Kissinger model, from which, the activation energy of the crystallization process is obtained. Using X-ray diffraction, Raman spectroscopy and optical microscope measurements, we have observed that during heating at different heating rates, crystallization of film is accompanied by Te phase segregation. The number and size of Te inclusions depend on the heating rate and film thickness. From our measurements we found that the capacitance measurements is the new highly sensitive method to control the crystallization process in the thin films. It provides additional information not obtained using other methods.

Thin Films Division
Room 615 - Session TF-FrM

In-situ Characterization and Material Process Imaging

Moderator: J.S. Zabinski, Air Force Research Laboratory

8:40am **TF-FrM2 Ion Beam Induced Defects and Phonon Confinement in 2H-WS@sub 2@ by "In-situ/Real-Time" Raman Measurements**, ***F.S. Ohuchi***, University of Washington; *K. Ishioka, M. Kitajima,* National Institute for Metals, Japan

Ion beam bombardment induces chemical and structural changes in the solid surface. This occurs because a large fraction of the incident ion energy goes into bulk processes like atomic mixing, dissociation and reduction, forming defects in the material. Ra man scattering is sensitive to small changes that occur in the lattice symmetry of a crystal, thus it has been used as a sensitive structure probe to study the defects in solids. In this paper, we report "in-situ" and "real-time" Raman measurements on tu n gsten disulfide (WS@sub 2@) single crystals during the bombardment of 5 keV He@super +@ ion beam. Changes in the peak intensity, energy and broadening for the E@sub 2g@ phonon mode were measured as a function of ion dose (1x10@super 12@-4x10@super 16@ i o n s/cm@super 2@), and the phonon correlation lengths were obtained using "spatial phonon correlation (SPC)" model. The phonon correlation length decreased with ion irradiation dose, and their changes were correlated with our previous investigation on t h e surface stoichiometry change with ion bombardment (JVST A12(4) 2451, 1994). Appearance of a new shoulder peak at around 416 cm@super -1@ to the A@sub 1g@ peak became evident when the dose exceeded more than 10@super 14@ions/cm@super 2@. This peak is considered as a forbidden mode originated from defect-induced coupling of the longitudinal acoustic (LA) and transverse acoustic (TA) phonons at the K point in the Brillouin zone of the WS@sub 2@ lattice. .

9:00am **TF-FrM3 Toward 'Virtual' Materials Processing Research**, ***S.R. LeClair***, Air Force Research Laboratory **INVITED**

Of the many research challenges in materials science is the development of more comprehensive methods for materials process design and control ranging from bulk materials transformation at the macro scale to increasingly small systems at the nano scale. The unavoidable frontier of the future is 'small-systems', wherein thin-films and MEMs are merely the bow wave to a world of atomic-scale ordering and transitions which will manifest in the interfacial designs of nano-functional building blocks for more portable and efficient systems. Although small-systems have widespread application to Air Force pursuits in becoming a Space Force, the technology will be inevitably driven by the need for more powerful but compact computing and telecommunication devices. Let us assume the inevitability of small-systems, and focus on the more immediate and prerequisite issues relative to materials research and the methods for design, analysis and control of processes to realize small-systems. To enable these methods will require investments - first, in the area of molecular modeling - transforming the various molecular modeling methods from their current use as a limited means of atomic-scale perusal to the simulation of growth processes for the manufacture of small-systems. Also at issue, and potentially more pivotal, is atomic-scale sensing for in situ monitoring of the deposition and self-assembly of nano-functional building blocks and their associated interfaces. We will need in situ, but non-destructive, methods for imaging surfaces and subsurface structures to assess defect densities, electrical, optical and thermal conductivities, size and continuity of granular orientations, etc.

9:40am **TF-FrM5 Stress Evolution during Growth of Epitaxial and Polycrystalline Metal Multilayers**, ***V. Ramaswamy***, *W.D. Nix, B.M. Clemens,* Stanford University

A complete understanding of the relationship between film stress and microstructure at the various stages of growth and an ability to measure film stress in-situ during growth, provide an opportunity to study film microstructural evolution. In this study, stress evolution during growth of epitaxial and polycrystalline, (111)-oriented Pd/Pt and Pd/Ag multilayers is monitored by in-situ substrate curvature measurement. The initial stress behavior of Pd grown on Ag and Pt is similar in epitaxial and polycrystalline films, with Pd exhibiting a sharp tensile change when grown on Ag and a smaller compressive change followed by a tensile change when grown on Pt. This initial behavior is ascribed to the effects of coherency and surface energy differences between film and underlayer. However, with increasing Pd thickness, remarkable differences are observed in the stress behavior in the epitaxial and polycrystalline samples. In polycrystalline Pd/Pt and Pd/Ag, the tensile stress relaxes with increasing Pd thickness and eventually turns compressive at about 30 Å whereas in the epitaxial samples, the stress in Pd remains tensile even at large thicknesses. The stress behavior of Ag and Pt in Pd/Ag and Pd/Pt multilayers are similar in the epitaxial and polycrystalline cases, with Ag on Pd relaxing completely after the growth of the first monolayer and the development of compressive stress in Pt grown on Pd. The effects of the structural differences between epitaxial and polycrystalline films on the stress behavior are discussed in terms of strengthening mechanisms and susceptibility to the effects of atomic peening.

10:00am **TF-FrM6 Metallic Sputtered Film Evolution Via Real-time/In-situ X-ray Diffraction**, *J.F. Whitacre, Z.B. Zhao, B.A. Rainey,* ***S.M. Yalisove***, *J.C. Bilello,* University of Michigan

A laboratory-based in-situ x-ray diffractometer is described. This equipment allows the evolution of sputtered metallic films to be studied during growth. An 18kW rotating anode x-ray source is used in conjunction with an Inel(tm) curvilinear position sensitive detector, which is aligned in the asymmetric or symmetric grazing incidence x-ray scattering (GIXS) geometry. Complete diffraction patterns can be acquired in as little as 2 seconds from films of adequate thickness. The development of texture, stress, grain size, and phase content is observed in coatings consisting of Ta, Cr, and/or CrN. Traditional ex-situ analysis methods are applied to these films after growth and are correlated to the in-situ findings, providing a powerful tool for in-situ process control and optimization. Using this system, films and multilayer coatings can be tailored to have specific microstructural characteristics as they are grown. Data from a number of different experiments will be presented and discussed. This work funded by ARO contracts with numbers DAAH 04-95-1-0120 and 8c DAAG55-98-1-0382.

10:20am **TF-FrM7 In Line Measurement of Ti and TiN Thickness and Optical Constants using Reflectance Data through a Vacuum Chamber Window**, ***M.F. Tabet***, Nanometrics Inc.; *U. Kelkar,* Applied Materials

The thickness and optical constants of titanium and titanium nitride thin films were measured by visible reflectometry through a window of a vacuum deposition system while the wafer is cooling from deposition to room temperature. The measurement system is ultra-compact and was designed for integration into semiconductor processing equipment. This in-line metrology tool does not affect the system throughput. The Ti and TiN films were deposited on 3000 @Ao@ silicon dioxide film on 200 mm silicon wafers using an Applied Materials Endura PVD deposition system. The system was used to measure thin metal films with various thicknesses and deposited using conventional DC magnetron sputtering and Ionized Metal Plasma (IMP) techniques. The optical constants of the Ti and TiN films were modeled through the use of a Lorentz oscillator dispersion model. A standalone production metrology tool was used to measured both ellipsometer and reflectometer data from the same location on the wafer and simultaneously determined the thickness and optical constants model parameters. The dispersion model obtained from the analysis of the combined ellipsometry and reflectometry data was then used to fit the visible reflectance data measured in line. This measurement system can monitor Ti and TiN depositions on every wafer in a production environment.

10:40am **TF-FrM8 Morphology and Growth of Metal Thin Films on Si Probed by In Situ Spectroscopic Ellipsometry@footnote 1@**, ***C. Liu***, *J. Erdmann, A. Macrander,* Argonne National Laboratory

Here we present results of in situ spectroscopic ellipsometry studies of sputtered thin films of Au, Pt, Pd, Rh, Cr, Cu grown on Si wafers. This study was carried out systematically on incrementally grown metal thin films. Multiple data sets obtained for each film material with incremental thicknesses were analyzed using both flat-film and rough-film models. We found that the initial growth of these metal films on Si is correlated with their chemical bond strength with oxygen in the native oxide of Si. Metals with higher bond strength (such as Cr) grow smoother at the early stage of growth and have a better adhesion to the Si wafer. In metal/Si systems, a Cr thin film is thus commonly added as a "glue" layer between the metal and Si for better adhesion. The Cr film however, becomes rougher as its thickness increases. A glue layer of Cr should not exceed 10 nm to keep the film smooth. Rh films grow smoothly on a thin (6-nm) Cr-covered Si wafer. But on a thick (100-nm) Cr/Si film, they were initially as rough as the thick Cr film. The roughness decreases as the Rh film thickness increases. A relaxation effect was also observed on Rh/Si films. An increase of ~10% in measured Rh thickness was observed two hours after the growth when a

flat-film model was used. This puzzle was solved when a rough-film model was applied. The Rh film simply became rougher in vacuum at room temperature and the total mass of Rh did not change. The same Rh film stored in air shrunk to small individual droplets 6 months later. These findings are important in our x-ray mirror applications. @FootnoteText@ This work is supported by the U.S. Department of Energy, BES, under contract no. W-31-109-ENG-38

11:00am **TF-FrM9 Stabilization of High Deposition Rate Reactive Magnetron Sputtering of Oxides by In-Situ Spectroscopic Ellipsometry and Plasma Diagnostics**, ***M. Vergöhl***, *N. Malkomes, B. Hunsche, B. Szyszka, T. Matthée,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany

High deposition rates are of essential importance in reactive magnetron sputtering on architectural glass. To reach high deposition rates and a high transparency of oxide films with constant properties during the full target lifetime, it is required that the process can be stabilized in a specific window within the transition mode. In general, the control of the plasma parameters alone (i.e. partial pressure, optical emission intensity, plasma impedance) is not sufficient for the definition of an operating point with constant film parameters. Therefore, a control system is proposed that is based on a combination of a short-term stabilization of the plasma and a long-term stabilization employing an in-situ spectroscopic ellipsometer. For niobium and titanium oxide, both an optical emission monitor and reactive gas partial pressure measurement were employed. In addition, it turns out that the specific deposition rate, i.e. deposition rate divided by the power density, is a suitable control parameter. Compared to the oxide mode, the deposition rate of Nb2O5 and TiO2 films deposited in the transition mode could be enlarged by a factor of 3-4. The films were grown at different process parameters (oxygen partial pressure, target power, absolute pressure, mid-frequency and DC-technique) onto unheated substrates. Nearby in-situ ellipsometry, ex-situ spectroscopic ellipsometry at different angles of incidence was applied to study the optical properties and the morphology of the films.

11:20am **TF-FrM10 In-situ Structural, Chemical and Electrical Characterization of WO@sub 3@ Sensor Films**, ***S.A. Ding***, *C.S. Kim, R.J. Lad,* University of Maine, U.S.

Tungsten trioxide thin films are useful as active elements in semiconducting metal oxide conductance-type gas sensors. To explore the correlation between deposition parameters/post-deposition processing and sensing characteristics of the films, we have used a multi-chambered UHV system to deposit WO@sub 3@ films on r-cut sapphire. In-situ chemical and electrical characterizations of the films were then carried out before and after the exposure to target gases such as H@sub 2@S, Cl@sub 2@ and DMMP. The films were grown using rf magnetron sputtering of a W target in O@sub 2@/Ar mixtures ranging from 0 to 80% O@sub 2@. Additional deposition parameters included growth temperature, rf power and total pressure. Both in-situ RHEED and ex-situ XRD data indicate that a variety of film structures including amorphous, polycrystalline and highly textured films can be achieved by varying those parameters. In-situ conductivity measurements acquired using a four-point van der Pauw method show that the stoichiometry and microstructure have an influence on the electrical behavior of the sensor films. One other important parameter in dictating the electrical characteristics of the sensor films is found to be the deposition rate, which is altered by varying the rf power, O@sub 2@/Ar ratio and the total pressure. The conductivity measurements indicate that the higher rate yields higher baseline conductivity. In-situ XPS study of the films shows the formation of stable surface species upon exposure to the target gases. The observed chemical modification of the surface is discussed within the context of a dependence of sensor behavior on the post-deposition processing of the films.

11:40am **TF-FrM11 Growth and In Situ Characterization of Thin Films by a Dual-Plasma System**, ***E.C. Samano***, *G. Soto, R. Machorro,* CCMC-UNAM, Mexico

Thin films of CN@sub x@, SiO@sub x@Nsub y@ have a tremendous potential to be used in the mechanical and optical industry due to its unique mechanical and dielectric properties, respectively. The stoichiometric control of these films is highly important to manage their desired properties. A dual-plasma system has been set up to provide free radicals from a solid target by laser ablation, and atoms and ions in gas phase by an ECR source. These highly reactive species are deposited on a single crystal silicon substrate. The stoichiometry and properties of carbon nitride and silicon oxynitride films are studied as a function of N@sub 2@ and O@sub 2@ gas pressure, respectively, and the several PLD and ECR deposition parameters. The films are in situ analyzed in an adjacent analysis chamber by AES, XPS and EELS to determine the chemical stability and bonding of their compounds.

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