Thin Films
Room 123 - Session TF-TuM

Optical Thin Films
Moderator: J. Verhoeven, FOM Institute, The Netherlands

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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