Thursday Afternoon, October 5, 2000

Thin Films
Room 203 - Session TF-ThA
Transparent Optical Coatings

Moderator: J.R. Doyle, Macalester College

2:00pm **TF-ThA1 Criteria for Choosing Transparent Conductors*, R.G. Gordon,*** Harvard University **INVITED**

Transparent, electrically conductive films (TCOs) have been prepared from a wide variety of materials. These include oxides of tin, indium, zinc and cadmium, nitrides of titanium and chromium, and metals such as silver and gold. The physical properties of these materials are reviewed and compared. A figure of merit for a transparent conductor may be defined as the ratio of the electrical conductivity to the optical absorption coefficient of the film. The materials having the highest figures of merit are fluorine-doped zinc oxide and cadmium stannate. Physical, chemical and thermal durability, etchability, conductivity, plasma wavelength, work function, thickness, deposition temperature, uniformity, toxicity and cost are other factors that may also influence the choice of material for any particular application. The TCO materials are ranked according to each of these factors. The main applications of TCOs will be examined to see how these factors entered into the selection of the materials actually used.

2:40pm **TF-ThA3 Preparation of Transparent Conducting Thin Films using Multicomponent Oxides Composed of ZnO and V@sub 2@O@sub 5@ by Magnetron Sputtering*, T. Miyata,*** *S. Suzuki, H. Toda, T. Minami,* Kanazawa Institute of Technology, Japan

Recently, multicomponent oxides consisting of a combination of different binary or ternary compounds have recently attracted much attention as new transparent conducting oxide (TCO) materials. In this paper, we describe the preparation of TCO thin films using new multicomponent oxides of the ZnO-V@sub 2@O@sub 5@ system. Films were prepared on substrates at temperatures ranging from room temperature (RT) to 350@super o@C by conventional planar magnetron sputtering using powder mixtures of ZnO and V@sub 2@O@sub 5@ as the target. The carrier concentration of vanadium-doped ZnO (ZnO:V) films prepared using ZnOV@sub 2@O@sub 5@ targets markedly increased as the V@sub 2@O@sub 5@ content was increased from 0 to about 15 wt.%, whereas the Hall mobility decreased gradually. As a result, the resistivity of ZnO:V thin films reached a minimum at a V@sub 2@O@sub 5@ content of about 15 wt.%, and markedly increased with V@sub 2@O@sub 5@ contents above about 20 wt.%. Films prepared with V@sub 2@O@sub 5@ contents of about 50 to 70 wt.% were highly resistive or insulators and identified as a ternary compound, ZnV@sub 2@O@sub 4@. In contrast, the resistivity of films markedly decreased as the V@sub 2@O@sub 5@ content was increased from about 80 to 100 wt.%. A 100 wt.% vanadium oxide film with a thickness of 25 nm exhibited a resistivity of 5-10@super -4@@ohm@cm and an average transmittance above 70% in the visible range. In addition, this report describes the chemical properties and the impurity doping effect of TCO films using new multicomponent oxides of the ZnO- V@sub 2@O@sub 5@ system.

3:00pm **TF-ThA4 Properties of Transparent conducting CdO-In@sub 2@O@sub 3@-SnO@sub 2@ Thin Films Prepared by Pulse Laser Deposition (PLD)*, M. Yan,*** *R.P.H. Chang, T.O. Mason, T.J. Marks, K.R. Poeppelmeier,* Northwestern University

Transparent conducting oxides (TCO) have extensive application in display devices, solar cells and sensing elements Various techniques have been applied to deposit TCO films including: thermal evaporation, sputtering, reactive ion plating, chemical vapor deposition (CVD), pulse laser deposition (PLD), atomic layer epitaxy (ALE), etc. The ternary alloy system of CdO-In@sub 2@O@sub 3@-SnO@sub 2@ has received much attention recently. Several compounds in this ternary systems, Cd@sub 2@SnO@sub 4@, CdIn@sub 2@O@sub 4@ and In@sub 4@Sn@sub 3@O@sub 12@, exhibit encouraging electrical and optical properties, while most of the ternary phase diagram (CdO, In@sub 2@O@sub 3@, SnO@sub 2@) remains unexplored. Furthermore, it is believed that there are some metastable phases and solution ranges not available in the bulk form but can be obtained as thin films. In our research, we synthesized and examined the electrical, optical and structural properties of thin films on Si and Corning 1737 substrates with different compositions deposited in a multi-target PLD system. Films were formed by first creating multi-layers of elemental oxides of CdO, In@sub 2@O@sub 3@ and SnO@sub 2@. The stoichiometry of the complex oxide was adjusted during this process. The multi-layered films were then annealed in certain gas environment for a range of time and temperature to form polycrystalline ternary oxides. Preliminary results show that 5% In@sub 2@O@sub 3@ doped CdO has conductivity of 20,000S and bandgap of 2.75eV. Stoichiometric Cd@sub 2@SnO@sub 4@ has conductivity of 1600S and bandgap of 3.02eV. Stoichiometric CdIn@sub 2@O@sub 4@ has conductivity of 600S and bandgap of 3.05eV. When CdIn@sub 2@O@sub 4@ is doped with 5% SnO@sub 2@, its conductivity raised to 3,300S and its bandgap remains unchanged. It is believed that further improvements can be achieved through proper doping and annealing strategies.

3:20pm **TF-ThA5 Expanding Thermal Plasma Deposition of Natively Textured ZnO for Thin Film Solar Cell Applications*, R. Groenen,*** Eindhoven University of Technology, The Netherlands*; J. Loeffler,* Utrecht University, The Netherlands*; J.L. Linden,* TNO-TPD, The Netherlands*; R.E.I. Schropp,* Utrecht University, The Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

A new approach for low temperature deposition of natively textured ZnO is developed, utilizing an expanding thermal argon plasma created with a cascaded arc. (Co)precursors are oxygen, diethylzinc and -additionally for doped films- trimethylaluminum, which undergo ionisation via charge exchange and consecutive dissociative recombination by respectively argon ions and electrons created in the arc. Films are deposited on Corning 1737 F glass at substrate temperatures of 200 - 350°C at a rate of 0.65 - 0.75 nm s@super -1@. The optical and electrical properties relevant for solar cell applications are comparable to those obtained for Asahi U-type SnO@sub 2@:F. Measurements of haze and angular resolved scattering intensity reveal increased light scattering with increasing deposition temperature and film thickness because of a rougher surface texture as confirmed by AFM and SEM measurements. In addition, virtually no loss in transmission of the ZnO films due to hydrogen plasma exposure is observed. In order to demonstrate the suitability for solar cell applications, p-i-n a-Si:H solar cells were co-deposited both on the natively textured low temperature material and Asahi U-type SnO@sub 2@:F, showing comparable efficiencies around 10%. The TCO / p-layer interface leads to effective light scattering, which results in high spectral response especially for long wavelengths.

3:40pm **TF-ThA6 Effects of Excess Oxygen Introduced during Sputter Deposition and Post Annealing under a High Oxygen Pressure on Carrier Mobility in Indium-tin Oxide Films*, N. Kikuchi,*** *E. Kusano, E. Kishio, A. Kinbara, H. Nanto,* Kanazawa Institute of Technology, Japan

Post-annealing for tin dope indium oxide films deposited at a low substrate temperature is sometimes needed to improve their optical properties. While the transparency in the visible range is enhanced by the annealing, the electrical conductivity of the film is deteriorated generally. The deterioration in the electrical conductivity is not only because of the reduction in carrier density, but also because of the reduction in carrier mobility. The reduction in the carrier mobility is thought to strongly relate to the introduction of excess oxygen into or on the film by the annealing. In this paper, indium tin oxide films with excess oxygen was prepared by deposition with a high oxygen concentration or by post-annealing under a high oxygen pressure in order to discuss its effects on electron mobility have been investigated. ITO films were deposited on glass substrates by r.f. sputtering under various oxygen concentrations in the discharge gas (0.3-100 %). Substrate temperature was kept at 773 K during deposition. Single phase of In@sub 2@O@sub 3@ was observed for all films deposited. A minimum resistivity of 1.8x10@super -4@ @ohm@cm was obtained for a film with a Sn concentration of 8 wt%, deposited at an O@sub 2@ concentration in the discharge gas of 0.3 %. With increasing oxygen concentration in the discharge gas from 0.3 % to 100 %, the Hall mobility decreased from 45 cm@super 2@V@super -1@s@super -1@ to 27 cm@super 2@V@super 1@s@super -1@ and the carrier density decreased from 1.0x10@super 21@ cm@super -3@ to 1.0x10@super 19@ cm@super -3@. By the post-annealing at 473 K for 30 min. in air, the Hall mobility of 27 cm@super 2@V@super -1@s@super -1@ increased to 37 cm@super 2@V@super -1@s@super -1@ and the carrier density of 1.0x10@super 19@ cm@super -3@ increased to 2.0x10@super 19@ cm@super -3@. The similar behavior of the Hall mobility and carrier density was observed for an ITO film annealed in O@sub 3@. These increases in the Hall mobility and carrier density during a low temperature annealing is thought to relate to desorption of excess oxygen existed at grain boundaries or the surface of the films because the annealing temperature is too low to improve the film crystallinity further and because it is hard to assume the formation of oxygen vacancies under the condition of the annealing. The results obtained support the hypothesis that the oxygen introduced into grain boundaries or adsorbed at the surface of the films act as charge traps and carrier scattering centers.

4:00pm **TF-ThA7 Preparation and Properties of Transparent Conductive Aluminum-doped Zinc Oxide Thin Films by Sol-Gel Process***, M. Alam, D. Cameron,* Dublin City University, Ireland

Recently, numerous electrically conductive oxides have been discovered and extensively investigated. Of these, indium tin oxide (ITO) and ZnO are well known for their transparency when made into thin films and are expected to find wide use as transparent electrodes for many devices, such as Electrochromic (ECDs), Liquid crystal displays (ELs) and solar cells. Zinc oxide is one of the most promising transparent conducting oxides currently under investigation. Zinc oxide holds considerable promise as an optically transparent conducting material due to its wide band gap (~3.3 eV), its amenability to defect or impurity doping and other desirable properties such as low cost and non-toxicity. Thin films of transparent conducting zinc oxide have been prepared by a variety of techniques, such as sputtering, chemical vapor deposition, reactive evaporation, spray pyrolysis and more recently by sol-gel process. Amongst the different techniques available, the sol-gel method seems to be the most attractive one due to coating on the desired shape and area, easy control of the doping level, solution concentration and homogeneity without using expensive and complicated equipment when compared to other methods. Highly conductive and transparent aluminum-doped zinc oxide thin films have been prepared from the solution of zinc acetate and aluminum chloride in ethanol by sol-gel process. The effect of changing the aluminum-to-zinc ratio from 0 to 6 at. % and annealing temperature from 0 to 600°C in vacuum has been thoroughly investigated. As-deposited films have high resistivity and high optical transmission. Annealing of the as-deposited films in vacuum leads to a substantial reduction in resistivity without affecting the optical transmission. The films have a minimum value of resistivity of about 1.5x10@super-3@ ohm-cm for 0.8 at. % aluminum-doped zinc oxide and a visible transmission of about 90%.

4:20pm **TF-ThA8 Synthesis and Characterization of TCO Cobalt-Nickel Spinel Films***, **C.F. Windisch, Jr.**, K. Ferris, G.J. Exarhos,* Pacific Northwest National Laboratory

Cobalt-nickel oxide films of nominal 100 nm thickness, and resistivities on the order of 0.01 ohm-cm have been prepared by spin-casting from both aqueous and organic precursor solutions followed by annealing at 450 C in air. Films deposited on sapphire substrates exhibit a refractive index of about 1.7 and are relatively transparent in the wavelength region from 600 to 8000 nm. They are also magnetic. The electrical and spectroscopic properties of the oxides have been studied as a function of Co/Ni ratio. An increase in film resistivity was found upon substitution of other cations (Zn@super 2+@, Al@super 3+@) for Ni in the spinel structure. However, some improvement in the mechanical properties of the films resulted. Conducting films also have been prepared upon substitution of cobalt by palladium. A combination of XRD, XPS, UV/Vis and Raman spectroscopy indicated that NiCo@sub 2@O@sub 4@ is the primary conducting component and that the conductivity is maximum at this stoichiometry. When Co/Ni < 2, NiO forms leading to an increase in resistivity; when Co/Ni > 2, the oxide was all spinel but the increased Co content lowered the conductivity. The influence of cation charge state and site occupancy in the spinel structure markedly affects calculated electron band structures and likely influences an anomalous switch of p-type conductivity to n-type conductivity seen at a Co/Ni ratio of 2. Electronic structure modeling studies also suggest the important role of the Ni@super +3@ cation in the conductivity mechanism. Finally, Raman spectra of the films were relatively easy to obtain and therefore were useful as a routine tool for identifying composition and optimizing conductivity.

4:40pm **TF-ThA9 Effect of Vacuum Deposited Polymer Substrate Roughness on ITO Electrical and Optical Properties***, **M.A. Roehrig**, C.I. Bright,* Presstek, Inc.

Increasing interest in next generation flexible flat panel display (FPD) materials and substrates has spurred research into improved/optimized ITO thin films deposited on polymer substrates. Requirements for FPD on flexible substrate are such that high conductivity and optical transmittance must be achieved for very thin ITO thin films, e.g. d@sub ITO@ - 5 nm to 100nm. At these thicknesses, polymer substrate roughness is expected to effect optical and electrical performance of the deposited ITO films making it difficult to achieve the high quality FPD requirements. An organic material vacuum deposition technique with the ability to control polymer film thickness from a few 10's of nanometers to several microns has been combined with ITO deposition from both ceramic (90% In@sub 2@O@sub 3@/ 10% SnO@sub 2@) and metal (90% In/ 10% Sn) targets. The effects of vacuum deposited polymer layer thickness and surface roughness effects on the electrical and optical properties of ITO thin films have been measured. Visible range optical performance, surface profilometry and electrical conductivity measurements, including carrier concentrations and mobilities, have been correlated with the vacuum deposited polymer layer thickness and surface roughness measurements.

5:00pm **TF-ThA10 Properties of Sol-Gel Prepared (ZnO)@sub y@(CdO)@sub 1-y@ Thin Films, with Low Concentrations of Cd in Solution***, C.I. Zúñiga-Romero, **G. Torres-Delgado**, L. Licea-Jiménez, S. Jiménez-Sandoval, O. Jiménez-Sandoval, R. Castanedo-Pérez,* Unidad Querétaro, Mexico

(ZnO)@sub y@(CdO)@sub 1-y@ thin films were prepared by the sol-gel method, with low atomic concentrations (x) of Cd in solution, i.e. 0@<=@x@<=@0.32, at @Delta@x = 0.04 intervals. The precursor solution was mainly based on zinc acetate dihydrate, cadmium acetate dihydrate, and ethylene glycol. The films were deposited on slide glass substrates, and annealed at 400°C, in open atmosphere for 60 min. The X-ray diffraction data show that the films are formed by a polycrystalline mixture of wurtzite-type ZnO and cubic-type CdO; the patterns, as well as electron dispersion spectroscopy (EDS) data, are indicative of a larger concentration (y) of CdO in the films, i.e. 0@<=@y@<=@0.7, with respect to that in solution. In support, the resistivity of the films decreases from @rho@=10@super 2@@ohm@cm for x = 0 (y = 0), to @rho@=5 x 10@super -2@@ohm@cm for x = 0.32 (y = 0.7). The UV-Vis spectra show that the films, throughout the composition range, display a high transmission, above 90%, at @lambda@@>=@600 nm.

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