Monday Morning, November 2, 1998

Thin Films Division
Room 310 - Session TF-MoM

Transparent Conductive Oxides

Moderator: T.J. Coutts, National Renewable Energy Laboratory

8:20am **TF-MoM1 Atmospheric Pressure Chemical Vapor Deposition of Transparent Conducting Films of Fluorine-Doped Zinc Oxide***, H. Liang, **R.G. Gordon**,* Harvard University **INVITED**

Transparent conducting fluorine doped zinc oxide was deposited as thin films on soda lime glass substrates by atmospheric pressure chemical vapor deposition (CVD) at substrate temperatures of 480@super o@C to 500@super o@C. The precursors diethylzinc, tetramethylethylenediamine and benzoyl fluoride were dissolved in xylene, and this solution was nebulized ultrasonically and then flash vaporized by a carrier gas of nitrogen preheated to 150 @super o@C. Ethanol was vaporized separately, and these vapors were then mixed to form a homogeneous vapor mixture. Good reproducibility was achieved using this new CVD method. Uniform thicknesses were obtained by moving the heated glass substrates through the deposition zone. The best electrical and optical properties were obtained when the precursor solution was aged for more than a week before use. The films were polycrystalline and highly oriented with the c-axis perpendicular to the substrate. More than 90% of the incorported fluorine atoms were electrically active as n-type dopants. The electrical resistivity of the films was as low as 5x10@super -4@ ohm-cm. The mobility was about 45 cm@super 2@/V-s. The electron concentration was up to 3x10@super 20@/cm@super 3@. The optical absorption of the films was about 3-4% at a sheet resistance of 7 ohms/square. The diffuse transmittance was about 10% at a thickness of 650 nm. Amorphous silicon solar cells were deposited using the textured fluorine doped zinc oxide films as the front electrode. The short circuit current was increased over similar cells made with fluorine doped tin oxide.

9:00am **TF-MoM3 Effects of Layered Structure on Properties of Transparent Conductive Films of ZnO/ZnO:Al***, **K. Tominaga**, T. Murayama, Y. Sato, I. Mori, T. Ushiro, T. Moriga, I. Nakabayashi,* The University of Tokushima, Japan

Recent data for transparent conductive films show that film resistivity seems to saturate at 10@super -4@ ohm-cm or above. This circumstance is common in ZnO and ITO films. To overcome this difficulty, approaches different from conventional parameter controls should be examined. In ZnO film preparation, we tried additional Zn adding during the film deposition. Recent investigations showed that the additional Zn during the sputtering of ZnO:Al target (doped 2 wt% aluminum oxide) induced an increase of both carrier concentration and Hall mobility. As the result, film resistivity was decreased. This suggested that an incorporation of oxygen deficient ZnO phase (ZnO:O@sub v@) in ZnO:Al phase improves the film crystallinity of ZnO:Al and decreases defects in ZnO:Al. This effect may be observed in general for the case of layered films of ZnO:Al and ZnO. To confirm this, we produced a multilayered film of ZnO:Al and ZnO:O@sub v@ film and investigated the role of the inserted ZnO:O@sub v@ layer in electrical conduction and optical property. Films were deposited by alternative sputtering method, where a ZnO:Al(2 wt%) target and a conductive ZnO target which only contains native donors were sputtered alternatively in pure Ar gas at 1 mTorr for a definite time. This process was succeeded to deposit a definite film thickness. The results showed that the film resistivity is decreased by inserting ZnO:O@sub v@ layer. This is due to an improvement of doping efficiency of Al donors in ZnO:Al layer by inserting ZnO:O@sub v@, in addition to carrier redistribution between two layers.

9:20am **TF-MoM4 Chemical State Effects on Doped ZnO Film Properties***, **G.J. Exarhos**, L.-Q. Wang, C.F. Windisch, Jr.,* Pacific Northwest National Laboratory

Zinc oxide is representative of the class of transparent conducting oxides which exhibit high transmission at visible wavelengths and concurrent low electrical resistivity. The resident conductivity and associated long wavelength reflectivity of these II-VI semiconductor films arises from the introduction of defect levels within the bandgap generated during the deposition process itself or during subsequent processing. In this work, films are prepared by means of rf-sputter and solution deposition methods. The deposition parameters are varied in order to increase conductivity in films which incorporate multivalent cationic dopants (Ga@super +3@, In@super +2@, Cu@super +2@, Au@super +3@, Pt@super +4@,...) within the wurtzite lattice. Post deposition modification of films on silica, Si, Al, or Pt substrates involves annealing in Ar/4% H2 or cathodic reduction in an electrochemical cell. Electrochemical film modification is carried out in aqueous solution (pH 7) or in an organic solvent such as CH@sub 3@CN. As-deposited and modified films are characterized using a cadre of analytical methods including XPS, AFM, TEM, XRD, Raman spectroscopy, and Electrochemical Impedance Spectroscopy. EIS measurements enable selective characterization of polarization effects within the oxide film and localized chemistry at the film-solution interface as a function of applied potential. The defect structure of the oxide is readily probed by means of in situ Raman spectroscopy during electroreduction. Results indicate that the LO Raman E@sub 1@ mode intensity, linewidth, and resonance frequency are particularly sensitive to the nature and concentration of defect states present in the film. Based upon these studies, a surface hydroxyl species is proposed to explain the observed reversible changes in conductivity. Such measurements complement the XPS studies which probe dopant oxidation state. Insight into film properties stability is based upon the electrochemical studies and measured variations in film properties upon subsequent annealing.

9:40am **TF-MoM5 Photoemission Spectroscopy Analysis of ZnO Films for Display Applications***, E.W. Forsythe, Y. Gao,* University of Rochester*; **G.S. Tompa**, L.G. Provost,* Structured Materials Industries, Inc.*; J. Doyle,* Advanced Display Systems

An important factor in the performance of most displays is the quality of at least one transparent conductive oxide contact layer. Presently, indium tin oxide (ITO) is predominantly used because it is an accepted standard and has a great deal of invested development. However, for several reasons, including work function, physical stability, and band alignment, ITO is not always the ideal contact layer for a given display technology. We will report the physical properties of ZnO based films prepared by metal organic chemical vapor deposition (MOCVD) using ultraviolet and x-ray photoemission spectroscopy (UPS and XPS). In addition, the surface characteristics of the films are modified with series of cleaning and polishing steps. Using UPS, the work function for ZnO is 4.23eV. XPS results show an oxide layer more than 5nm on the surface of the as-received MOCVD films, with a small fraction of Zn and Ga. This oxide layer is removed by a cleaning and plasma treatment, which enhances the conductivity of the ZnO films. Finally, we will report atomic force microscopy results before and after cleaning and polishing as well as chemical etching results. This work was supported in part by DARPA DAAL01-96-K-0086, NSF DMR-9612370.

10:00am **TF-MoM6 Transparent and Conductive Multicomponent Oxide Films Prepared by Magnetron Sputtering***, **T. Minami**,* Kanazawa Institute of Technology, Japan **INVITED**

Recently, multicomponent oxides composed of combinations of binary compounds or ternary compounds have attracted much attention as new materials for transparent and conductive thin films. This paper introduces transparent conducting multicomponent oxide films prepared with varied chemical compositions by magnetron sputtering. It was found that most multicomponent oxides composed of combinations of binary compounds contained at the least one ternary compound; highly transparent and conductive films could be prepared in the ternary compound. In addition, if binary or ternary compounds which produced transparent and conductive films when prepared by magnetron sputtering were used as the starting materials, transparent and conductive films composed of combinations of these binary or ternary compounds could be also produced from all compositions in the resulting multicomponent oxides. In addition, it was found that most of the properties of transparent conducting multicomponent oxide films were mainly determined by the metal element contained in the oxide. It can be concluded that transparent conducting multicomponent oxide films are suitable for specialized applications because their electrical, optical and chemical properties as well as physical properties such as band-gap energy, refractive index and work function can be controlled by changing the chemical composition.

10:40am **TF-MoM8 Improvement of Microstructure of Indium-Tin-Oxide Films by Thin Film and Surface Technologies***, **Y. Taga**, T. Satoh, M. Ishii, T. Ohwaki,* TOYOTA Central Research & Development Labs., Inc., Japan

A rapid progress has been made in the practical device applications of flat panel displays (FPD) such as liquid crystal display, electroluminescence display, etc. In accordance with this trend, strong demands have been actually appeared in the quality of transparent conductive films such as indium-tin-oxide (ITO). Up to now, a lot of studies have been devoted mainly to the electrical and optical properties of ITO films. However, it becomes clear that microstructure of ITO films gives an important influence on the performance and durability of FPD's. In this paper, we tried to improve the microstructure of ITO films by controlling the sputter deposition and plasma treatment conditions in thin film preparation. Furthermore, we investigated the effect of microstructure of ITO films on the electrical properties of Ta-Sn-O films in the system of Al/Ta-Sn-O/ITO layered structure in inorganic electroluminescence displays. It was found that the microstructures of ITO films changed drastically with oxygen partial pressure in Ar-O@sub 2@ sputtering gas; i.e., with increasing oxygen partial pressure, grain size become small and surface morphology become smooth. Measurements of I-V characteristics in Al/Ta-Sn-O/ITO revealed that the leakage current at low electric field has been diminished by the improvement of microstructure of ITO films.

11:00am **TF-MoM9 Work Function Modification of Indium Tin Oxide**, ***S.M. Tadayyon***, *K. Griffiths, P.R. Norton,* University of Western Ontario, Canada*; C. Tripp, Z. Popovic,* Xerox Research Centre of Canada, Canada

Indium-tin-oxide (ITO) is a transparent conducting material widely used in electronic devices such as flat panel displays, solar cells, IR detectors and OLED's where it is used as the hole injecting electrode. It is desirable to have an electrode possessing as high a work function as possible, and so extensive investigations into properties and modification of ITO have been undertaken. The objective of the present study is the possible modification of ITO work function (WF) using evaporated metal overlayers. We have therefore studied gold overlayers because of the high WF of gold, and its inertness. ITO films on glass substrates (resistance ~ 10 Ohms/sq) were cleaned with a UV-ozone treatment before entry into a UHV system. Auger electron spectroscopy (AES) was used to determine the surface composition. The change of work function (WF) of the surface (± 10mV) was determined by a Kelvin probe technique and correlated with the absolute coverage (@theta@) of Au in the range 0<@theta@ 5x10@super 15@ Au cm@super -2@. The final WF values were not very different from the non-UV-ozone treated samples. Studies on bulk Au and ITO covered by Au in a single deposition, showed that the low final WF value in the sequential experiments was attributable to adsorption of hydrocarbons from the 5x10@super10@ torr vacuum, and that useful increases in WF are attainable on transparent ITO electrodes

11:20am **TF-MoM10 Application of High Speed Four-Parameter Stokes Vector Spectroscopy to the Characterization of Textured and Specular Transparent Conducting Oxide Thin Films**, ***P.I. Rovira***, *R.W. Collins,* Pennsylvania State University

A rotating-compensator multichannel ellipsometer has been used to measure the four unnormalized Stokes vector elements associated with the polarization state of polarized light reflected from both specular and textured transparent conducting SnO@sub 2@:F films. This technique provides not only the ellipsometry angles (@PSI@, @DELTA@), but also the reflectance R and the degree of polarization p. With a photodiode array detector, spectra in (@PSI@, @DELTA@), R, p) having 100 points from 1.5 to 3.75 eV can be collected with a minimum acquisition time of ~32 ms. In contrast to rotating-polarizer multichannel ellipsometry which tends to be inaccurate when @DELTA@ equals 0° or ±180°, or p<1, the rotating-compensator approach provides high accuracy measurements of the phase shift @DELTA@ over its full range (-180° to 180°) even when p<1. Therefore, this new configuration permits us to make accurate ellipsometric measurements for SnO@sub 2@:F films on glass substrates, which is the structure of choice for large area device applications such as photovoltaics. In addition to conventional microstructural characterization using the ellipsometry angles (@PSI@, @DELTA@), we have incorporated light scattering due to the textured surfaces into the analysis using the reflectance and degree of polarization. From the latter analysis, information on the SnO@sub 2@:F texture can be extracted. The results are consistent with direct images by scanning electron microscopy and atomic force microscopy. A comparison of the degree of polarization measured for the specular and textured SnO@sub 2@:F films suggests that deviations in p from unity for the latter are due to the detection of light multiply-scattered by the texture into the specular direction. Finally, the rotating-compensator multichannel ellipsometer developed here can be readily adapted to real time analysis of solar cells prepared on textured transparent conducting oxide films in commercial processes.

11:40am **TF-MoM11 Transparent Conductive Oxides with Improved Performance for Plastic Flat Panel Displays**, ***C.I. Bright,*** Delta V Technologies

The major use of Transparent Conductive Oxides (TCO) is in Flat Panel Displays (FPD). One of the major issues preventing the use of a plastic film substrate for FPD is its moisture and oxygen permeability. The permeation of water and oxygen limits the long-term stability of the display device. Another issue with plastic substrates is the low conductivity of the TCO that must be deposited at a low temperature. The Polymer MultiLayer (PML) process for vacuum evaporation of organic monomers and in-situ e-beam or UV polymerization has been shown to produce excellent substrate smoothing and when combined with other layers, outstanding barrier properties on plastic films, e.g., polypropylene and polyester (PET). Oxygen and moister permeation rates for an aluminum film with PML base coat, are one to two orders of magnitude lower than with just an aluminum layer alone. Similarly, permeation rates with PML plus an aluminum oxide layer, are another one to two orders of magnitude lower than PML with aluminum. Thus, it is proposed to combine a PML base coat and the necessary TCO transparent electrode layer, to form a barrier and solve the permeability problem of plastic substrates. This PML base coat layer should also provide a pristine surface for nucleation of the deposited TCO. Therefore, the surface resistivity of the TCO should be lower, for a given film thickness, due to its improved microstructure. The experimental results for an evaporated acrylic base coat on PET substrate, follow by DC sputtering of ITO from a ceramic target in a single pass through a web coater, are reported. Results for ITO sputtered directly onto the PET substrate without the smoothing base coat are also reported. The optical, electrical and barrier properties for both constructions were measured and compared. Three-layer constructions are also considered with, for example, a silicon dioxide barrier layer deposited either onto the PET substrate, TCO or on the base coat. The potential benefits of these configurations are compared with the two-layer configuration results reported.

Author Index

Bold page numbers indicate presenter