Wednesday Afternoon, October 27, 1999

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).

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