Characteristics of Tin doped Indium oxide films

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Abstract: Tin doped Indium oxide films were deposited by the sol gel dip coating technique using the acrylamide route. X-ray diffraction studies indicated cubic bixbyte structure. The percentage of Tin incorporated in Indium oxide was same as the precursor concentration. X-ray photoelectron spectroscopic studies also supported the incorporation of Tin in the Indium oxide lattice. Resistivity of the films was 0.01 ohm cm. Both carrier density and mobility increased with formation temperature. Room temperature Raman spectrum indicated superposition of the contribution of the In–O vibrational modes with frequency 630 cm^{-1} and the Sn–O vibrational modes with frequency 633 cm^{-1} supporting the fact that Tin was completely incorporated in the Indium oxide lattice.
Keywords: TCO, ITO, electrical properties, electronic material.

Introduction

Tin-doped Indium Oxide (ITO) has many applications due to the unique combination of high transparency and low resistivity. The low resistivity value of ITO films is due to a high carrier concentration caused by both oxygen vacancies and substitutional Tin dopants. The high transparency in the visible and near-IR region is also caused by wide band gap of a TCO. Tin-doped Indium oxide (ITO) is the most widely used transparent-conducting oxide material. The transparent conducting thin films of this oxide are used as electrodes in a variety of optoelectronic devices, as heat-mirror coatings in 'smart windows' for buildings, in automobile and airplane windshields, in incandescent light bulbs, in flat-plate and concentrating solar collectors [1–3]. Indium oxide being a wide band gap oxide semiconductor (e.g. 3.75 eV), absorbs UV radiation due to band to band transitions and reflects in the IR region due to free-electron oscillation. In between these two limits it has a transparency window covering the visible spectrum and near-IR. This transition between the transmitting and reflecting regions takes place at a wavelength λ_P, called the plasma reflection edge. The location of λ_P in an ITO film depends on the free-electron concentration (n). As n increases, the plasma reflection edge moves towards shorter wavelengths. In this connection, to produce ITO thin films various deposition techniques have been employed viz. spray pyrolysis [4], sol–gel process [5], evaporation [6], magnetron sputtering [7], electron beam evaporation [8], pulsed laser deposition [9], etc. Among these, the sol gel dip coating technique is one of the techniques used for preparation of transparent and conducting oxides owing to its simplicity, non-vacuum of the deposition and inexpensive method for large area coatings. In this work, the acrylamide sol gel dip coating technique was used for the deposition of ITO films.

Experimental Techniques

ITO thin films (10 % Sn doped Indium oxide) were deposited by the sol gel dip coating method adopting the following procedure. Clean glass substrates were used for the deposition of the films. 10 ml of

G. Ramanathan *et al* /Int.J. ChemTech Res. 2015,8(8),pp 260-264.

261

0.45 M solution of Indium (III) chloride and 0.05 M $SnCl_4$ were taken in a clean glass beaker. The solution was heated to 70°C and the pH was brought to 9 by the addition of ammonia, then 1 gm of Acrylamide was added followed by the addition of 0.25 gm of N,N,bis methylene acrylamide. After 20 min, 2 mg ammonium persulphate initiator was added to this mixture. The solution became viscous. Cleaned microglass slides (2.5 cm x 7.5 cm) were immersed into the viscous solution and withdrawn at the rate of 1cm min^{-1}. The film formed on the surface was dried in an air oven for about 15 min followed by annealing in air at different temperatures in the range of 350 - 450°C for different durations in the range of 15 min to 90 min. The optimized duration for heat treatment was 50 min. Thickness of the films measured by Mitutoyo surface profilometer increased from 450 nm – 950 nm with increase of post heat treatment temperature. The films were characterized by **Xpertpanalytical** x-ray diffraction unit with Cukα radiation. Composition of the films was estimated by EDS attachment to JOEL SEM. Electrical measurements were measured by providing evaporated silver ohmic contacts at the four corners of film surface. Hall – Vander Pauw geometry was used for the electrical measurements.

Results and Discussion

The In_2O_3–SnO_2 films deposited by the sol–gel method were characterized by XRD studies. Fig.1 shows the XRD patterns of the In_2O_3–SnO_2 films of 10 % SnO_2 formed at different temperatures. The samples have the same cubic, bixbyite structure, of In_2O_3, (JCPDS 6-0416). Also, none of the spectra corresponding to higher annealing temperatures indicate any characteristic peaks of Sn, SnO, SnO_2, which indicates that the Sn atoms are probably incorporated substitutionally into the In_2O_3 lattice [10,11]. The mean crystallite size of the ITO films, as determined by the Scherrer equation from the line broadening of the (2 2 2) reflection was 38 nm.

EDS was performed to further determine the doping level. We surveyed several samples. The EDS spectra taken on the sample is shown in figure.2, from which the SnO_2 content was determined to be 10 at % for the films. This analysis shows that the atomic percentages are, In (51.33%) Sn (6.58%) and O (42.09%)
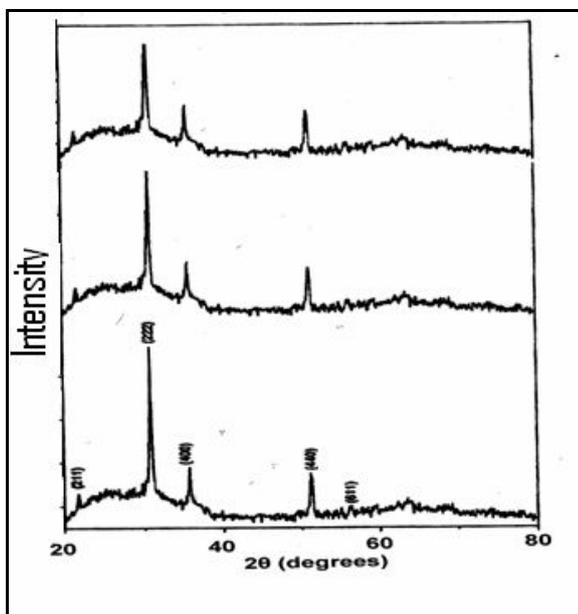

Fig.1. X-ray diffraction pattern of 10 % Tin oxide in ITO films formed at different temperatures (a) 350°C (b) 400°C (c) 450°C
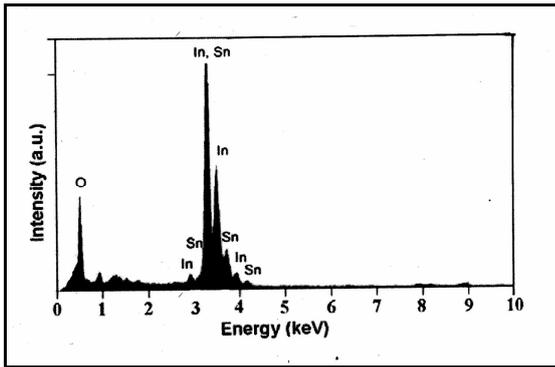
G. Ramanathan *et al* /Int.J. ChemTech Res. 2015,8(8),pp 260-264.

262

Fig.2. EDAX spectrum of ITO films (90 % In_2O_3 – 10 % SnO_2)

      XPS spectra of ITO films of different composition are indicated in Fig.3. Peaks corresponding to O 1s, In $3d_{5/2}$ and In $3d_{3/2}$, Sn $3d_{5/2}$ are observed in all cases. The binding energy of the O 1s photoelectron peak is at 534 eV. A C 1s peak at a binding energy of 284 eV is also observed on the surface of the film. The presence of this peak is related to the surface pollution which corresponds to the fact that the samples were exposed to air before the XPS measurements. The XPS spectra for O 1s peak, In 3d doublet and Sn $3d_{5/2}$ are shown in the figures. These show the evidence of only one binding state for In and Sn since there is no sign of broadening or splitting of the peaks. It is observed from the figures that oxygen is bonded to the Indium and Tin and that ITO is formed. The binding energy of In $3d_{5/2}$ at 445.1 eV measured from ITO film can be attributed to the In^{3+} bonding state from In_2O_3 which corresponds to the previous studies [11, 12]. The binding energy of Sn $3d_{5/2}$ is at 487.1 eV and corresponds to the Sn^{4+} bonding state from SnO_2 [11,13].
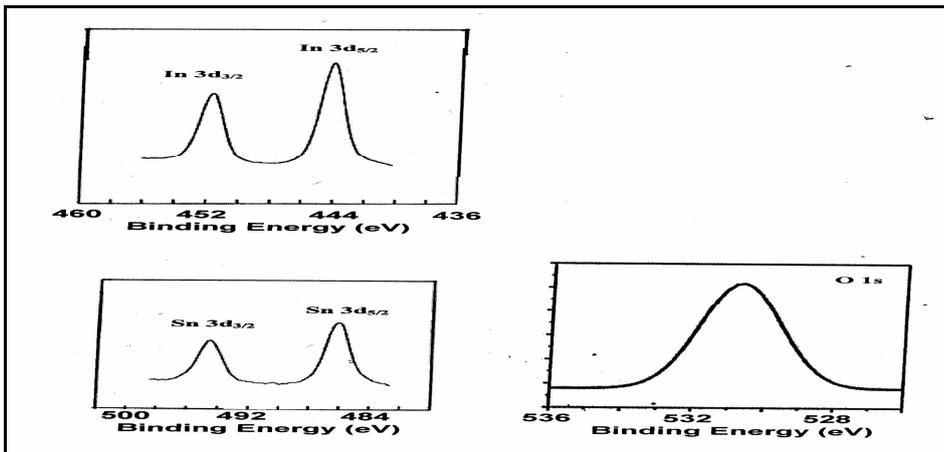

Fig.3. XPS spectrum of ITO films with 10 % Tin oxide formed at 450°C

      Fig 4 shows the surface morphology of ITO films formed at 450°C with different concentration of Tin was observed. It is observed that the grain size decreased with increase of Tin concentration. The surface roughness increases from 0.20 nm to 1.25 nm as the Tin concentration decrease. The films are porous in nature.
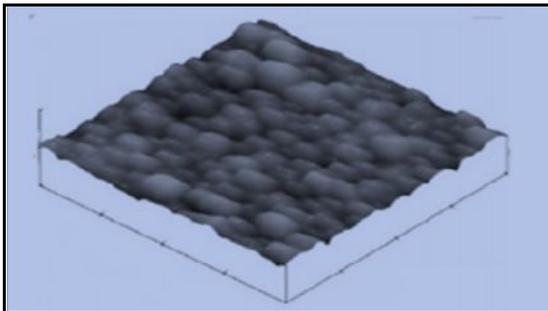

Fig.4. Atomic force micrographs of ITO films with 10 % Tin oxide formed at 450°C (1 µm x 1 µm area). Z direction: 1 div – 5.0 nm

The resistivity of the films decreased from 10 ohm cm (films formed at 350°C) to 0.01 ohm cm as the temperature increased to 450°C. The carrier density and mobility increase with increase of temperature from 350°C to 450°C. The N_d increased from 3.85×10^{17} cm^{-3} to 1.25×10^{20} cm^{-3}. The value of mobility increased from 1.35 cm^2 V^{-1}s^{-1} to 49.93 cm^2 V^{-1}s^{-1}. The resistivity value obtained for the films could be explained in terms of solubility of Sn atoms in the In$_2$O$_3$ lattice. As shown in the literature [14], the maximum solubility of Sn-atoms in the In$_2$O$_3$ lattice is reached at approximately 10 at. %.

Raman spectrum of undoped In$_2$O$_3$ shows vibrational modes at 109, 135, 307, 366, 495, 517 and 630 cm^{-1} which is an unambiguous signature of the cubic In$_2$O$_3$ structure [15]. These same features are readily observed in the ITO spectra because the main contribution to the vibrational modes comes from the cubic In$_2$O$_3$ host lattice. The high frequency line in the ITO spectrum at 631 cm^{-1}is due to the superposition of the contribution of the In–O vibrational modes with frequency 630 cm^{-1} and the Sn–O vibrational modes with frequency 633 cm^{-1}, in this work, vibration modes appeared at 144, 175, 248, 476 and 584 cm^{-1} in the ITO spectrum (Fig.5). This is similar to an earlier report [16].
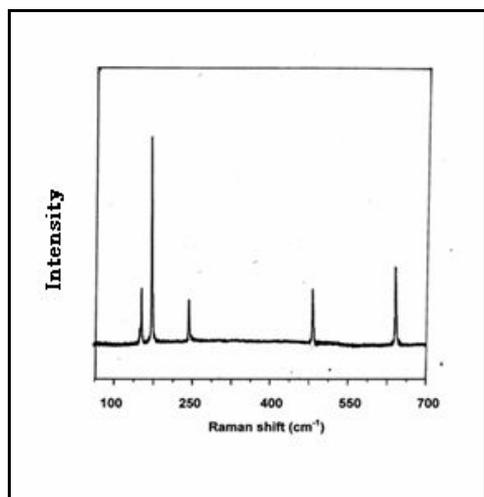

Fig.5. Room temperature Raman Spectrum of ITO films formed at 450°C with 10 %   tin oxide

Conclusions

The results of this investigation clearly points to the possibility of using them in solar cells. Single phase material can be obtained by the sol gel dip coating technique. Low resistivity films can be obtained. The process can be scaled up for large area deposition of films.

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