Dye Sensitized Solar Cells with Ito Films Prepared By the Acrylamide Sol Gel Route

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Abstract: *Tin doped Indium oxide films were prepared by the acrylamide Sol gel dip coating method. The films were post heat treated in air at different temperatures in the range 350 - 450°C. The films exhibited cubic structure. The films showed 85 % transmission and exhibited a resistivity of 1.0×10^{-4} Ohm cm. Dye sensitized solar cells fabricated with the ITO electrodes/dye/electrolyte/ tin oxide configuration yielded efficiency in the range of 1.59 – 2.20 % at 100 mW cm^{-2} illumination.*
Keywords- *Acrylamide route, ITO, Semiconductor, Thin films*

I.   Introduction

Transparent conducting oxide (TCO) films have been widely used for a variety of optoelectronic devices, energy efficient windows, light emitting diode (LEDs), flat panel displays (FPD), storage-type cathode ray tubes, solar cells, gas sensors, photo catalysts, and surface layers in electroluminescent applications. Among the existing TCOs, Sn doped In_2O_3 (ITO) is one of the most frequently used material because of its unique characteristics such as low resistivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates and chemical stability. ITO is an n type semiconductor with a band gap between 3.5 and 4.3 eV at room temperature with bixbyte structure. Several techniques have been employed for the deposition of ITO thin films. In this work, the polyacrylamide gel route was employed for the deposition of ITO thin films.

II.   Experimental Method

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 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 Cleaned micro glass slides (2.5 cm x 7.5 cm) were immersed into the viscous solution and withdrawn at the rate of 1cm min^{-1}.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. The films were characterized for their structural, optical and electrical properties.

III.   Result And Discussion

X-Ray Diffraction Patterns of ITO films as a function of the post heat treatment temperature are shown on Fig.3.1.The ITO thin films are polycrystalline and crystallize in a cubic structure of the bixbyite Mn_2O_3 (I) type structure, since (222) and (400) oriented peaks, characteristic of a cubic structure, are present on the diffractograms. The preferred growth orientation of ITO thin films depends on the post heat treatment temperature. The ratio (400) *I (*222) increase with increasing temperature. Others peaks corresponding to (411); (622); (440) reflections are also observed, but their intensity is very small compared to that of the (400) peak. Nevertheless, their presence indicate that others orientations are possible on the films and that these orientations do not disappear with increasing temperature. The mean crystallite size *D* was calculated from the (222) diffraction peaks using Debye-Scherer's formula:

$$D = K\lambda/\beta cos\theta \;\ldots\ldots\ldots\ldots(3.1)$$

in which λ is the X-ray wavelength (1.548 A° for Cu (Kα)), K =180/π, θ is the diffraction angle and β is the full line-width at half maximum of the (400) and (222) peaks. The line-widths were measured at a narrow slit width for better resolution. The mean size increases from 30 nm to 40 nm with increasing post heat treatment temperature.
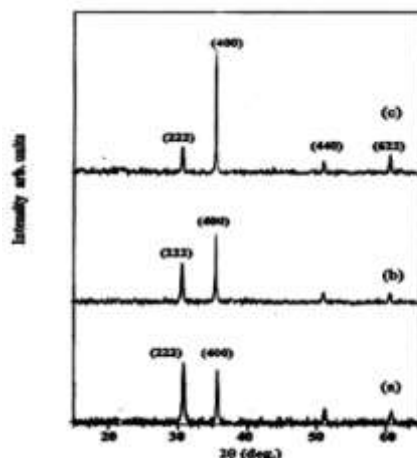
Fig. 3.1 – XRD patterns of Sn doped indium oxide films post heat treated in air at different temperatures (a) 350°C(b) 400°C (c) 450°C

Fig.3.2 confirms qualitatively the presence of indium, tin and oxygen elements. This analysis shows that the atomic percentage are, In (51.33 %), Sn (6.58 %) and O (42.09 %).
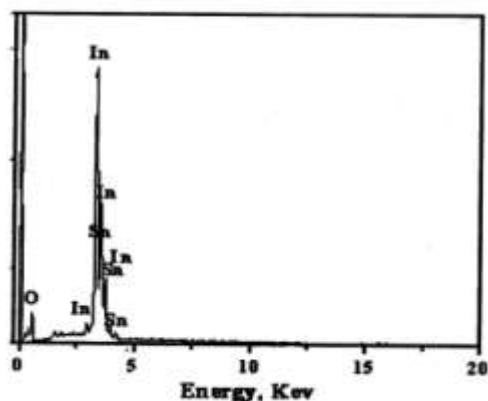

Fig. 3.2 – EDAX spectrum of ITO films post heat treated at 450°C

XPS spectra for O 1s peak, In 3d and Sn 3d doublets are shown in Fig.3.3. 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. The figures clearly indicate that oxygen is bonded to the indium and tin and that ITO is formed [1]. The binding energy of In $3d_{5/2}$ at 445.1 eV measured from ITO film shown in Fig.3.3 can be attributed to the In^{3+} bonding state from In_2O_3 which corresponds to the previous studies [2]. The binding energy of Sn $3d_{5/2}$ is at 487.1 eV of the fig.3.3 and corresponds to the Sn^{4+} bonding state from SnO_2[2].
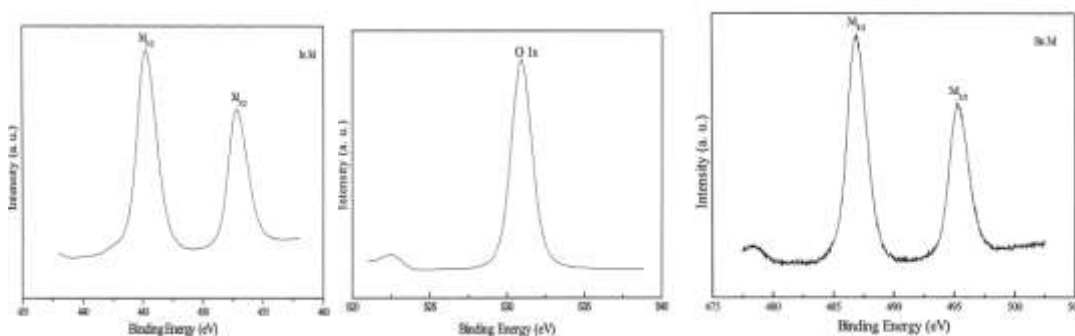

Fig. 3.3 – XPS spectra of 10 % Sn doped indium oxide

Fig.3.4 Shows typical transmittance curves plotted as a function of wavelength for the films post heat treated at different temperatures. In addition to the high transmittance (visible range), high infrared reflectance was also obtained in the Sn-doped ITO films. A shift of the absorption edge to shorter wavelengths with changes in heat treatment temperature was also apparent and is related to the Burstien–Moss effect [3].
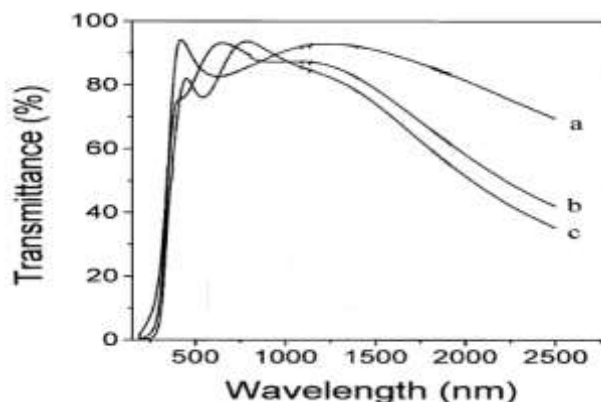
Fig. 3.4 – Transmission spectra of ITO films post heat treated at different temperatures
(a) 450°C (b) 400°C (c) 350°C

Transport parameters like mobility and carrier density were obtained from Hall measurements. Resistivity was obtained by the four probe resistivity method. The resistivity of the films varied from 10^{-4} to 10^{-3} ohm cm as the post deposition temperature decreased. Mobility values varied from 25 to 15 cm^2 $V^{-1}s^{-1}$. The carrier density values decreased from 1.0 x 10^{21} cm^{-3} to 1.0 x 10^{20} cm^{-3} as the post heat treatment temperature decreased. The resistivity value is comparable with electron beam evaporated ITO films [4].

All the ITO films post heat treated at different temperatures were sensitized in a dye solution of cis-di (thiocyanate) bis (2, 2'-bipyridyl-4,4'-di-carboxylate) ruthenium (II) (R535, N3-dye, Solaronix) for 12 h at room temperature. Carbon paste coated on a FTO substrate was used as a counter electrode. The Dye sensitized solar cell (DSSC) was fabricated by clamping the dye-sensitized ITO photo electrode against carbon counter-electrode and filling the inter-electrode space by the electrolyte of 0.5M KI, 0.05M I_2 and 0.05M 4-tert-butylpridine using capillary force. The active cell area was 0.25 cm^2. The cell was irradiated with a 250 W Xenon lamp with ultraviolet and an infrared-blocking filter. The intensity of light was 100 mW cm^{-2}. The cell configuration was ITO/Dye/Electrolyte/FTO.

The important parameter of the DSSC is the photoelectric conversion efficiency. The photoelectric conversion efficiency of solar cells is the ratio of the output power to the incident power. The efficiency (η) of the DSSCs can be calculated from the expression [5]

$$\eta = (J_{SC}V_{OC}FF)/P_{in}............(3.2)$$

Where J_{SC} is the photocurrent, V_{OC} is the open-circuit voltage, FF is the fill factor: FF = $(I \times V)_{max}/J_{SC}V_{OC}$, and the P_{in} is the intensity of the incident light. Fig.3.5 shows the photocurrent–photo voltage characteristic curve of DSSCs using the ITO films heat treated at different temperatures. The η, FF, V_{OC}, and J_{SC} of the DSSCs are summarized in Table 3.1, from the figure it is observed that the DSSC with the ITO photo electrode heat treated at 450°C, shows the maximum efficiency of 2.20 %.
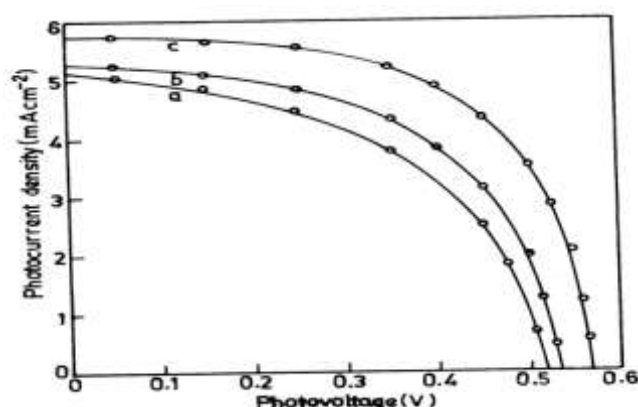

Fig. 3.5 - Photocurrent – photo voltage characteristics of ITO photo electrodes heat treated at
different temperatures (a) 350°C (b) 400°C (c) 450°C

3.1 Table -Photovoltaic performance of ITO photo electrodes

Température (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	ff	η (%)
450	0.57	5.60	0.69	2.20
400	0.53	5.30	0.65	1.82
350	0.52	5.10	0.60	1.59

IV.   Conclusion

ITO films with crystallite size in the range of 30 – 40 nm can be obtained. Films with Transmission in the range of 80 – 90 % can be obtained. Resistivity in the range of 10^{-3} ohm cm to 10^{-4} ohm cm can be obtained. DSSC cells with ITO/dye/electrolyte/FTO configuration have yielded efficiencies in the range of 1.59 % - 2.20% can be fabricated.

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