Effect of Annealing on Structural and Optical Properties of Mn: ITO Thin Film

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Abstract

Thin films of Mn (5 at.%) doped ITO were coated on corning glass substrates using the electron beam evaporation technique. The substrates were maintained at a temperature of 350 °C. The deposited thin films were then air annealed at 100 °C, 200 °C, 300 °C and 400 °C for 1 hr. The structural properties of as deposited and air annealed films were studied. The effect of annealing temperature on the structural, compositional and optical properties of the thin films was studied using X-ray diffractometer (XRD) and UV-Vis-NIR Diffuse reflectance spectrophotometer (DRS).

Keywords: *annealing, (Mn,Sn) codoped ITO, thin films*

1. Introduction

Different transparent conducting oxides (TCO) like ZnO, In_2O_3, TiO_2, SnO, CdO were doped with varied transition metals and studied the structural and optical properties of them [1-4]. The researchers are trying to find a way to increase the properties of TCO by annealing them. Annealing is a type of heat treatment to enhance the crystallinity and decrease the dislocation of atoms. The annealing affects the macroscopic characteristics of TCO in nanostructured state. This leads to change in structural and optical property of TCO on annealing. The TCOs find applications in LED, photodiodes, energy efficient windows, touch screens, surface layers in electroluminescent applications, solar cells etc. [5-13]. Among them, In_2O_3 is one of the best TCO material having high hardness, efficient chemical stability, high adhesion quality and photochemical properties. It finds applications in photovoltaic devices, biocatalytic redox transformations and flat panel displays [14-20]. The influence of annealing on the properties of ITO has already been reported by many researchers [21-24]. The crystallite size is affected by the annealing temperature. Some of the researchers have shown that there is an increase in the crystallite size as well as enhancement in the optical properties on increasing the annealing temperature [25-28].

This manuscript deals with the effect of annealing on the structural and optical properties of Mn doped ITO thin film.

2. Experimental Method

The precursor powders of In_2O_3, SnO_2 and MnO_2 were taken in stoichiometry and milled for 16 hrs using planetary ball mill to form $(In_{0.90}Mn_{0.05}Sn_{0.05})_2O_3$ nanoparticles. After sintering the grinded $(In_{0.90}Mn_{0.05}Sn_{0.05})_2O_3$ nanopowder at 950 °C for 8 hrs, it was taken as sample in the graphite crucible. The deposition of $(In_{0.90}Mn_{0.05}Sn_{0.05})_2O_3$ on glass substrate was carried out using electron beam evaporation coating method. The substrate temperature was maintained to be at 350 °C and the vacuum is maintained at 2*10-3 mbar throughout the coating period. The deposited thin films were then annealed at various temperatures such as 100 °C, 200 °C, 300 °C and 400 °C in presence of air for 1 hr in horizontal tubular furnace. The structural and optical properties of as deposited and annealed samples were studied using X-ray diffractometer (XRD) and Diffuse reflectance spectra (DRS). The obtained results were compared and the influence of annealing on the properties was studied.

3 Results and Discussion

Fig.1(a). depicts the XRD profiles for as deposited and annealed $(In_{0.90}Mn_{0.05}Sn_{0.05})_2O_3$ thin films at different temperatures. The bottom layer depicts the XRD pattern for as deposited $(In_{0.90}Mn_{0.05}Sn_{0.05})_2O_3$ thin film. The layers above the bottom layer depict the XRD pattern of $(In_{0.90}Mn_{0.05}Sn_{0.05})_2O_3$ thin films annealed at different temperatures. From the figure it was confirmed that the XRD patterns of all the samples match with the XRD profile of In_2O_3 [JCPDS card no. 06-0416]. So, it was reported that the thin films have cubic structure. From the fig. absence of secondary phase was reported. This suggests that the Mn and Sn replace the In ions in the host lattice. The absence of secondary phases or cluster of metals indicates the complete substitution of dopants in the host lattice

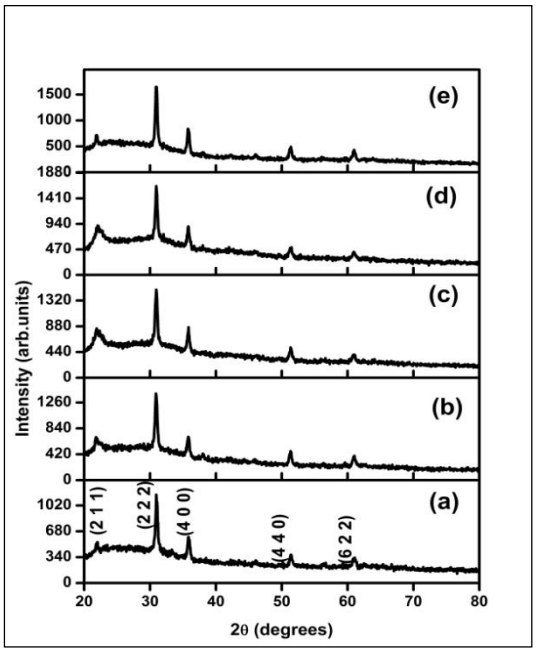

Fig. 1(a). XRD pattern for Mn doped ITO thin films (a) as deposited and annealed at (b) 100 °C (c) 200 °C (d) 300 °C and (e) 400 °C.

Fig. 1(b) shows the XRD pattern of as deposited and air annealed $(In_{0.90}Mn_{0.05}Sn_{0.05})_2O_3$ thin films in the range of 30°-32°. From the fig.1(b), it was observed that there is increase in the intensity of the predominant peak (2 2 2) at 31° on increasing the annealing temperature. It has also been observed from fig.1(b) that the predominant peak shifts to lower angle on increasing the annealing temperature. The crystallite size was found to increase from 17 nm to 21 nm on increasing the annealing temperature. This suggests that increase in the annealing temperature helps in the enhancement of crystalline properties of thin films. The slight shift in the peak position to lower angle confirms the substitution of dopants in the host lattice. The lattice parameter was found to increase from 9.38 Å to 10.37 Å on increasing the annealing temperature. The strain and dislocation density of thin films were found to decrease from 25 * 10-4 to 17 * 10-4 and 64 * 1014 to 24.8 * 1014 m-2, respectively. These behaviors of decreasing strain and dislocation density with increasing annealing temperature confirms that annealing helps to enhance the crystallinity of the sample[29,30]. The increase in crystallite size also indicates that the tensile strain is dominant as suggested by Gupta et al. [32]. Similar behavior was obtained on annealing of transition metal doped ZnO by Mathew et al. [31].

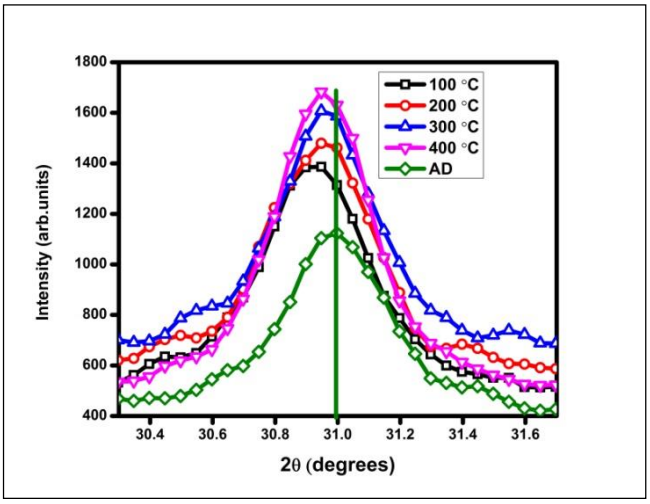

Fig. 2(b). XRD pattern for Mn doped ITO thin films in the range of 30°-32°.

Fig.2 (a). depicts the decrease in absorption band on increasing the annealing temperature. Fig. 2 (b). depicts the increase in transmittance of Mn doped ITO thin films on increasing the annealing temperature after 100 °C. The transmission value for as deposited $(In_{0.90}Mn_{0.05}Sn_{0.05})_2O_3$ thin film was found as 70 %. On annealing to 100 °C, the transmittance decreases to 65%. On further increasing the annealing temperature from 200 °C to 400 °C, the transmittance increases from 65% to 88%. The increase in transmission on increasing annealing indicates the enhanced diffusion of Mn and Sn ions in the In_2O_3 lattice of thin films. The same kind of behavior was observed for Titanium (Ti) and Gallium (Ga) codoped ZnO by Chen et al.[33].

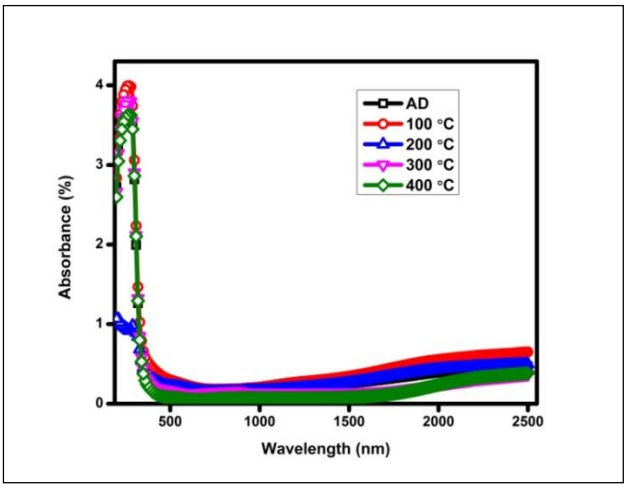

Fig. 2. (a) Absorption spectra of Mn doped ITO thin films both as deposited and annealed at 100 °C , 200 °C, 300 °C and 400 °C.

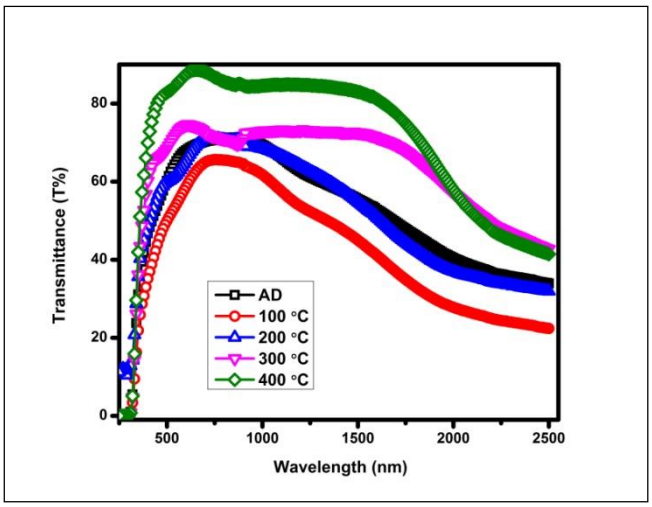

Fig. 2. (b) Transmittance spectra of Mn doped ITO thin films both as deposited and annealed at 100 °C , 200 °C, 300 °C and 400 °C.

From Tauc's plot in Fig. 3, it was found that the optical band gap decreases on increasing the annealing temperature. This decrease in band gap energy is due to the increase in defect states formation on increasing the annealing temperature [34]. This is also due to the degradement of quantum confinement effect as increase in the size of crystallite on increasing the annealing temperature. This type of behavior was observed for indium tin oxide thin film on thermal annealing by Xu et al [35]. Such behavior is termed as Burstein Moss shift [36].

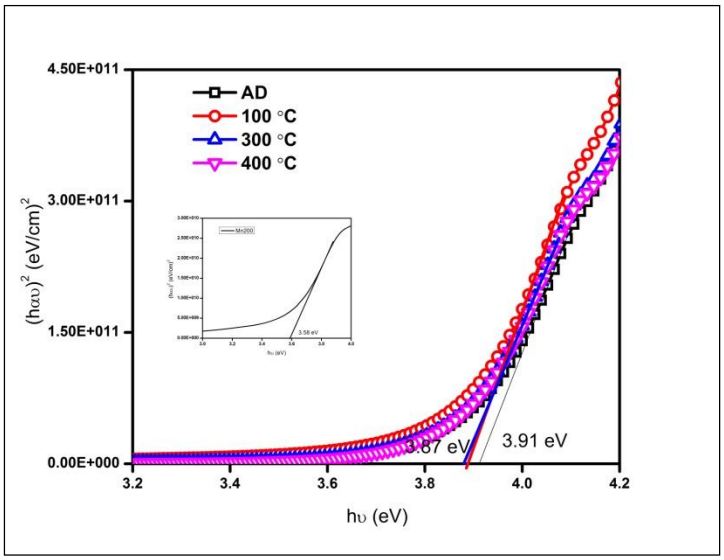

Fig. 3. Tauc's plot for Mn doped ITO thin films both as deposited and annealed at 100 °C , 200 °C (inset), 300 °C and 400 °C.

Fig.4. shows the refractive index of as deposited and annealed thin films with respect to wavelength. From the fig. it was observed that the refractive index decreases on increasing the wavelength. The refractive index was found to decrease on increasing the annealing temperature. This is due to the increase in crystallinity of the sample on increasing the annealing temperature. The increase in crystallite size with decrease in optical bandgap energy forms the background for decrease in refractive index on increasing annealing temperature [37]. Similar kind of behavior was observed by Sanjeev et al.[38].

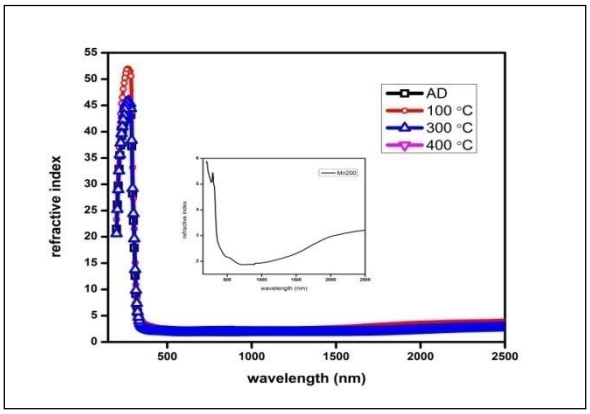

Fig. 4. Refractive index plot for Mn doped ITO thin films both as deposited and annealed at 100 °C , 200 °C (inset), 300 °C and 400 °C.

4 Summary

Mn (5 at.%) doped ITO thin films were coated on corning glass substrate at Ts = 350 C. The XRD pattern confirms the absence of any kind of impurities or formation of any secondary phases on increasing the annealing temperature. The crystallite size was found to increase on increasing the annealing temperature. The optical band gap and refractive index was found to decrease on increasing the annealing temperature.

Thus the increase in annealing temperature increases the crystallite size and decreases the optical band gap of the thin film.

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