Structural and optical properties of Tin Oxide and Indium doped SnO_2 thin films deposited by thermal evaporation technique

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ABSTRACT

Tin Oxide and Indium doped Tin Oxide (SnO_2:In) thin films were deposited on glass and Silicon substrates by thermal evaporation technique. X-ray diffraction pattern of pure SnO_2 and SnO_2:In thin films annealed at 650^{o}C and the results showed that the structure have tetragonal phase with preferred orientation in (110) plane. AFM studies showed an inhibition of grain growth with increase in indium concentration. SEM studies of pure SnO_2 and Indium doped tin oxide (SnO_2:In)) thin films showed that the films with regular distribution of particles and they have spherical shape. Optical properties such as Transmission, optical band-gap have been measured and calculated.

KEYWORDS

Tin Oxide, Indium doped Tin Oxide , Silicon substrate , Structural Properties , Optical properties

SUBJECT CLASSIFICATION: Physics subject classification: library of congress classification QC170-197

INTRODUCTION

Polycrystalline tin dioxide (SnO_2) is an important transparent material due to its potential use in many technological applications. Recently, there has been much interest in wide band gap transparent oxide semiconductors due to the huge commercial desire for short-wavelength luminescent devices, such as blue and ultra-violet (UV) light emitting diodes and laser diodes [1]. Among the various semiconductor materials SnO_2 is an n-type wide band gap semiconductor (3.6 eV) [2]. As a wide band gap semiconductor SnO_2 and doped SnO_2 are known to have a wide range of applications such as gas sensors, solar cells, photovoltaic solar energy conversion devices and transparent electrodes [1- 3]. Oxide semiconductors occur in a variety of crystal structures and exhibit diverse electronic and optical properties. Controlling the electrical conductivity in oxide thin films is an important step towards their application in electronics and optoelectronics [4]. SnO_2 has n-type conductivity because of the intrinsic defects such as oxygen vacancies and tin interstitials. It can be easily doped with a wide variety of ions to meet the demands of several application fields. SnO_2 can exhibit n-type and p-type conductivity behavior depending on type of dopants. Theoretically, if SnO_2 is substituted with III-family elements, then p-type SnO_2 can be fabricated. The elements used as dopants such as Li, Fe, Sb and In act as an acceptor in SnO_2 [4–5]. Among them, being noted for the high conductivity and good optical transmittance is indium doped SnO_2 (SnO_2:In) films, which have drawn considerable attention for transparent conducting electrodes [6]. Indium has one less valance electron than tin, so substitution doping; indium in SnO_2 can act as an acceptor. In general; the indium dopant can inhibit the growth of crystallite and play an important role in the optical properties including transmittance and luminescence .The surface roughness of thin films has been reported to show the influence on the electrical and optical properties [7]. The RMS. roughness values of range greater than 4 % of the film thickness makes the films suitable for solar cell applications [8]. Also, the smooth films (approximately equal to 1 % of the film thickness) finds applications in optoelectronics [9]. Thin films of indium tin oxide are widely used as transparent and conductive oxide layers for many microelectronics applications, such as transparent electrical contacts in liquid crystal displays, organic light-emitting diodes (OLEDs), plasma displays, thin film solar cells, etc.[10]. SnO_2:In films have been prepared by various techniques such as chemical vapor deposition, spray pyrolysis, reactive RF sputtering, sol–gel technique[11].

In this research we prepared thin films of pure SnO_2 with different thickness and SnO_2:In films with different concentrations by thermal evaporation technique. Structural and Optical properties of these films were studied.

EXPERIMENTAL PROCEDURE AND MEASUREMENT

Tin Oxide and Indium doped Tin Oxide film with doping levels ((5 , 10 , 15) wt%) was deposited on corn glass substrate by thermal evaporation coating unit model (Edward 306) with ultimate pressure of vacuum chamber $1x10^{-6}$ torr. Tin oxide powder and Indium powder with purity 99% supplied from Aldrich company are considered as source materials and were taken into Tungsten boats which are connected to the respective electrodes. The pressure of the vacuum chamber was maintained at 2 x 10^{-5} torr, target- substrate separation of 10 cm was maintained during the entire deposition process. Before the deposition, the glass and Silicon substrate was thoroughly cleaned with cleaning liquid soap and then with acetone to remove organic particles on the surface and then washed with distilled water. To prevent local hydrolysis the substrates were then soaked in diluted isopropyl alcohol for 10 minutes and then dried. Optical characterization was studied from transmission with wavelength curve which was plotted from the data obtained from transmission spectrum analysis of the film in the wavelength range 300nm to 1100nm. The refractive index and the thickness of the film were calculated using the formula. By using the idea of **Swanepoel's method** by using equations (1) , (2) and (3) [12].

$$\mathrm{d} = \left(2\left[\frac{n(\lambda_1)}{\lambda_1} - \frac{n(\lambda_2)}{\lambda_2} \right] \right)^{-1} \qquad (1)$$

$$n_{film} = \frac{1}{2}\left(\left[8n_{sub}C(\lambda) + (n_{sub}+1)^2 \right]^{0.5} + \left[8n_{sub}C(\lambda) + (n_{sub}-1)^2 \right]^{0.5} \right)$$

$$C(\lambda) = \frac{\left[T_{\max}(\lambda) - T_{\min}(\lambda) \right]}{2T_{\max}(\lambda)T_{\min}(\lambda)},$$

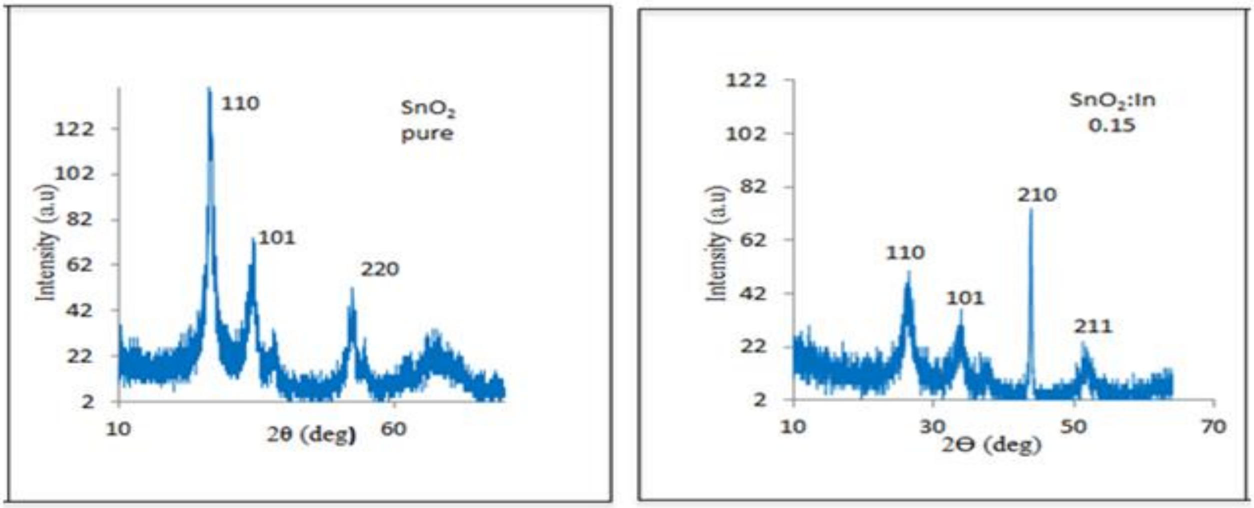
where *(d)* is the film thickness, $n(\lambda)$ is the refractive index of film, $n_{sub.}$ is the refractive index of substrate, n_{film} the refractive index film, $T_{Max}(\lambda)$ is the maximum transmittance and $T_{Min}(\lambda)$ is the minimum transmittance in the λ values. The optical band gap was obtained from the plot of $(\alpha h\upsilon)^{1/2}$ Vs. hυ in thin film

RESULTS AND DISCUSSIONS

1-X-ray diffraction studies

The X-Ray diffraction patterns of pure and Indium doped SnO_2 prepared by thermal evaporation at R.T. showed that the structures of the films are amorphous and the structure of these films after annealing at 650^{o}C for Two (2) hours showed a nice X-ray diffraction pattern as shown in Figure (1) the emergence of a number of peaks in the composition of the films which shows that this films were found to be polycrystalline as shown in the figures. We observed three characteristic diffraction peaks for pure SnO_2 corresponding to the (110) , (101) and (220) reflections at Bragg angles ($2\theta_s$); (26.548^o) , (32.760^o) and (50.687^o) respectively . While, we observed four characteristic diffraction peaks for SnO_2:In corresponding to the (110), (101) , (210) and (211) reflections at Bragg's angles ($2\theta_s$) ; (25.909^o) , (33.419^o) , (43.853^o) and (51.607^o) respectively . These results indicate that the structure of the films is polycrystalline , and according to ((ICDD 00-021-1250) card , these reflections represent a tetragonal unit cell. Indeed , the X-Ray diffraction has been used to ensure that the structure of the semiconductor film (pure and doped SnO_2) which were evaporated on the glass and Silicon substrate , has not been changed after evaporation. indicates that the main features of diffraction pattern are the same but only the peaks intensity are varied and there is slight shifting of peaks position. The results obtained in figures (a-1) , (b-1) were consistent with the previous workers [13] .

Table (1) showed the values of d_{hkl} and average grain size , where we observed that the average grain size were decreased with doping of the films with Indium (In) .This results can be attributed to the effect of impurities within the crystal structure , because it could affect on the size of the crystal and thus the distance between crystalline surfaces. The effect of impurities on the crystal structure have a significant role in the change of physical properties , because they depend on the radius of atoms , for example , in our research Indium impurity atoms with a radius (1.93 A^o) have been substituted site of host material Tin Oxide with a radius (2.17 A^o) . from the table (1) we can see that the values of calculated d_{hkl} when comparing with the standard values of d_{hkl} [ICCD- 00021-1250 .] are almost identical**.**

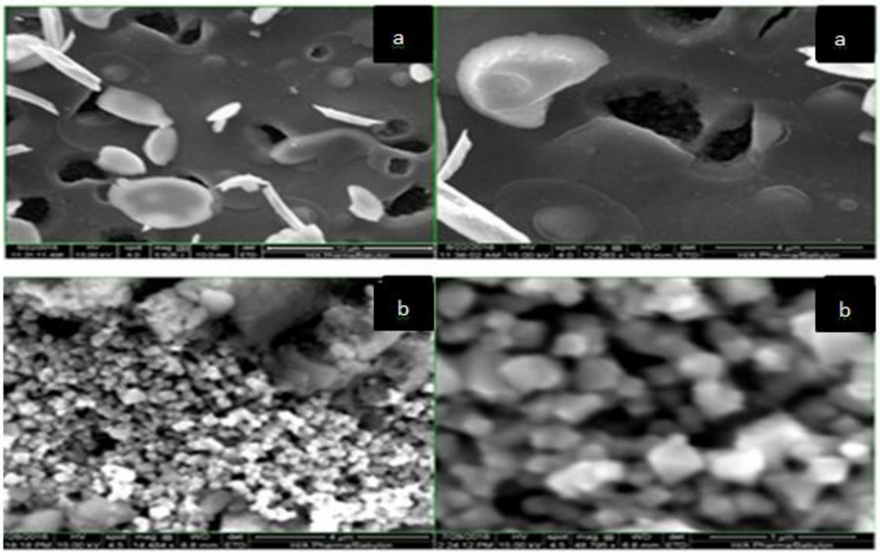


"Figure 1". XRD patternof(a) SnO2, (b) SnO2:In(0.15) thin films

Compound	(hkl)	d(A°) (Observed)	d(A°) (Standard)	Average grain size(nm)
SnO_2 (Pure)	110 101 211	3.3548 2.7314 1.7995	3.3510 2.6440 1.7650	50.16
SnO_2:In (0.15)	110 101 210 211	3.4360 2.6790 2.0628 1.7696	3.3510 2.6440 2.1200 1.7650	32.53

2-Morphological Properties

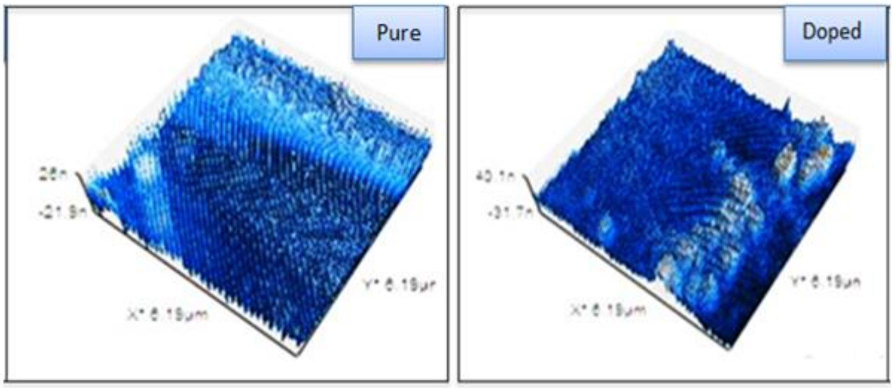
Figure (2) showed the results of measurements of scanning electron microscopy (SEM) for pure SnO_2 and SnO_2:In (with 15%). The substrate of the films is Silicon (Si), and the films were annelid at temperature 650 ^oC for 2 hr. From the figure , we can observe a large number of particles with regular distribution on the surface of the pure films as shown in figure(a-2) . While for Indium doped films , we showed that the shape of particles become approximately spherical with also regular distribution figure (b-2) . On the other hand , the grain size as shown in the figure for Indium doped film is smaller than that for pure film. This results are consisted with the results that obtained by X-Ray diffraction. were consistent with the previous workers [14] .



"Figure 2". Scanning Electron Microscopy micrographs. (a) for pure sample , (b) for doping films.

3-Surface morphological studies.

The surface roughness plays a major role in optical and electrical properties of thin films. The AFM images taken for SnO_2 and SnO_2:In thin films for doping Indium 0.15 are shown in Fig. (3) . It can be seen that the surfaces of all films are uniform and crack free. It is seen that the grains appear to be less dense in nature with increase in indium content (Table2). This shows that the grain growth is inhibited at higher indium doping concentrations. This observation agrees with the XRD results. The unique properties of the semiconducting oxides are related to the microstructural properties of the thin films were consistent with the previous workers [15] .



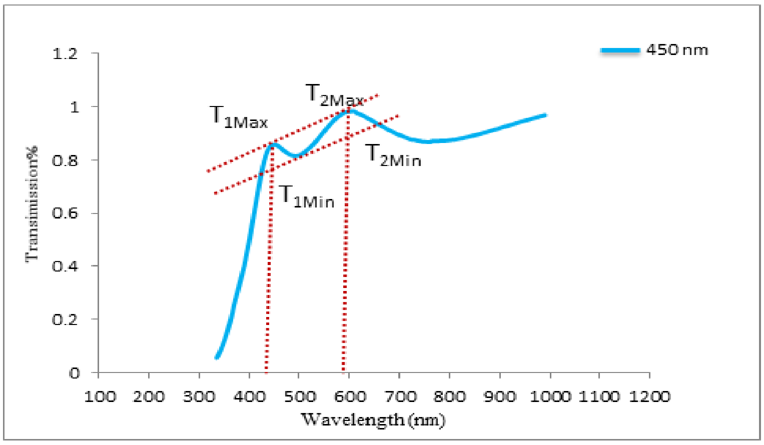
"Figure 3" AFM images of Pure(a) SnO_2 and indium doped (b) SnO_2:In films

" Table 2" AFM of SnO_2 and SnO_2:In thin films

Sample	(RMS) (nm)	Surface Roughness (nm)
SnO_2 (pure)	17.78	13.77
SnO_2:In (0.15)	13.18	10.49

optical analysis

Optical analysis of SnO_2 on glass substrate was studied from transmission Vs. wavelength curve in the wavelength range 300nm to 1100nm which is shown in the fig.4. From fig.4 it was clear that the surface quality and homogeneity of the thin film were excellent and this confirms that tin oxide thin film exhibits semiconducting properties also as it was established by the pure semiconducting compounds have a sharp absorption edge [16]. If the thickness (d) of the film is uniform , interference effects give rise to a spectrum shown by the full curve in figure (4). These fringes can be used to calculate the optical constants of the film by using equations (1),(2),(3) . From the figure , we can see three regions of absorption strong , medium-weak and transparent . In the visible region of the spectra, the transmission of film was very high, due to the fact that the reflectivity is low and there is less absorption due to excitation of electrons from the valence band to conduction band [17]

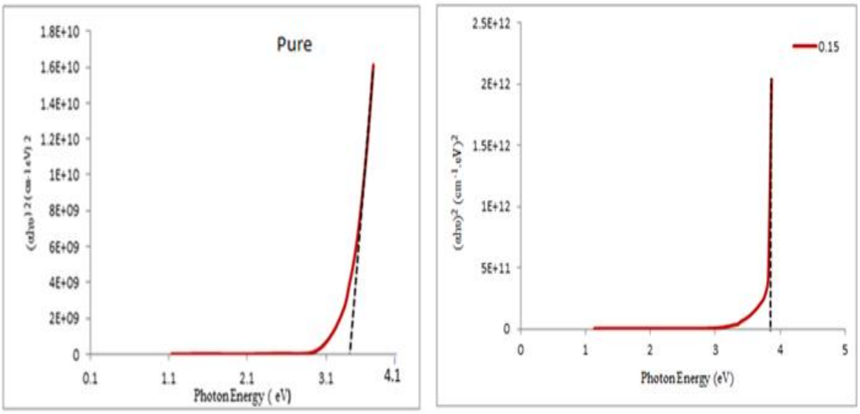


"Figure 4". Transmittance Vs. λ in nm in the wavelength range 300nm- 1100nm.

From fig.2 it may be concluded that the transmittance was more which may be due to high porosity and larger grain size and less absorption in the film. The lower and upper envelop were used to find out refractive index of the film material and thickness of the film. We found that the thickness of the films are 450 nm and the refractive index 1.78. .

optical band-gap

The direct band-gap for pure Tin Oxide was estimated to be 3.48 eV, which it increased to a value of 3.85 eV for Indium doped Tin Oxide with 15 at.% in the film , these results are shown in the figure (5). Generally, the band-gap energy for doped metal oxides films is higher than that of the un-doped type. This is because the energy gap between the valence band and the lowest empty state in the conduction band is found to increase due to the filling of low lying energy levels in the conduction that is caused by the increase in the carrier concentration (Burstein-Moss effect) [18]. The shift in the band-gap can also be related to the variation in the mean crystallite size, the internal stress or due to the free carrier concentration [19].



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