Structural and Optical Studies of In_2S_3 Thin Films Prepared by Sulferization of Indium Thin Films

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Abstract: The In_2S_3 thin film is prepared using sulfurate method under a vacuum in a sealed tube of amorphous indium thin film. The later film is pre-deposited on glass with thermal evaporation. We have studied the effect of the temperature and the annealing time on the structural and morphological properties In_2S_3 thin films. The X-ray diffraction (XRD) shows a good crystallinity found until the annealing temperature reach 280°C for an annealing duration of 30 mn. The scanning electron microscopy (SEM) for the thin films of In_2S_3 layer, synthesized at different temperature for the annealing time at 15mn, revealed more homogenous layer until 320°C. Optical analyses by absorption spectroscopy show that the energy band gap is a function of the annealing condition. This band gap decreases from 3 eV to 2.6 eV when the annealing temperature is varied from 200°C to 400°C. The obtained In_2S_3 thin films have a transmittance higher than 65%.

Keywords: Indium sulphide, optical properties, thermal annealing, thin film.

INTRODUCTION

The In_2S_3 thin film is an interested II-VI material, which has applications in optoelectronic [1] and in photovoltaic industries. Also, it is reported that In_2S_3 has applications in photo-electrochemical solar cell devices [2]. An important research goal in developing photovoltaic devices is the replacement of toxic heavy metals (such as Cd) with more benign elements to replacement of n-type CdS layers in polycrystalline heterojunction thin film solar cells. The indium sulphide can be a binary base material to be a suitable substitute for the deposition of semiconductors compound such as CuInS2, a popular absorber material in hetero-junction solar cell device structures [3]. It is investigated like buffer layer on solar cells due to their high optical transmission. On the other hand, the optical proprieties of the In_2S_3 thin films obtained by chemical bath deposition (CBD) method have a higher band gap that it takes values between 2 eV and 2.75 eV [4, 5]. Moreover, there are several reports on the growth of In_2S_3 thin film, by various chemical bath deposition [6], spray pyrolysis [7] and metal-organic chemical vapor deposition [8]. Generally, it is always preferable technically to form the desired thin film by a simple inexpensive, less time consuming and environment friendly method. In this paper, we described the structural and optical characterization of the prepared indium sulphide.

EXPERIMENTAL SET-UP

The substrates used for In_2S_3 deposition were a Pyrex glass (2 cm x 1cm). The glass substrates were chemically cleaned before deposition. The process for preparing an In_2S_3 thin film can be divided in two stages, the deposition of the indium onto substrates, and sulfering of the samples evaporated. The deposition of the Indium was carried out by vacuum thermal evaporation at gas pressure of $1x10^{-4}$ Pa using a tungsten crucible. In order to obtain the film, thin indium and amount of sulfer were sealed in a Pyrex tube under vacuum at pressure of $4x10^{-6}$ Pa. The sulferization is achieved after a thermal annealing in tubular furnace. The thickness of the In_2S_3 films was measured by using gravimetric method by means of a microbalance and found to be in the range of 900–1200 nm. In order to study the effect of the annealing temperature and duration on the structural and optical properties of In_2S_3 thin films, the annealing temperature was varied from 200 °C to 400 °C and the annealing duration from 15 mn to one hour 30 mn. The effect of increasing rate of the temperature was also taken into account in this study.

RESULTS AND DISCUSSION

Several crystalline phases have been reported for In_2S_3 films (α, β, and γ) deposited by several techniques, when the tetragonal β phase being the most stable at room temperature. It is also the most common crystalline phase observed in In_2S_3 films. The X-ray diffraction patterns of In_2S_3 films as a function of temperature are shown in Fig. (**1**). The In_2S_3 films are polycrystalline and crystallized in the tetragonal structure of β-In_2S_3 the PDF numbers (JCPDS Data 73-1366). As seen from the XRD the crystallization process presents a threshold temperature (280°C). Until this temperature, the films have a good crystallization. The predominance is clear for the (109) peak.

Fig. (**2**) shows the evolution of XRD diagram for In_2S_3 thin films obtained at an annealing temperature of 280°C as a function of the annealing time. From those diagrams it was found the threshold annealing time is about 15 mn. However, this figure indicates that the crystallization of In_2S_3 films increase with the annealing duration and the films are

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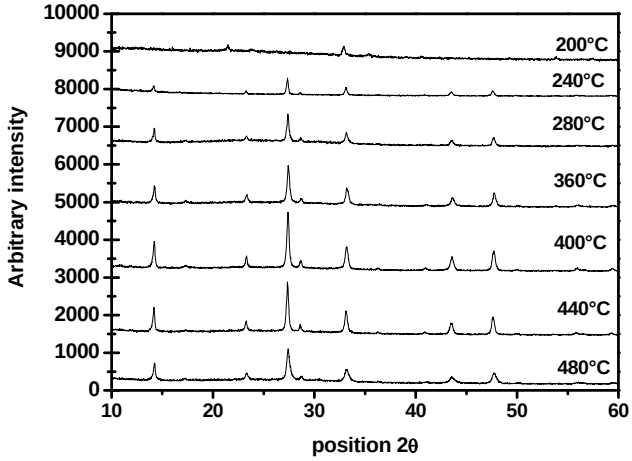


Fig. (1). X-ray pattern of In_2S_3 thin films are prepared at various substrate temperature with 45 mn annealing time.

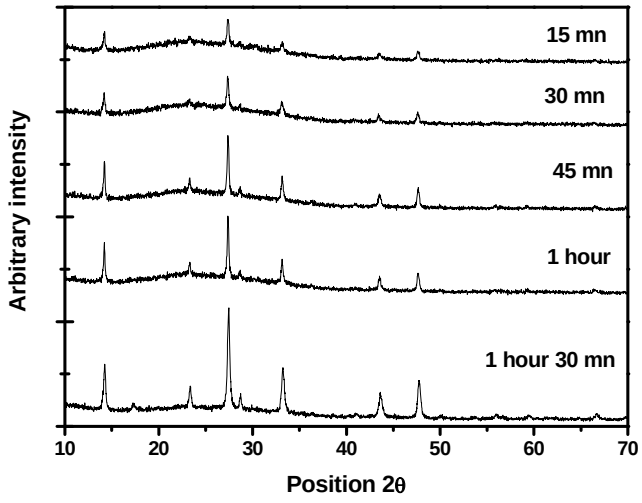


Fig. (2). X-ray pattern of In_2S_3 tin films are prepared at 280°C annealing temperature with various annealing times.

completely crystallized after 1h 30mn. We can qualitatively explain these results by using the critical optimization concept described by Vincett [9]. This author observes that the films deposited at low temperatures are a mixture of crystallized and amorphous regions. At the boiling point of the substance, the amorphous regions vaporize during the film growth. Furthermore, the diffusion in the bulk becomes relatively important at the optimal temperature and contributes to the filling of the lacunas created by the evaporation of the disordered regions. Consequently, the crystallinity improves leading to well-ordered and well-oriented films.

Fig. (**3**) shows the optical transmittance curves as function of the wavelength. The films present a high transmittance in the visible wavelength range (above 65%). Comparison between curves of Fig. (**3a**, **c**) show that the average optical transmittance increase as the pre-deposited indium thin film thickness decrease. The decrease of transmittance might be due to the stoichiometric deviation in the films. From Fig. (**3a**, **b**) it can be concluded that the increasing rate of the temperature doses not have a significant influence on the average optical transmittance.

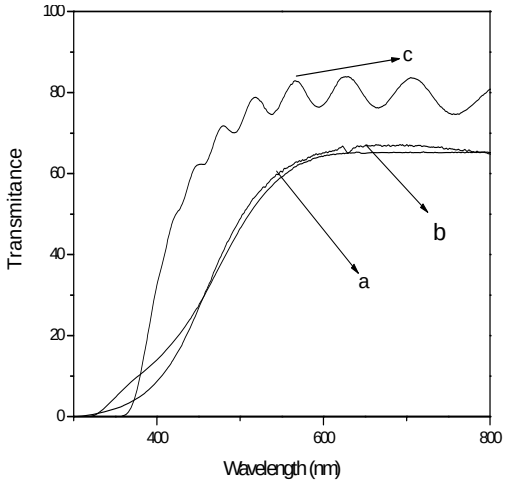


Fig. (3). Optical transmission spectra of: (**a**) annealing rate 10°C/mn and 1 μm thickness (**b**) annealing rate 50°C/mn and 1 μm thickness (**c**) annealing rate 50°C/mn and 0.9 μm thickness.

The absorption coefficient (α) is determined by the following equation:

$$\alpha = \frac{1}{e}\ln\left(\frac{1}{T}\right) \quad (1)$$

where T is transmittance and e is film thickness. The optical band gap (Eg) can be determined by the absorption coefficient (α) and photon energy (E=hν) from:

$$(\alpha E)^2 = A(h\nu - E_g) \quad (2)$$

where A is a constant [10]. The band gap energy value Eg was determined from the spectra by extrapolation of the linear part of the curve. Results are shown in Fig. (**4**) where the $(\alpha*E)^2$ versus energy. The optical properties of In_2S_3 films are restricted to their absorption spectra (Fig. **5**). For wavelength in the absorption edge region, we observe a shift towards high wavelengths. The dependence of the energy band gap with the annealing temperature shown in Fig. (**6**) depicts a decrease in the band gap value as a consequence of an increase of the thermal annealing temperature. Generally, the behavior of the energy band gap as a function of temperature suggests that there is structural transition (order–disorder transition) of In_2S_3 thin films. Thus, the decrease of the energy band gap could be produced by an increase in the structural order induced during the structural change from amorphous to crystalline stable phase. On the other hand, several authors have observed a broadening of the optical band gap of In_2S_3 thin films and they explain this behavior by the excess of sulfur in the film [11] or by the quantum size effect [12]. Moreover, the size of the grains constituting our films is more than 300 nm therefore the shift of the optical transmission threshold observed can not be induced by the quantum size effect. Furthermore, the study of EDAX of the thin films elaborated at low annealing temperature has shown that there are two types of grains, smaller ones that have proper ratios of In_2S_3, and greater ones that have an excess of sulfer. Then the evolution of the band gap value in our case can be explained by the sulfer excess.

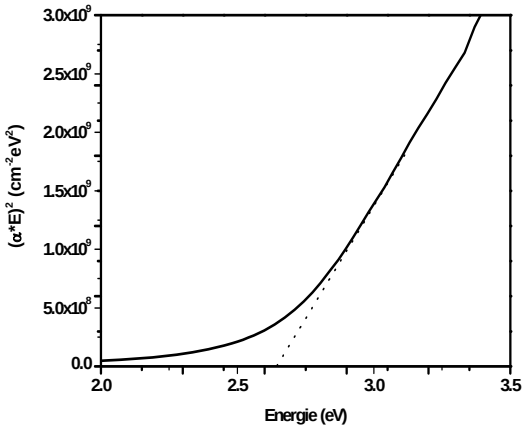


Fig. (4). Shows the relationship between $(\alpha*E)^2$ versus E for In_2S_3 films annealed at 360 °C with 30mn duration of annealing.

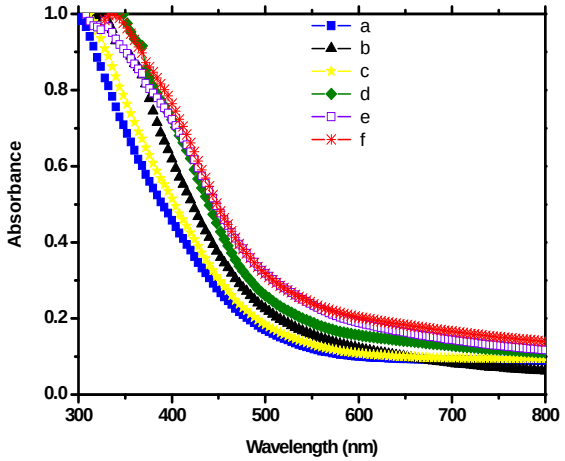


Fig. (5). Shows the absorbance spectra as versus of annealing temperature with 30mn duration of annealing: (**a**) for 200°C, for (**b**) 240°C, (**c**) for 280°C, (**d**) for 320°C, (**e**) for 360°C and (**f**) for 380°C.

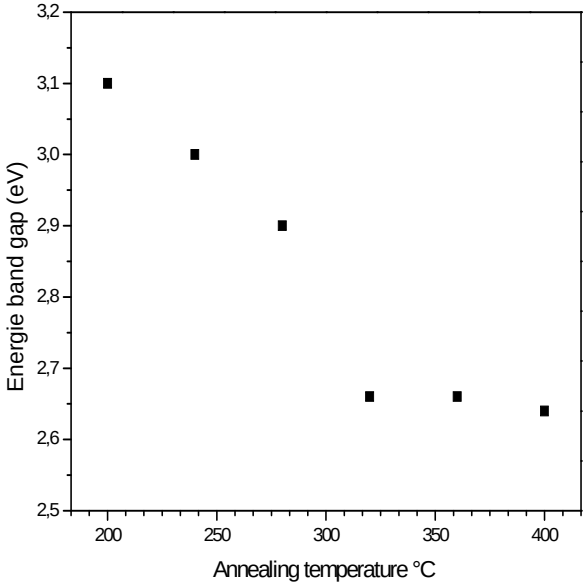
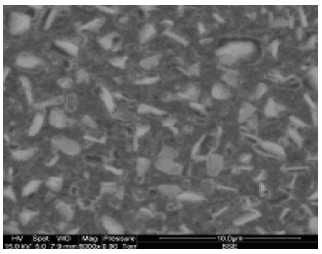


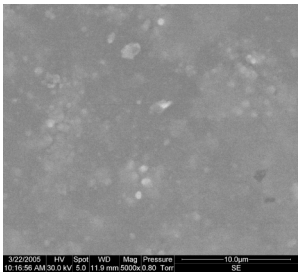
Fig. (6). Dependence on annealing temperature of direct energy band gaps of In_2S_3 films for 30mn duration of annealing.

Fig. (**7**) shows SEM micrographic surface views of the In_2S_3 thin films prepared at different annealing temperatures. We can see that the surface morphology of In_2S_3 films change when changing the annealing temperature. In all cases we obtain continuous films consist of crystalline grains. For an annealing temperature of 200 °C (Fig. **7a**) the film appears with large grains with a large size distribution. By increasing the annealing temperature to 280 °C, the film (Fig. **7b**) presents plate-like grains. The large grains seem to disappear and very small particles appear when the temperature increase. The last remark remains valid for the sample images of Fig. (**7c**, **d**). For higher temperatures the surface is entirely covered by grains with a narrow size distribution. The XRD results are therefore confirmed by SEM imaging, the crystallization of In_2S_3 films increase with the substrate temperature.

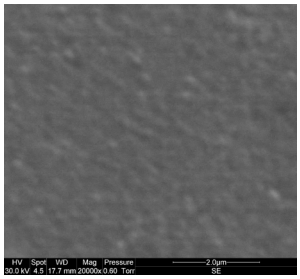
(**a**)



(**b**)



(**c**)



(**d**)

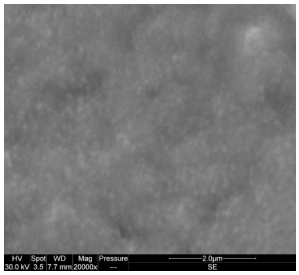


Fig. (7). SEM of In_2S_3 films sulfurated from indium layer for 30mn and thermal treated: (**a**) at 200°C, (**b**) at 280°C, (**c**) at 320°C and (**d**) at 400°C.

CONCLUSION

The results from this work show that the In_2S_3 thin film with good crystallinity and purity can be obtained by sulferization of indium thin films. The optical transmission spectra of the films exhibit that the coefficient depends on the pre-deposited indium thin film thickness. The XRD and SEM investigations show that the annealing process induces a threshold at annealing temperature and duration. The behavior of the direct energy band gap of the films could be varied between 2.6 eV and 3 eV by varying the annealing condition.

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