

STRUCTURAL AND OPTICAL PROPERTIES OF In_2S_3 THIN FILMS PREPARED BY FLASH EVAPORATION

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In_2S_3 thin films were deposited by flash evaporation of In_2S_3 powder. The effect of annealing in vacuum and under sulphur atmosphere on the structural and optical properties of these films was investigated. X-ray diffraction studies reveal that the as-deposited films are amorphous. The formation of $\beta\text{-In}_2\text{S}_3$ phase is obtained after annealing under vacuum at 693 K. Heat treatments under sulphur pressure lead to the formation of the above phase at a less annealing temperature (573 K). The energy dispersive X-ray (EDX) analysis reveals that the sulphurized films are nearly stoichiometric and those annealed in vacuum are sulphur deficient. Optical transmission spectra showed a slight shift of the absorption edge towards lower wavelengths. The optical gap value varied between 2.4 and 3 eV as a function of the film thickness and the annealing temperature.

Keywords: $\beta\text{-In}_2\text{S}_3$; Flash evaporation; Photovoltaic; Thin films

1 INTRODUCTION

Recently, there has been a renewed interest in the III–VI materials such as In_2Se_3 and In_2S_3 because of their interesting electrical and optical properties. In_2S_3 is a direct band gap semiconductor with a large band gap that can be varied from 2 to 3.25 eV [1–3] by addition of oxygen or Na. Therefore, it can be used as a buffer layer in solar cells instead of CdS which is very hazardous. Moreover, In_2S_3 finds application in photochemical solar cell devices [4]. In_2S_3 exists in three different structures: a defect cubic structure $\alpha\text{-In}_2\text{S}_3$, which transforms into a defect spinal, $\beta\text{-In}_2\text{S}_3$, at 693 K and into a layered structure, $\gamma\text{-In}_2\text{S}_3$ at 1013 K [5, 6]. In_2S_3 films were prepared by a variety of methods, including thermal evaporation [7, 8], rf-sputtering [1, 9], spray pyrolysis [10, 11], chemical vapour deposition [12] and chemical bath deposition [13, 14]. The flash evaporation technique, based on thermal vacuum evaporation from a single source, is a relatively cheap, simple and very attractive method to produce large area films for photovoltaic applications.

In this article, we report some results on the structural and optical properties of In_2S_3 thin films obtained by the above-mentioned method. The effects of annealing at different temperatures under vacuum and sulphur atmosphere on these properties are also presented.

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2 EXPERIMENTAL PROCEDURE

In_2S_3 films with different thicknesses were obtained by flash evaporation of a 99.9% In_2S_3 powder onto a cleaned glass or indium tin oxide (ITO)-coated glass substrates. The unheated substrates were held at a distance of 6 cm from the molybdenum boat. The substrates were kept at room temperature and under a vacuum of 10^{-6} torr.

The samples were then annealed under a vacuum of 10^{-6} torr and under a sulphur atmosphere in a closed reactor, for one hour, at temperatures between 100 and 693 K.

The structure of the films was determined by using a Phillips PW X-ray diffractometer 1840. The morphology of the films was studied by (JEOL5500) scanning electron microscopy; and their composition was determined by energy dispersive X-ray (EDX) analysis. The optical transmittance and reflectance were measured at normal incidence in the wavelength range 320–3200 nm, using a Shimadzu UV-3101 PC spectrophotometer.

The optical constants and the thickness of the films were extracted from the optical transmission spectra using a technique based on exploiting the interference fringes as described in detail in Refs. [15, 16]. The absorption coefficient is deduced with precision in the order of 5%. The optical band gap is determined, with an error in the order of 5 meV, by fitting the experimental data with the well-known law:

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

3 RESULTS AND DISCUSSION

The first argument deduced from the XRD diagrams is the amorphous nature of the evaporated films independently of the evaporated mass and the substrate nature. For the annealed samples under vacuum (Fig. 1), the crystallization begins only when the annealing temperature reaches 693 K. The film deposited on Mo and annealed at 693 K is crystallized. The

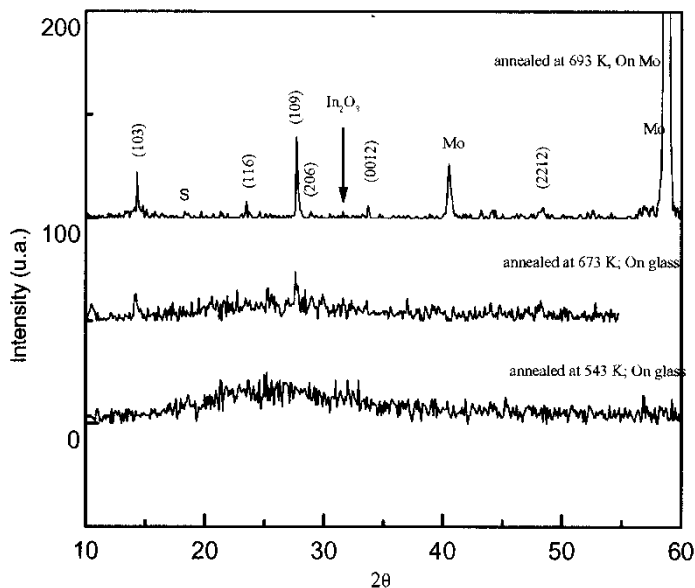


FIGURE 1 XRD diagrams of samples annealed in vacuum for one hour at 573, 673 and 693 K.

observed XRD peaks were assigned to (1 0 9) and (1 0 3) planes of β -In₂S₃ although they are small and broad. However, for films annealed under a sulphur atmosphere, the crystallization appears at 573 K (Fig. 2). One can see that reflections planes of sulphur-treated films are sharper and stronger than those of vacuum-treated ones. The intensity of X-ray diffraction peaks observed increases with the annealing temperature. No preferred growth direction is noticed on the XRD diagrams. The structure of these layers was identified as β -In₂S₃ tetragonal system (JCPDS Card no. 250-0390). For samples treated at 693 K a peak of In₂O₃ at $2\theta = 30.8^\circ$ is also observed.

The annealed In₂S₃ films exhibit a very small grain size as calculated from the full width at half-peak maximum (FWHM) of the (1 0 9) reflection using the Scherrer's equation [17]. It ranges between 20 nm for the films annealed under sulphur and 35 nm for films annealed in vacuum.

SEM micrographs of the surface and the cross-section (Fig. 3(a) and (b)) reveal that the evaporated layers are smooth, continuous and very homogeneous. The surface morphology of the annealed film at 693 K under sulphur atmosphere (Fig. 3(c)) did not change; however, the sample heat-treated under vacuum at 693 K (Figure 3(d)) shows a slight roughness because of its crystalline quality degradation.

Energy dispersive X-ray measurements on as-deposited and annealed films are presented in Table I. The average atomic ratio S/In of as-deposited films is in order of 1.52 showing that the films are nearly stoichiometric to In₂S₃ powder evaporated. The ratios S/In of annealed samples under vacuum at 693 K show that the films are sulphur deficient, as a result of evaporation of sulphur from the film. On the other hand, for films sulphurized at 573 K, the ratio S/In is higher of about a 1.67 and decrease to 1.56 for those sulphurized at 693 K. The improvement in the crystallinity of these films could be attributed to a rapid reaction of S vapor with In which would lead to β -In₂S₃ phase. Furthermore, EDX analysis indicates that the layers contain a little oxygen.

The transmission curves of In₂S₃ films before and after heat treatment at 693 K in vacuum and under sulphur ambient are shown in Figure 4. As can be seen, these films have a high transmission in the infrared region and present a steep absorption edge at low wavelengths. The

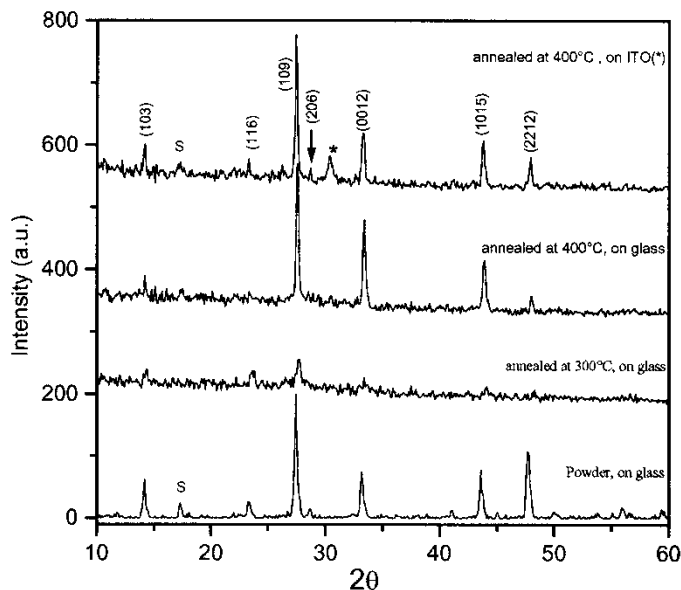


FIGURE 2 XRD diagrams of In₂S₃ powder and of samples annealed in sulphur ambient at 573 and 673 K.

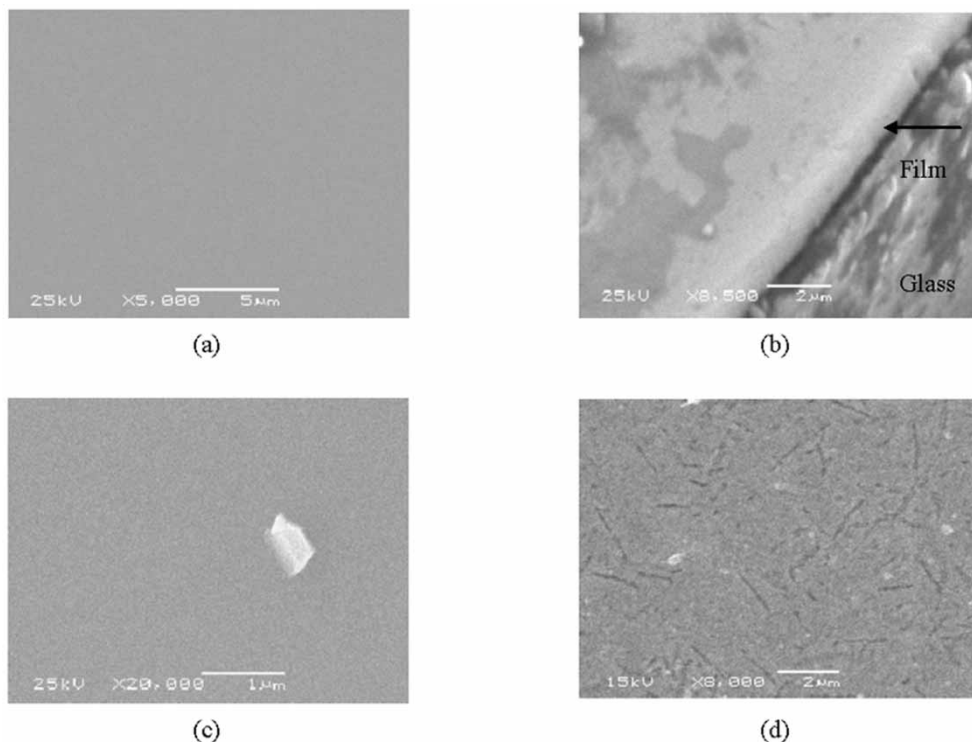


FIGURE 3 SEM micrographs of the surface of as-deposited film (a); the cross section of as-deposited film (b); the films annealed at 693 K under sulphur ambient (c); and in vacuum (d).

presence of fringes makes possible the determination of thickness and the index of refraction of these films. It was observed in both cases that the value of transmission decreases slightly after heat treatment. This can be explained in terms of an increase of micro-stresses in the film.

Figure 5 depicts the variation of the index of refraction $n(\lambda)$ of the thin films as a function of the wavelength and the fit of the data with the dispersion Sellmeier law given in Ref. [18]:

$$n^2(\lambda) = n_\infty^2 + \frac{b^2}{\lambda^2 - \lambda_0^2}$$

where n_∞ is the infrared extrapolated refractive index, and λ_0 and b are the constants. The refractive index for evaporated films is about 2.5 for thickness in order of $0.33 \mu\text{m}$ and decreased slightly with the increasing of the thickness.

TABLE I Atomic Percentage of Indium (In) and Sulphur (S) vs. the Annealing Temperature.

Temperature of annealing	Composition		
	In (%)	S (%)	S/In
As-deposited	39.74	60.26	1.52
573 K under In_2S_3	37.63	62.36	1.63
573 K in vacuum	42.90	63.10	1.47
573 K under S	36.90	61.78	1.67
693 K in vacuum	42.60	57.40	1.35
693 K under S	38.77	61.22	1.57

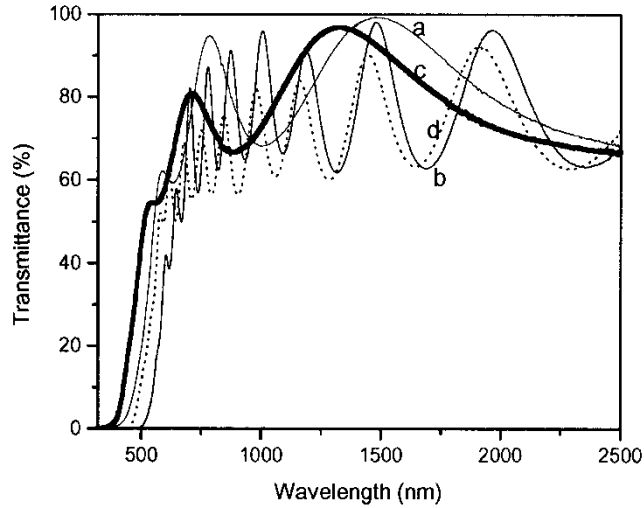


FIGURE 4 Transmission spectra of films obtained by one deposition (a) and three depositions (c); and annealed at 693 K in vacuum (b) and under sulphur (d), respectively.

As seen in Figure 6, the thickness of the film annealed in vacuum decreases significantly with increasing temperature. However, that of sulphurized films decreases slightly when the temperature increases to 373 K and becomes constant at higher temperatures. The thickness decrease is due to the loss of sulphur during annealing in vacuum at high temperatures. Kumaresan *et al.* [19] have reported on a similar observation.

It is well known that β -In₂S₃ has a direct band gap [20, 21]. The band gap energy is determined by extrapolating the linear portion of $(\alpha h\nu)^2$ vs. $h\nu$ to the photon energy as seen in Figure 7. This quasilinear variation shows in fact that the transitions are direct. The band gap energy values of as-deposited films were varied between 2.5 and 2.65 eV. These values

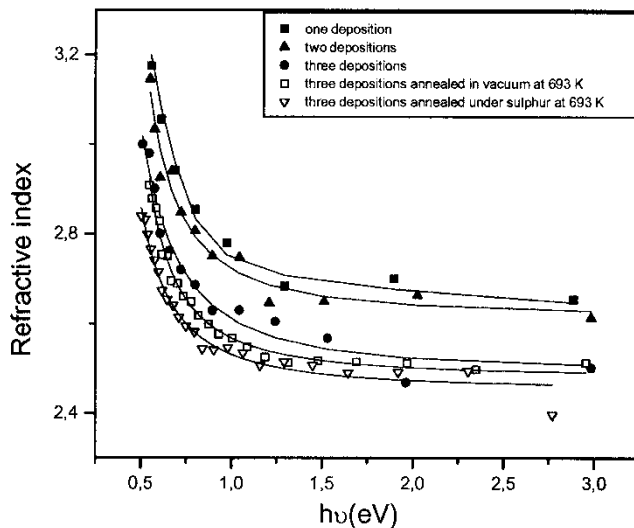


FIGURE 5 Evolution of the refractive index vs. the wavelength for as-deposited and annealed films.

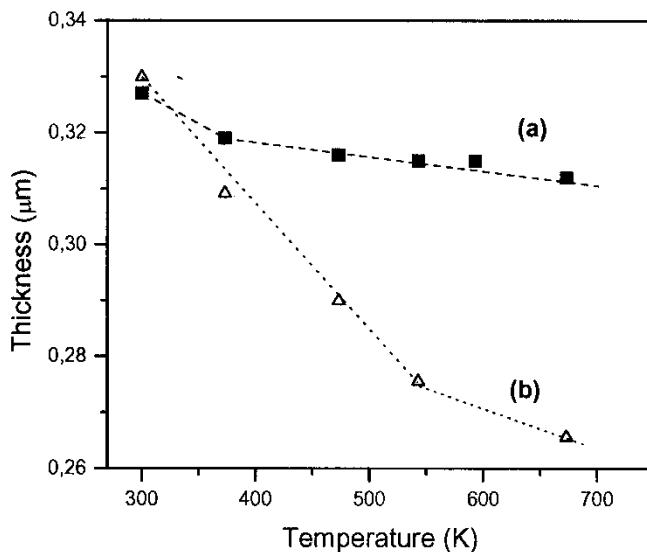


FIGURE 6 Effect of annealing temperature under different atmospheres on film thickness: (a) under sulphur and (b) in vacuum.

are somewhat larger than the 2–2.4 eV reported in literature for bulk material [1, 5, 22] but are in agreement with those reported for In_2S_3 thin films prepared by thermal evaporation or by chemical bath deposition [7, 14]. In general, it has been found that the band gap has a tendency towards lower energies in the case of increases of number of depositions. This could be due to the band gap narrowing between the conduction band and defect levels.

Figure 8 shows the plot of E_g of films as a function of annealing temperature in vacuum and under sulphur atmosphere. One can see that band gap values of the films annealed in vacuum increase with the annealing temperature. However they remain unchanged when

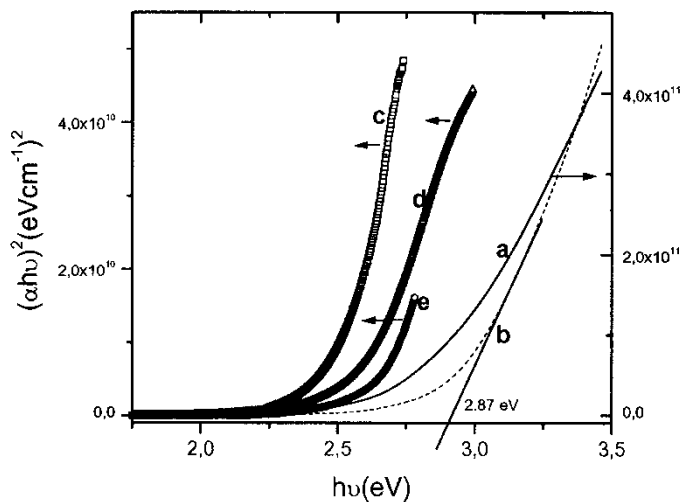


FIGURE 7 Evolution of $(\alpha h\nu)^2$ vs. the energy for films obtained by: (a) one deposition, (c) three depositions; and effect of annealing at: (b) 693 K in vacuum; and under sulphur ambient at: (d) 573 K and (e) 693 K.

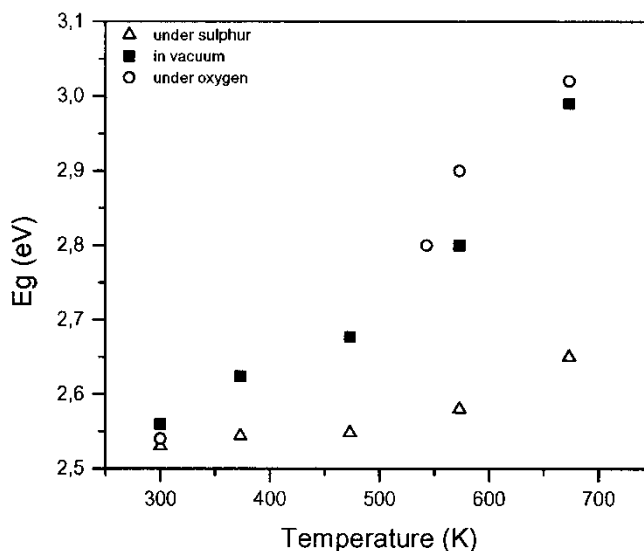


FIGURE 8 Evolution of optical band gap of In₂S₃ samples vs. the annealing temperature at different atmospheres.

the films were sulphurized. The band gap increases can be attributed to oxygen incorporation during heat treatments. Several workers [23, 24] have reported that the E_g of In₂S₃ increases with oxygen content. Indeed, we have observed the increases in E_g when the films were heat treated under oxygen atmosphere above 573 K. The oxygen present at the surface diffuses into the bulk during annealing at high temperatures. The oxygen is partially substituted to sulphur in the crystalline matrix and bonded to indium to form In₂S_{3-x}O_{3x} [23, 24].

Some workers [25, 26] have attributed this increase in the optical band gap to the quantum size effect if the individual grain sizes are smaller than 5 nm. Therefore, the size of the grains constituting our films is higher than 20 nm.

4 CONCLUSION

In₂S₃ thin films have been successfully deposited using the flash evaporation method. The as-deposited films are amorphous, smooth and very homogenous. The annealing under vacuum at 693 K leads to the formation of β -In₂S₃ tetragonal phases. This structure can be obtained by sulphurization at lower temperature 573 K. The optical transmission of the films was very high, 80–90%, for wavelengths greater than 500 nm and their optical band gap was in order of 2.5–2.65 eV depending on thickness and annealing temperature. These values correspond to the optimum range for solar energy conversion. One can conclude that our material can be used as transmissive windows in low-cost solar cells.

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