

Research article

Thickness dependent physical properties of evaporated In_2S_3 films for photovoltaic application

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Abstract

In recent years, In_2S_3 is considered as a promising buffer layer in the fabrication of heterojunction solar cells. Film thickness is one of the important parameters that alters the physical characteristics of the grown layers significantly. The effect of film thickness on the structural, morphological and optical properties of evaporated In_2S_3 layers has been studied. In_2S_3 thin films with different thicknesses in the range, 600–900 nm were deposited at a constant substrate temperature of 240°C.

The films were deposited by vacuum thermal evaporation technique on glass substrates. Films were characterized using X-Ray Diffraction (XRD), Energy Dispersive X-ray Analysis (EDX), Scanning Electron Microscopy (SEM) and optical absorption and transmission measurements. XRD pattern revealed that the layers are amorphous in nature and recrystallized after annealing in nitrogen atmosphere at 300°C during 30mn. The optical properties of the films were studied as a function of the thickness layers varied from 600 to 900nm. The optical transmittance of the films was decreased from 90% to 65% and the band gap varied in the range, 1.95–2.22 eV with increase of film thickness.

The refractive index is about 2.44 for the thinnest In_2S_3 films. The preparative parameters have been optimized in order to obtain a good quality of In_2S_3 film used for solar cells. The detailed study of these results was presented and discussed. **Copyright © IJRETR, all right reserved.**

Keywords: In_2S_3 , Thin films, Thickness layers, vacuum thermal evaporation technique, Photovoltaic.

1. Introduction

Indium Sulphide thin films appear to be promising candidates for many technological application due to their stability, large band gap and photoconducting [1, 2]. It is an important material for opto-electronic, photovoltaic applications [3] and photo electrochemical solar cell devices [4]. A number of techniques have been used to prepare this compound [5, 6, 7]. Then, In_2S_3 thin films have exhibited a direct optical transition with a band gap energy takes values between 2.0 and 2.75 eV, depending on the composition and deposition parameters [8, 22].

Using Cu(In, Ga)Se₂ (CIGS) absorber film, photovoltaic conversion efficiencies higher than 10% have been achieved [9]. These higher efficiency values are tied to the use of a CdS interfacial buffer layer. Therefore, for environment protection and for industrial production, it would be preferable to replace CdS by a less toxic material, which can be achieved by evaporation in order to avoid any rupture of the physical vapour deposition (PVD) process. However, as discussed earlier, the use of an alternative PVD technique should be very interesting. Such PVD technique has been often used in the case of In_xS_y (X=S, Se) compounds [10, 11]. In our laboratory, successful deposition of the crystalline In₂S₃ compounds was achieved thanks to a careful control of vacuum thermal evaporation technique (VTET). In our paper [12], we have already described this method which allows obtaining n-type indium sulphide thin films which brood band gap.

Indium sulphide could be used as an effective replacement for CdS in CuInS₂ based solar cells. The motivation of searching for an alternative buffer layer is not only to eliminate toxic cadmium but also to improve light transmission in the blue wavelength region, by using a material having a wider band gap, than CdS [13]. An active area efficiency of 11% was obtained for a CuInS₂ based solar cell, in which CdS was replaced by In_x(OH, S)_y [14].

This paper presents the effect of thickness layers on the properties of In₂S₃ thin films, prepared using vacuum thermal evaporation technique. Detailed analyses of the structural, compositional, morphological and optical properties of the films were studied. Special attention has been paid to the accurate layer thickness control below 1µm, and to the achievement of high band-gap material, which are suitable for thin film photovoltaic applications.

2. Experimental details

Stoichiometric amounts of the elements of 99.999% and 99.9995% purity S and In, respectively, were used to prepare the initial ingot of In₂S₃. The mixture was sealed under 13×10⁻⁴ Pa (10⁻⁵ Torr) vacuum in a quartz tube. In order to avoid explosions due to the sulfur vapor pressure, the quartz tube was heated slowly (20 8C/h). A complete homogenization could be obtained by keeping the melt at 880°C for about 6 h. The tube was then cooled at the rate 10°C/h. So, the cracking due to the thermal expansion of the melt, during the solidification, was avoided. The compound obtained by the way of this method is dark red grayish color. X-ray diffraction of powder analysis showed that all peaks were identified as In₂S₃. Crushed powder of this ingot was used as raw material for the thermal evaporation. A crucible of graphite (resistively heated) was used as evaporator. The pressure of the chamber during evaporation was about 13×10⁻⁵ Pa (10⁻⁶ Torr). The variation of thickness of the layer is made by the change of the powder mass in the crucible. The In₂S₃ films obtained were homogeneous and very well adhered to the substrate. The structure of the samples has been analysed by X-Ray diffraction (XRD) using the nickel-filtered Kα1 emission (λ=1.752Å), in a PANalytical X'Pert PRO instrument.

Transmission (T) and reflectivity (R) spectra measurements were performed with an UV-Vis-NIR spectrophotometer (UV-3100, Shimadzu) in the 300-1800 nm wavelengths range, provided with a specular reflexion attachment including an integrating sphere to measure total and diffuse reflection as well as total transmission. Scanning electron microscopy (SEM) micrographs were performed using a Philips XL30

microscope. The compositions of the films were determined by EDX measurement. Film thicknesses were determined to use the extremes of the interference fringes.

3. Results and discussions

3.1 Structural analysis

X-ray diffraction (XRD) was used to identify the crystalline phases using X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.752\text{\AA}$). In the present experimental conditions, all the indium sulphide thin films prepared have an amorphous structure. Indeed, the transformation of amorphous structure leads an arrangement of atoms into volume. This leads us to undergo with our films of the heat treatments. Our layers were heated at 300°C in nitrogen atmosphere during 30 min in order to study the effect of annealing on the quality of the layers. From XRD patterns, it is found that annealing has great effects on the formation of polycrystalline In_2S_3 thin films. Fig.1 shows the XRD diagrams from In-S thin layer deposited at different thickness and annealed in nitrogen atmosphere. It is also observed that the cristallinity increases obviously with increasing thickness layers, which probably may be due to the decrease of the disorder component. On the other hand, few minor peaks associated to In_6S_7 phases can be observed from the patterns.

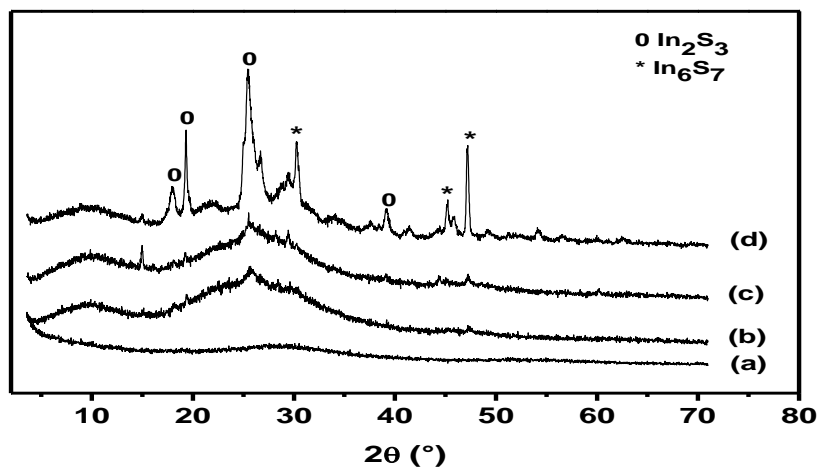


Figure 1: X-ray diffractograms of (a) as-deposited In_2S_3 thin films and annealed at 300°C during 30mn in nitrogen atmosphere as function of thickness layers with (b) $0.6\mu\text{m}$, (c) $0.75\mu\text{m}$ and (d) $0.9\mu\text{m}$.

3.2 Optical measurement

The optical properties of the buffer layers are of major importance for the solar cell performance. Thus, regardless of the band structure and assuming that the photons absorbed inside the buffer layer do not influence the collected carriers, it is particularly important that the buffer layer band gap be wide enough in order to avoid photon loss in the short-wavelength region. The optical characterization of the synthesized solid solutions shows that, although their band gap is observed to vary with the increasing thickness layers. Figs.2 and 3 show the spectral distributions both of the transmission and the reflection R at normal incidence, respectively. However, this decrease occurs mainly in transmission, while reflection is almost not affected.

The spectrum shows the presence of interference fringes due to multitude reflexions showing a fairly homogenous film [15]. The films show a widely increasing transmission in the long wavelength region (500-

800) nm, and it does not exhibit a clear absorption edge. This could be due to the amorphous nature of the as-deposited film and its associated presence of elementary sulphur. In addition this result confirms the X-ray analysis amorphous study for deposited layers. We marked that each spectrum made of a linear part and a part of absorption, the absorption part of the layer which locates at low energies is appreciably due to defects of absorption [16].

The presence of a linear part of optical transmission spectra for layers confirms that the optical threshold absorption is of a direct nature.

Fig.2 exhibits the optical transmittance of the In_2S_3 films grown at 240°C . All these films demonstrate good optical transmittance in the visible and near infrared spectrum. The optical absorption coefficient (α) was evaluated from the relation [17],

$$\alpha = 1/e \ln(T/(1-R)) ,$$

Where T is the transmittance; R, reflectance and e, film thickness.

The variation of α with photon energy ($h\nu$) was found to obey the relation

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2}$$

for the allowed direct transition where A is the edge width parameter and E_g is the optical band gap.

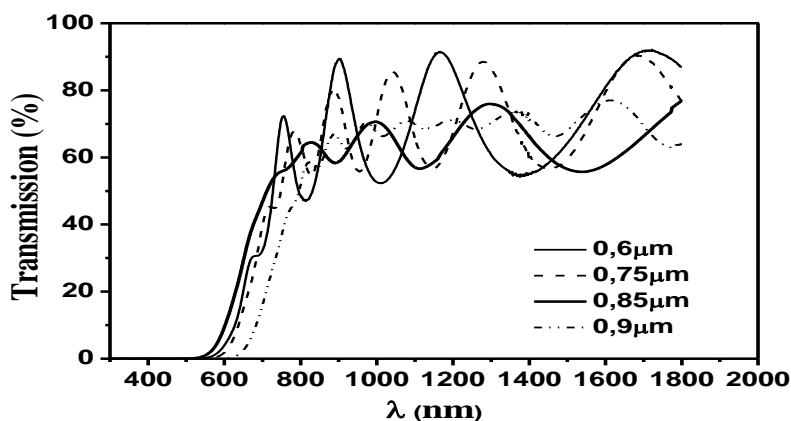


Figure 2: Variation of optical transmittance with annealed free air temperature.

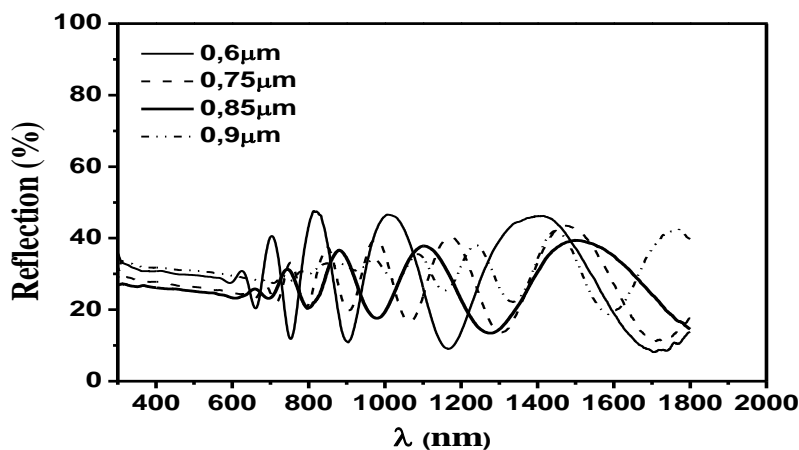


Figure 3: Variation of optical transmittance with annealed free air temperature.

The optical band gap values are obtained by extrapolating the linear portion of the plots of $(\alpha hv)^2$ versus (hv) to $\alpha = 0$. Fig.4 shows the plots of $(\alpha hv)^2$ versus (hv) for all samples. From the result considered above we note that the value of gap energies passes by a maximum for 0.85 μm layers. From this study we considered that the thickness is the optimum for our study.

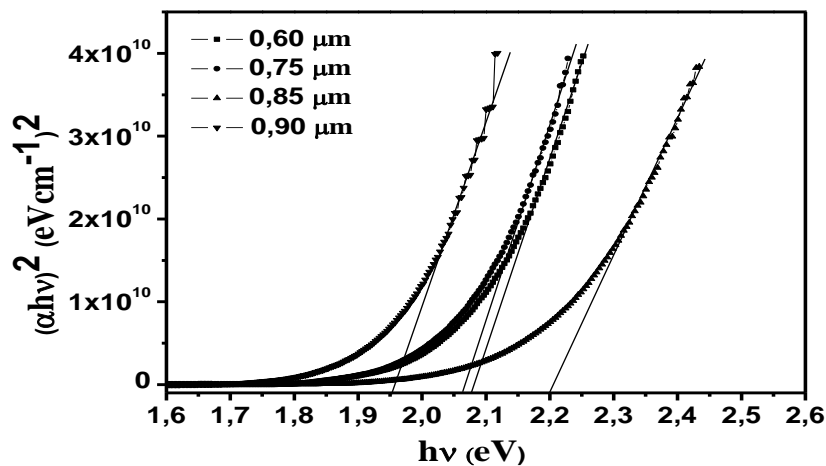


Figure 4: Plots of the square of (αE) as a function of the photon energy for vacuum annealed layers at different temperature.

The thickness was also calculated with the method of Swanpoel [18], which is based on the use of the extremes of the interference fringes and which is in accordance with the results found with the SEM characterisation. The films exhibited a direct band gap varying from 1.95 at 2.22 eV as a function of thickness layers (Fig.5); the measured of E_g -values are lower than those reported in [19]. In the literature, large variations of the band gap of indium sulphide thin films was reported [20, 21, 22, 23] which are generally related to structural effects. Such band gap energy increase is highly beneficial for photovoltaic applications since it allows for the absorber an increased collection of photons in the ultraviolet range.

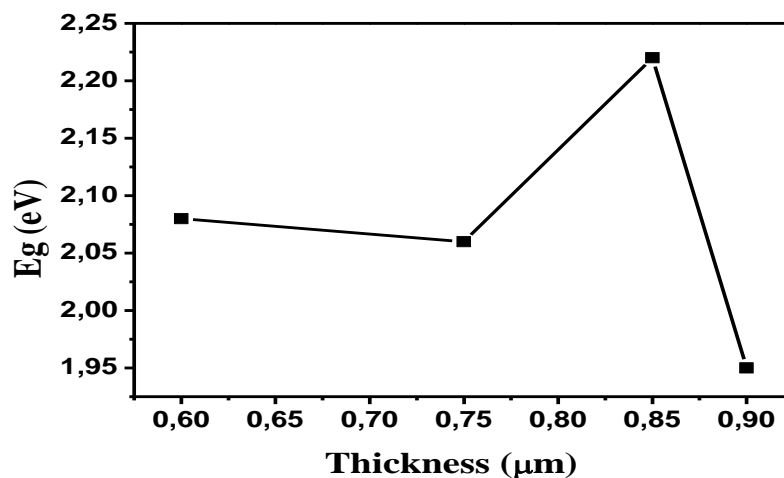


Figure 5: Variation of optical gap energy as function of thickness layers.

The refractive indexes, n , of the deposited In_2S_3 films were successfully determined from the transmission and reflection spectrum, the result is summarized in Fig.6.

From the results considered above we note that the value of refractive index passes by a minimum for optimum thickness layers 0.85 μm layers.

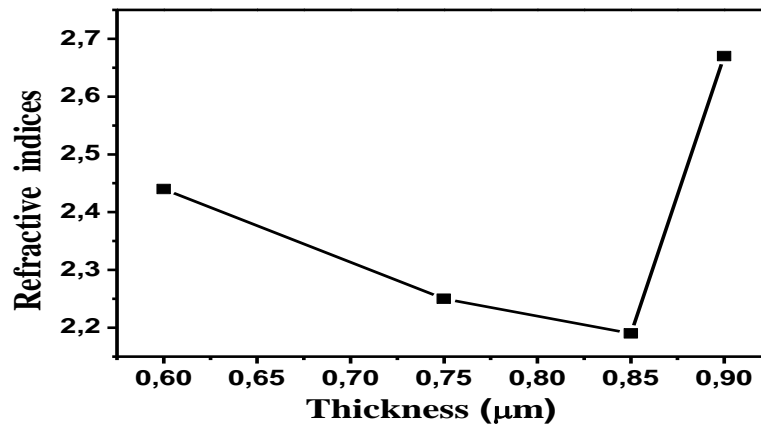


Figure 6: Variation of refractive index as function of thickness layers.

3.3 Morphology

The surface morphology of the indium sulphide thin films has been also studied by using SEM. Surface morphology was examined using scanning electron microscopy (SEM). It gives microscopic information of the surface topography. Fig.7 shows the SEM micrographs of In_2S_3 thin layers deposited on glass substrates. It can be seen that the surface is partially smooth and not uniform. The average crystallite size evaluated by a statistical analysis of these micrographs is in the range of 0.1 μm .

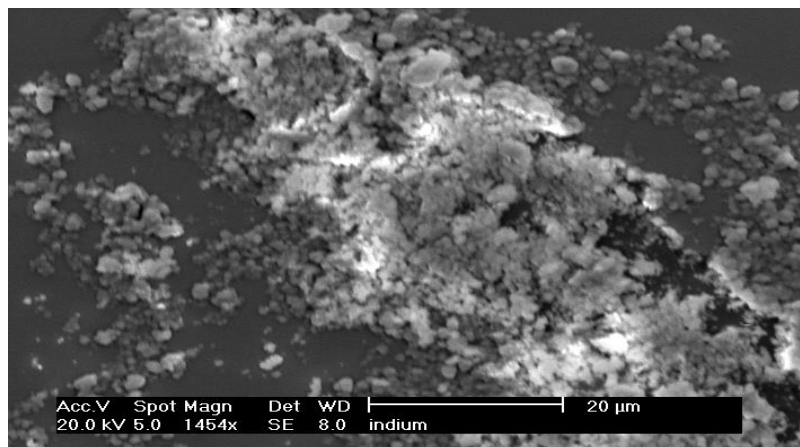


Figure 7: SEM micrograph for as-deposited In_2S_3 thin layer.

3.4 EDAX measurements

The quantitative analysis for energy dispersive X-ray analysis (EDAX), was performed for In and S on various samples at different points. The average ratio for atomic percentage of In:S was 2:3 showing that the samples are in good stoichiometric ratio. The presence of other compound is not detected in EDAX analysis. A typical EDAX spectrum is presented in Fig.

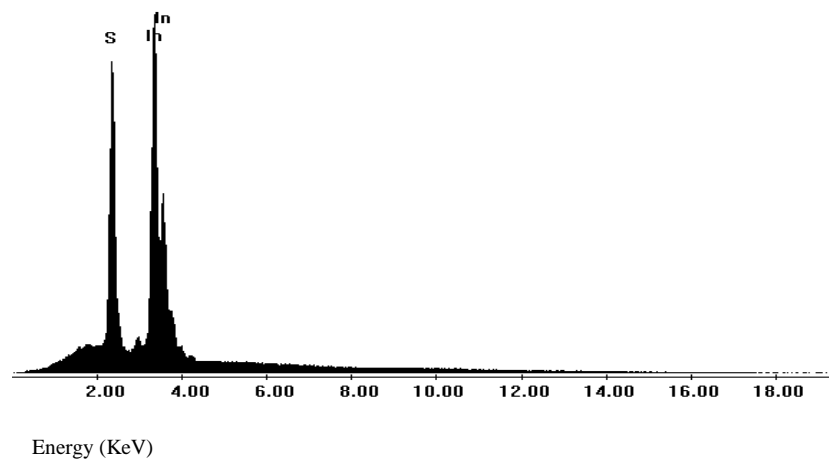


Figure 7: The EDAX spectrum of In₂S₃ film on glass substrate

4. Conclusion

In₂S₃ films have been prepared by vacuum thermal evaporation at different thicknesses by keeping the substrate temperature constant. The physical properties of In₂S₃ layers as a function of film thickness have been investigated. A good correlation between the results obtained from different characterization techniques with respect to film thickness was observed. The increase in film thickness improved the crystallinity of the layers.

The optical band gap of In₂S₃ films decreased from 2.22 –1.95 eV with increase of film thickness from 600 nm to 900 nm.

The films were amorphous in nature and the cristallinity was enhanced with annealing in nitrogen atmosphere during 30mn.

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