This is a pre-print of an article published in
Materials Today: Proceedings.
The final authenticated version is available online at:
https://doi.org/10.1016/j.matpr.2017.10.049

ICSEP 2016

Effect of Substrate temperature on Structural and Optical properties of In_2S_3 thin films grown by Thermal evaporation

S. Rasool[a], G. Phaneendra Reddy[a], K.T. Ramakrishna Reddy[a,*] M. Tivanov[b] and V.F. Gremenok[c]

[a]*Department of Physics, Sri Venkateswara University, Tirupati-517 502, India.*
[b]*Department of Energy Studies, Belarusian State University, Minsk, Belarus.*
[c]*Solid state Physics laboratory, Scientific and Practical Materials Research Centre, National Academy of Sciences of Belarus, Minsk 220072.*
[*]*e-mail: ktrkreddy@gmail.com*

Abstract

Indium sulfide (In_2S_3) is widely used as a buffer layer alternative to CdS for thin film solar cell applications. In_2S_3 thin films were deposited on glass substrates by using thermal evaporation technique at different substrate temperature that vary in the range, 200-350° C. The effect of substrate temperature (T_s) on structural and optical properties of In_2S_3 films was investigated by using Grazing incidence X-ray diffraction (GIXD), Raman Spectroscopy and Photon RT Spectrophotometer. The GIXD patterns showed that the films grown at 200°C and 250°C were amorphous in nature. For further increase of temperature T_s=300°C and 350°C, the films showed polycrystalline nature with mixed phases of tetragonal and cubic structure of β-In_2S_3 with (300) plane as preferred orientation. Also, it was observed that the crystallinity of the films increased with substrate temperature. Raman Spectroscopy analysis confirmed that the active modes present belong to the β-In_2S_3 phase. From the optical transmittance spectra, the band gap of the as-grown In_2S_3 films was evaluated that varied in the range, 1.72-2.64 eV. Further, the optical constants such as refractive index (n) and extinction coefficient (k) were also calculated for as-deposited In_2S_3 thin films, and the results were reported.

Keywords: *In_2S_3 thin films; thermal evaporation; tetragonal; cubic; GIXD; Raman; optical band gap; refractive index and extinction coefficient;*

* Corresponding author. Tel.: +0-9441137898 .
E-mail address: ktrkreddy@gmail.com

1. Introduction

Indium sulfide (In_2S_3) is a direct band gap semiconductor with n-type conductivity [1,2] that can exists in three different crystallographic phases such as α, β and γ-In_2S_3 [3]. Among these β-In_2S_3 has stable structure at room temperature and crystallizes in defect spinel lattice [4]. It has interesting properties such as stability, wider band gap (2.6 eV), photo conductive behavior [5], optical, photoelectrical [6,7] and acoustical properties [8]. In_2S_3 can be used as a buffer layer for hetero-junction thin film solar cells which showed a considerable conversion efficiency of 16.4% with CIGS based solar cells [9]. In the present work, In_2S_3 thin films were grown by thermal evaporation at different substrate temperatures and studied the effect of substrate temperature (T_s) on structural and optical properties of In_2S_3 thin films.

2. Experimental

In_2S_3 films were prepared by thermal evaporation technique using Hind Hi Vac Box Coater (model BC-300). The deposition was carried on ultrasonically cleaned glass substrates. Here, In_2S_3 powder (Sigma Aldrich 99.999%) was used as source material for thin film deposition. The chamber pressure during the deposition was maintained at 6×10^{-5} mbar and the source to substrate distance was 14 cm. The deposition rate (15 Å/sec) and thickness (~ 400 nm) of the films were monitored using the quartz crystal thickness monitor (model QTM-101). The films were deposited at different substrate temperatures that varied in the range, 200-350°C. The structural characteristics of samples were analyzed by using Ultima IV X-ray diffractometer in grazing incidence diffraction (GIXD) geometry at 1 degree of incident X-rays with CuKα radiation source (λ = 1.5406Å). The Raman spectra was performed in the backscattering configuration at room temperature with unpolarized light using a DILOR XY 800 spectrometer and an Ar laser with 514.5 nm wavelength as a light source. The optical characteristics were analyzed by using Photon RT Spectrophotometer with a spectral resolution better than 4 nm in the wavelength range, 400 – 2500 nm.

3. Results and discussion

The as-deposited In_2S_3 films were appeared dark reddish yellow in colour, pinhole free, uniform and strongly adherent to the substrate surface.

3.1. Structural studies

The structural characteristics of In_2S_3 thin films were carried out by using GIXD. Figure 1 shows the GIXD patterns of In_2S_3 films grown at different substrate temperatures. The films deposited at T_s = 200°C and 250°C exhibited amorphous in nature because the applied thermal energy is not sufficient to adsorb the atoms deposited on the substrate. However, when the substrate temperature was increased to 300°C and 350°C, the films showed polycrystalline nature with improved crystallinity and exhibited two different phases. The peaks obtained in these films at 2θ = 24.96°, 32.83°, 38.69° and 46.36° are related to (300), (400), (421) and (521) planes respectively, which indicates cubic β-In_2S_3 (JCPDS: 32-0456). These films also showed certain minor peaks related to (112), (105), (325) and (404) orientations that are corresponding to tetragonal β-In_2S_3 (JCPDS: 73-1366) as secondary phase. Sandoval et al. [10] also reported the existence of cubic and tetragonal mixed phases in chemical bath deposited In_2S_3 layers. It is observed that as the substrate temperature increased, the crystallinity of the films also increased which might be due to the increased ad-atom mobility on the substrate surface. The GIXD patterns showed an improved intensity of (300) plane, which is treated as the preferred orientation for the films grown at higher temperature. The crystallite size (D) was calculated using the Debye-Scherrer formula (relation 1) where β is the full width at half- maximum, λ is the wavelength of X-rays used and θ is the Bragg angle at the centre of the peak and the values were found to be 16.31 nm and 33.16 nm for the films grown at T_s = 300°C and 350°C respectively.

$$D = \frac{0.94\lambda}{\beta\cos\theta} \tag{1}$$

The structural properties of the as-grown In_2S_3 films were further analyzed by Raman spectroscopy, which is a nondestructive technique used for the phase as well as structural analysis of thin films. Figure 2 shows the Raman spectra of the In_2S_3 films deposited at different growth temperatures. The Raman spectrum of films formed at

T_s = 200°C showed two peaks at 134 cm^{-1} and 268 cm^{-1} that are related to tetragonal and cubic β-In_2S_3 phases respectively. Here, the tetragonal phase dominated the cubic phase at this lower growth temperature. Further increase of temperature, resulted with the appearance of active modes at 168 cm^{-1} and 268 cm^{-1}, both related to cubic phasewith a shoulder present at 134 cm^{-1} due to tetragonal phase. Therefore, the Raman analysis confirmed the existence of β- In_2S_3 with mixed phases at all temperatures and supported the GIXD results [11, 12].

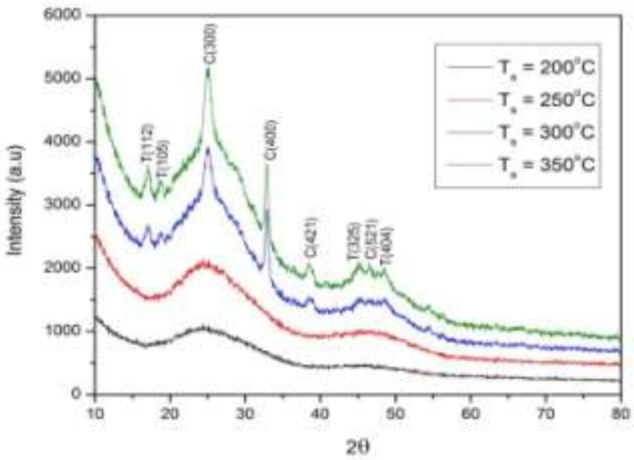

Fig.1. GIXD spectra of In_2S_3 layers.

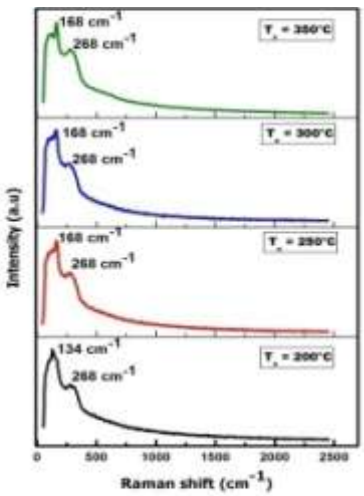

Fig.2. Raman spectra of In_2S_3 layers.

3.2. Optical studies

Figure 3 shows the optical transmittance versus wavelength spectra of all as-deposited In_2S_3 thin films, measured by using Photon RT Spectrophotometer in the wavelength range of 400 - 2500 nm. The figure exhibited high optical transmittance (T) of >80% at lower substrate temperatures of T_s = 200°C and 250°C, which might be due to the poor crystallinity of the films. The interference pattern in the transmittance spectra indicates good homogeneity and smooth surface of the films. At T_s = 300°C, a sudden fall in the optical transmittance of 40% was observed while at T_s = 350°C, the transmittance was slightly increased to 60% due to the surface scattering effect. The results obtained were in good agreement with earlier reported work of Zhao Yang Zhong et al. [13]. The optical absorption coefficient (α) was calculated by using the following relation (2), in which, 'd' is the thickness of the film. The optical band gap (E_g) of the films can be obtained by using the following relation (3) for direct allowed transition. In relation 3, 'A' is the constant related to the effective mass and $h\nu$ is the incident photon energy [14]. Figure 4 shows the extrapolation of the curve $(\alpha h\nu)^2$ versus hν, which gives the direct optical band gap of the as-grown In_2S_3 films that varied in the range, 1.72-2.64 eV. The optical band gap of the films initially decreased with increase of substrate temperature up to 300°C and then increased at 350°C. This might be due to the structural disorder at the grain boundaries of the films [15].

$$T = e^{-\alpha d} \tag{2}$$

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \tag{3}$$

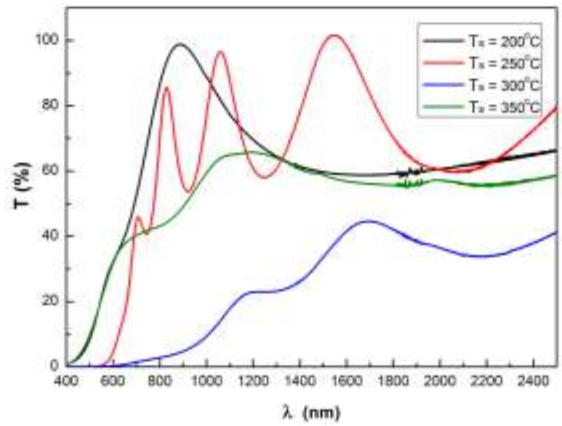

Fig.3. Optical transmittance of In_2S_3 thin films.

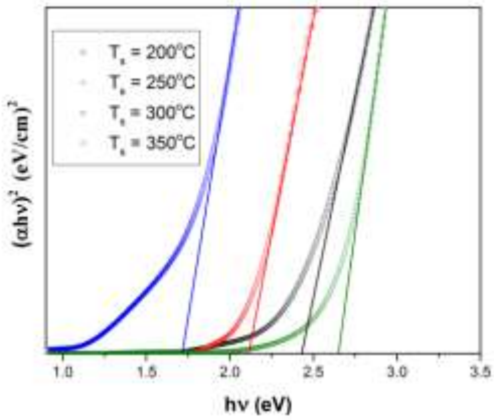

Fig.4. Variation of energy band gap with T_s.

The refractive index (n) of all the samples was calculated using Herve-Vandamme formula (relation 4). Here A and B are constants having values of 13.6 eV and 3.4 eV respectively and E_g is the optical band gap [16]. The evaluated refractive index was varied in the range of 2.46-2.84 with respect to temperature. The variation of refractive index with substrate temperature is presented in figure 5. The refractive index increased with substrate temperature up to 300°C and then decreased at 350°C. This may be attributed to the variation in packing density and band gap of the films [17]. The extinction coefficient (k) could be calculated from the following relation (5). Figure 6 shows the variation of extinction coefficient as a function of wavelength for the different substrate temperatures. It is observed from the figure that at low growth temperatures, T_s = 200°C and 250°C, the absorption index is low due to high optical transmittance and non-crystallinity of the films. At T_s = 300°C, k value was high because of less optical transmittance in the visible region as shown in figure 3, which indicates high absorption of incident photons in the film. While at T_s = 350°C, again k value was decreased that might be due to improved transmittance over the visible wavelength and less crystallographic defects present in the films.

$$n^2 = 1 + \left(\frac{A}{E_g + B}\right)^2 \tag{4}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{5}$$

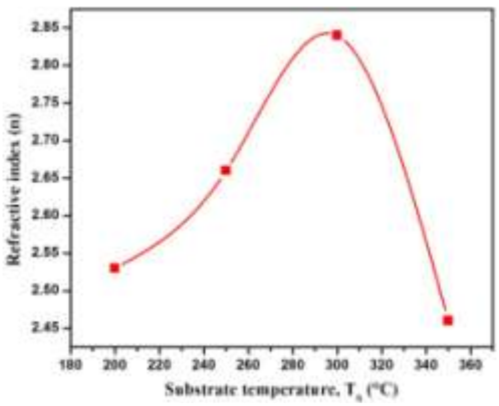

Fig. 5. Variation of refractive index (n) with T_s.

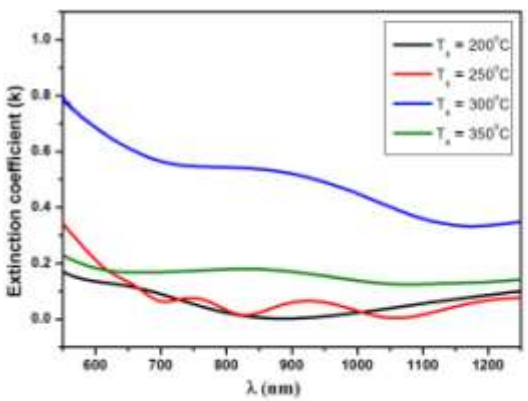

Fig. 6. Extinction coefficient (k) versus wavelength (λ).

4. Conclusion:

In_2S_3 thin films were grown by using vacuum thermal evaporation technique at different substrate temperatures that varied in the range, 200-350°C. The deposited films were characterized by using GIXD, Raman and Photon RT spectrophotometer for structural and optical analysis. The GIXD patterns exhibited the non-crystallinity of as-deposited films at lower substrate temperature (<300°C) while at higher temperature (≥300°C), cubic and tetragonal mixed phases of β-In_2S_3 was observed with improved crystallinity. Raman spectroscopy also confirmed the existence of β- In_2S_3 phase by showing active modes at 134 cm^{-1}, 168 cm^{-1} and 268 cm^{-1}. Further, the optical properties of the films were studied and the evaluated optical energy band gap varied in the range, 1.72-2.64 eV. The optical constants, refractive index and extinction coefficient were also evaluated. The present investigation reveals that the as-grown films require post annealing treatment to improve its physical properties, which then can be used as a buffer layer in solar photovoltaic cell fabrication.

Acknowledgments

The authors would like to acknowledge the financial support provided by the DST, New Delhi and the Belarusian Republican Foundation for Fundamental Research via the India-Belarus joint research project to carry out this work.

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