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Effect of Substrate temperature on Structural and Optical properties of In$_2$S$_3$ thin films grown by Thermal evaporation

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Abstract

Indium sulfide (In$_2$S$_3$) is widely used as a buffer layer alternative to CdS for thin film solar cell applications. In$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ phase. From the optical transmittance spectra, the band gap of the as-grown In$_2$S$_3$ 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$_2$S$_3$ thin films, and the results were reported.

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1. Introduction

Indium sulfide (In$_2$S$_3$) is a direct band gap semiconductor with n-type conductivity [1,2] that can exist in three different crystallographic phases such as α, β and γ-In$_2$S$_3$ [3]. Among these β-In$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ thin films.

2. Experimental

In$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ thin films were carried out by using GIXD. Figure 1 shows the GIXD patterns of In$_2$S$_3$ films grown at different substrate temperatures. The films deposited at T$_s$ = 200°C and 250°C exhibited amorphous 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$_2$S$_3$ (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$_2$S$_3$ (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$_2$S$_3$ 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.

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

The structural properties of the as-grown In$_2$S$_3$ 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$_2$S$_3$ films deposited at different growth temperatures. The Raman spectrum of films formed at
$T_s = 200^\circ C$ showed two peaks at 134 cm$^{-1}$ and 268 cm$^{-1}$ that are related to tetragonal and cubic $\beta$-$\text{In}_2\text{S}_3$ 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 phase with a shoulder present at 134 cm$^{-1}$ due to tetragonal phase. Therefore, the Raman analysis confirmed the existence of $\beta$-$\text{In}_2\text{S}_3$ with mixed phases at all temperatures and supported the GIXD results [11, 12].

3.2. Optical studies

Figure 3 shows the optical transmittance versus wavelength spectra of all as-deposited $\text{In}_2\text{S}_3$ 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 $T_s = 200^\circ C$ and $250^\circ C$, 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 $T_s = 300^\circ C$, a sudden fall in the optical transmittance of 40% was observed while at $T_s = 350^\circ C$, 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 ($\alpha$) 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 ($ah\nu)^2$ versus $h\nu$, which gives the direct optical band gap of the as-grown $\text{In}_2\text{S}_3$ 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$^\circ C$ and then increased at 350$^\circ C$. This might be due to the structural disorder at the grain boundaries of the films [15].

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

$$ah\nu = A(h\nu - E_g)^1/2 \tag{3}$$
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, $T_s = 200^\circ$C and 250°C, the absorption index is low due to high optical transmittance and non-crystallinity of the films. At $T_s = 300^\circ$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 $T_s = 350^\circ$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.

$$n^2 = 1 + \frac{A}{E_g + B}$$

(4)

$$k = \frac{e\lambda}{4\pi}$$

(5)
4. Conclusion:

In$_2$S$_3$ 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$_2$S$_3$ was observed with improved crystallinity. Raman spectroscopy also confirmed the existence of β- In$_2$S$_3$ 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.

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Reference:


