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The effect of annealing temperature on the structural and optical properties of In_2Se_3 thin films

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Thin films of In_2Se_3 were prepared by thermal evaporation. X-ray diffraction indicated that the as grown films were amorphous in nature and became polycrystalline γ- In_2Se_3 films after annealing. Optical properties of the films, investigated by using spectrophotometer transmittance spectra in the wavelength range 200-2500 nm. The increase in the value of Eg^{opt} with annealed treatment is interpreted in terms of the density of states model as proposed by Mott and Davis.

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1. Introduction

Studies of Indium Selenide films are attracting wide attention because of their importance as good photovoltaic materials. Moreover, In_2Se_3 has attractive properties for application in electro thermal devices such as solid solution electrodes [1]. Indium Selenide is a III-VI compound semiconductor having direct band gap. It can be used as a window layer [2] (in CIS/ In_2Se_3) as well as an absorbed layer [3, 4] (in CDS/In2Se3) in solar cells, depending upon the optical band gap of the film. γ- In_2Se_3 with wide band gap of 1.8 eV [5] is used as window layer while β-In2Se3 having a band gap 1.55 eV can be used as an absorber layer in solar cell fabrication. X-ray studies of the structure of In2Se3 have shown existence of four crystallographic modifications [6, 7]: the α-phase stable at room temperature, transforms at 200˚C into β-phase; the β-phase exists between 200˚C and 650˚C; the γ-phase between 650˚ and 750˚C; and the δ-phase above 750˚C.

In this paper, structural and optical properties of In_2Se_3 thin films, prepared by vacuum evaporation technique are studied with different annealing temperature (150˚C, 200˚C, 300˚C).

2. Experimental

Indium Selenide (99.99%, Sigma Aldrich) was evaporated from a resistive heated molybdenum boat onto glass substrates using a conventional coating unit (Hind Hivac 12A4). The pressure inside the chamber was lower than 10^{-6} Torr. The thickness of film was measured by Quartz crystal monitor. The crystalline structure of the film is analyzed using (Shimadzu XRD-6000) X-ray diffractometer with CuKα radiation (λ=1.5405Å). The optical transmittance was recorded using a (UV-VIS-NIR) Spectrophotometer in the wavelength range 200-2500 nm.

3. Results and discussion

3.1 Structural analysis

Fig. 1(a) shows the XRD pattern of as-deposited In2Se3 thin film of thickness 300 nm. It clearly indicated an amorphous in nature [8-11]. Annealing at 150˚C and 200˚C resulted in the formation of microcrystalline structure as shown in fig.1 (b, c). Samples annealed at 300˚C exhibit polycrystalline nature as shown in fig.1 (d). The orientation along (110) and (006) plane corresponds to hexagonal structure of γ-In_2Se_3 [12, 13]. The crystallographic data for this structure of In2Se3 thin film have been calculated as a = 7.04Å and c = 19.15Å. These values coincide well with the ASTM data (23-0294).

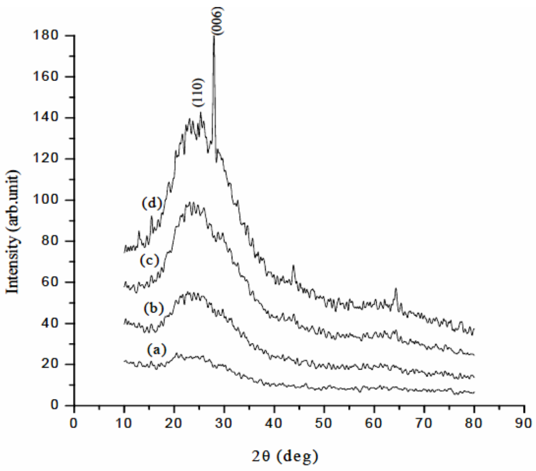

Fig. 1. X-ray diffraction patterns for In_2Se_3films (a) un annealed (b) annealed 150˚C (c) annealed 200˚C (d) annealed 300˚C

The grain size of the films annealed at 300˚C was calculated using Scherrer's relation [14]

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

where λ is the wavelength of radiation, K, the constant (0.94), β is the full width half maximum and θ, diffraction angle,.

The dislocation density (δ) and the microstrain (ε) were evaluated using the equations

$$\delta = \frac{1}{D^2} \tag{2}$$

and

$$\varepsilon = \frac{\beta \cos\theta}{4} \tag{3}$$

The values of D, δ and ε for the films were found to be 23.49 nm, 18.11×10^{14} lines/m^2 and 15.41×10^{-4} lines/m^2 respectively.

3.2 Optical properties

The transmittance spectra of In_2Se_3 films of various thicknesses (50,150,300nm) are presented in fig.2. As seen, the transmittance decreases with the increase in the film thickness, which leads to a decrease in light scattering losses [15]. High transmittance in the higher wavelength region and a sharp absorption edge were observed in the films [16]. The transmittance falls steeply with decreasing wavelength. It can be positively concluded that the material is of highly absorbing nature. Similar results were obtained for annealed film of thickness 300 nm and it shown in fig. 3.

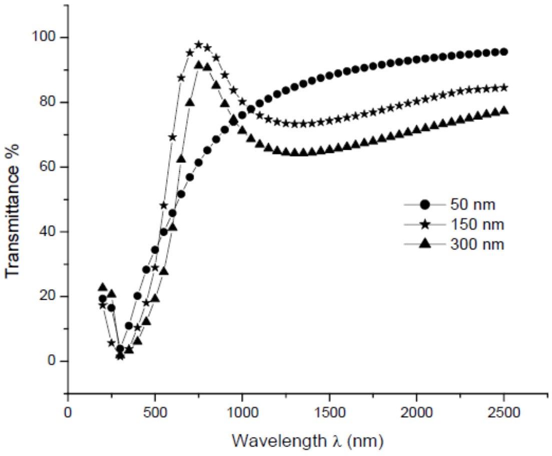

Fig. 2. Transmittance spectra of as deposited of In_2Se_3 films at different thickness.

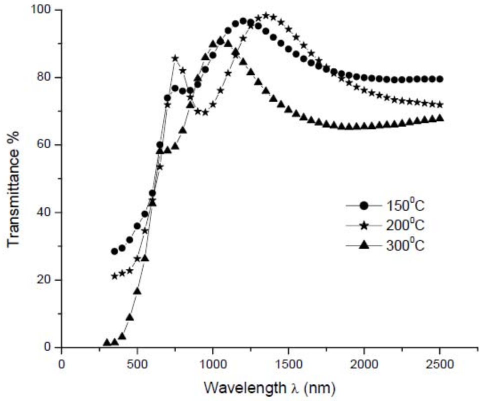

Fig. 3. Transmittance spectra of annealed of In_2Se_3 film of thickness 300 nm at different temperatures.

The band gap energy (Eg) was estimated based on the recorded optical spectra using the following relation

$$\alpha h\nu = A\,(h\nu - E_g)^{n} \tag{4}$$

where A is a constant, α the absorption coefficient, hν the photon energy, and n depends on the nature of the transition. For direct transition n =1/2 or 3/2, while for indirect case n = 2 or 3, depending on whether they are allowed or forbidden respectively. The best fit to the experimental data was obtained for n = 1/2. This is in agreement with literature data [16, 17] according to which, Indium Selenide is a semiconducting material with a direct band gap. The relation $(\alpha h\nu)^{1/2}$ versus hν yields to a straight line (Fig. 4). From the plot it was found that the band gap energy decreases as the film thickness increases. The decrease in the band gap may due to many reasons. It may be due to the presence of internal electric field associated with the defects present in the films; it may be due to the action of atmospheric oxygen on surface of the films, which produces an acceptor level in the forbidden band [18]. Table.1 represents the band gap energy of In_2Se_3 thin film at different thickness.

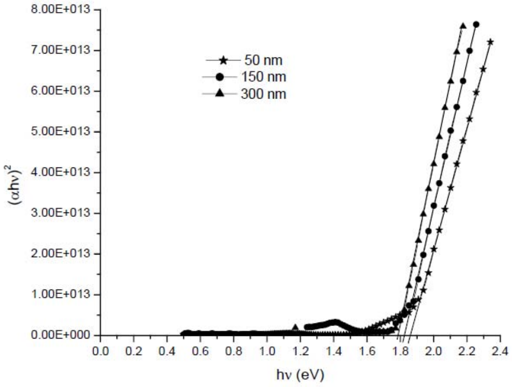

Fig. 4. Plot of hν versus $(\alpha h\nu)^2$ of as deposited In_2Se_3 films at different thickness

Table 1. Band gap energy for various thickness of as deposited In_2Se_3 thin film

Thickness (nm)	Band gap (E_g) eV
50	1.85
150	1.82
300	1.79

Fig. 5 shows annealed Indium Selenide films of thickness 300 nm. The annealed temperature increases with band gap energy increases. The optical band gap values changes from 1.81 to 1.95 eV. The value of E_g is in agreement with the reported values (1.8 – 2 eV) for γ-In_2Se_3 films. The table.2 shows the value of band gap energy for annealed In_2Se_3 thin film at different temperature.

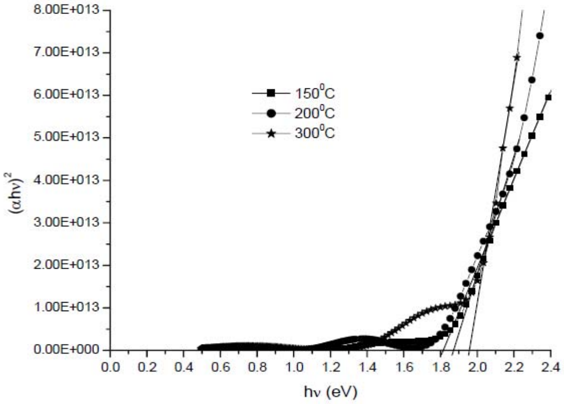

Fig. 5. Plot of $h\nu$ versus $(\alpha h\nu)^2$ of annealed In_2Se_3 films of thickness 300 nm at different temperature.

Table.2 Band gap energy for annealed In_2Se_3 thin film at different temperature.

Thickness (nm)	Annealed Temperature (˚C)	Band gap E_g (eV)
300	150	1.81
	200	1.86
	300	1.95

According to Mott and Davis model [19], the width of the localized states near the mobility edges depends on the degree of disorder and the defects present in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds (like dative bonds [20]) are produced because of an insufficient number of atoms deposited in the amorphous films. The unsaturated bonds are responsible for the formation of some defects in the films. Such defects produce localized states in amorphous solids. The presence of a high concentration of localized states in the band structure is responsible for the low value of E_g in the case of room temperature deposited amorphous films. In the process of annealed substrates deposited films (i.e. in polycrystalline films), the unsaturated defects are gradually annealed out producing a large number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure, consequently increasing the optical gap [5, 20-22].

4 Conclusions

Indium Selenide thin films were prepared by vacuum evaporation technique. The XRD pattern revealed that the as deposited films are amorphous in nature and annealed at 300˚C films exhibit γ-phase polycrystalline nature with hexagonal structure. Optical studies show that direct band gap values of annealed Indium Selenide films are higher compared to as deposited films. This may be due to reduction in the number of unsaturated defects that decreases the density localized states in the band structure, consequently increasing the optical band gap.

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