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Comparison of Morphological, Electrical and Optical Properties of as-deposited and annealed InSe Thin Films

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ABSTRACT
Indium selenide (InSe) thin films have been deposited on to glass substrate by e-beam evaporation technique. Scanning Electron Microscopy (SEM) has been used to study the surface morphology of the films. It is observed that the as-deposited InSe films have no sign of grains and the surfaces are almost smooth and uniform. While a number of grain boundaries are observed in the annealed films. Three different slopes in the conductivity *vs* temperature curves exhibits in as-deposited InSe films. If it is associated with three types of conduction mechanisms, then it might be interesting. The conductivity of annealed InSe films increases continuously with increasing temperature showing normal semiconducting behaviour. The direct optical band is found to decrease from 1.79 eV to 1.57 eV after annealing.
***Keywords* –**Activation energy, Band gap, Electrical conductivity, E-beam, Thin films

I. INTRODUCTION

Indium Selenide (InSe) is semiconducting compound which belongs to the III - VI group. InSe has become a promising material for their potential application in the fields of opto-electronic devices, solar energy conversion, solid solution electrode [1]. It has been the subject of extensive research because of its near band-edge optical and electrical properties [2]. A variety of physical and chemical deposition techniques, such as vacuum evaporation [3-5], flash evaporation [6], molecular beam deposition [7], electro deposition [8], sol-gel method [9], metalorganic chemical vapour deposition (MOCVD) techniques [10] etc. have been used for the preparation of InSe thin films. E- beam evaporation has become a popular and reliable technique, is widely used by researchers, among different techniques, for the deposition of thin films.

Strong exciton emissions were found at around 2.14 eV at 20 K in γ-In_2Se_3. The band gap of γ-In_2Se_3 at room temperature is estimated at approximately 1.93eV [10]. Device performances are strongly dependence upon the structural, electrical and optical properties [11].

Dependences of structural and optical properties on substrate temperature of InSe thin films deposited using e-beam evaporation technique was reported by Hossain et al. [2]. It was observed that InSe thin films are amorphous before phase-transition while they become polycrystalline after phase-transition [12]. The absorption coefficient of as-deposited InSe thin films shows a direct type transition with a band gap of ≈1.65 eV [2].

Although there are different deposition techniques and several studies on the growth and characterization of InSe thin films, there is still a lack of understanding of this properties.

This paper presents a comparison of morphological, electrical and optical properties of as-deposited and annealed InSe thin films and compare the results with other researchers' works.

II. EXPERIMENTAL DETAILS

Indium selenide (InSe) thin films have been deposited on glass substrate by e-beam evaporation technique at a pressure of 3×10^{-4} Pa from InSe granular powder (99.999%) obtained from Materials by Metron, USA.

Before deposition, the deposition chamber was thoroughly cleaned with emery paper and cotton wool by wetting acetone and was then dried with a dryer. When the chamber pressure reduced to ~ 3×10^{-4} Pa, the deposition was then started with 10 mA current by turning on the low-tension control switch. The deposition rate of the films is about 9.8 nms^{-1}. All the films were deposited at room temperature. As-deposited films were annealed by heating (temperature is changed slowly 1K/min) about 3 hours in open air at a temperature of 573K. The film thickness was measured by the Tolanasky interference method with an accuracy of ±5nm [13].

The electrical contacts required for conductivity measurement were made with silver paste (leading silver D-200) on the InSe thin films. Van-der-Pauw technique [13] was used for the measurement of the conductivity of thin film.

The optical transmittance spectra of InSe films have been recorded from 400 nm to 1100 nm wavelength using a SHIMADZU UV- double beam spectrophotometer at room temperature. To determine the optical band gap of the InSe thin films, the plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ was drawn for direct allowed transition. The value of the band gap was determined for the tangent of these curves which intersect the energy axis.

III. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM) study

SEM has been used to characterize the surface morphology and to find out the existence of grains in the InSe thin films. Fig. 1 shows the SEM micrographs of the as-deposited (top) and annealed (bottom) InSe thin films of thickness 200nm. These SEM images indicate that there is no sign of grains in the as-deposited InSe films and the surfaces are almost smooth and uniform. While there are a number of grains exhibit in the annealed films which agreed with the reported values [12]. It is noted that InSe thin films become polycrystalline after annealing which has also been verified by XRD study [12]. The presence of grain boundaries in annealed films in our experiment may be attributed to the polycrystalline nature of the films.

3.2 Electrical Properties

Temperature effect on electrical conductivity (σ) has been studied both for the as-deposited and annealed InSe thin films. The ln(σ) versus inverse temperature (1/T) curves for the as-deposited and annealed InSe films of thicknesses 100, 150 & 250 nm, respectively are shown in Fig. 2. It is seen from the Fig.2 (a) that conductivity increases continuously with increasing temperature and an abrupt increase in conductivity is observed at around 385K which varies with thickness, and the results agreed with the reported data [12]. The presence of three different slopes in the conductivity *vs* temperature curves most probably suggest the presence of three types of conduction mechanism in InSe films. In the room temperature range, conductivity almost independent of temperature, but then increased more sharply above 385 K, and then it increases linearly above 415K.

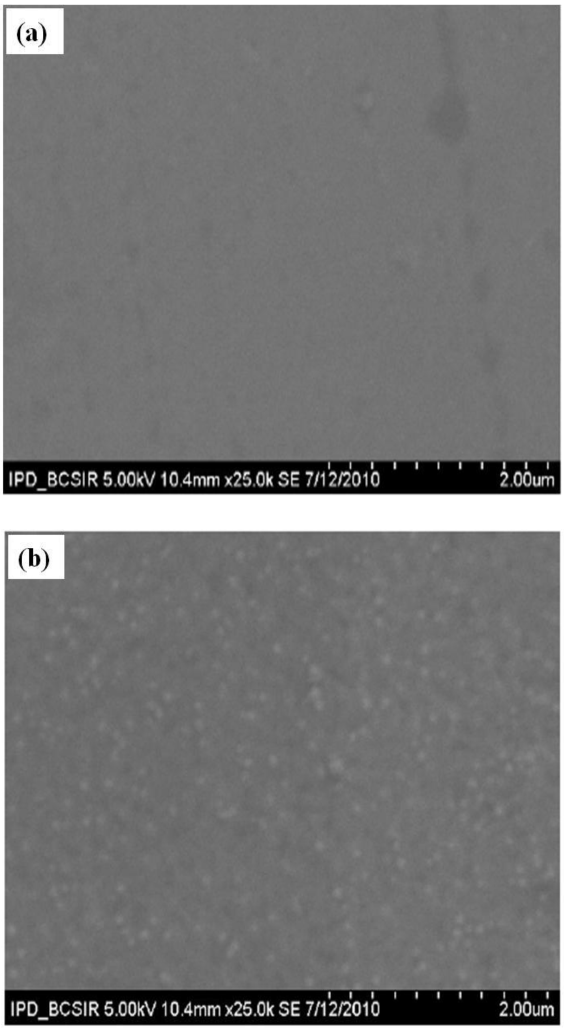

Fig. 1. SEM micrographs of (a) as-deposited and (b) annealed InSe thin films with a thickness of 200 nm

The conductivity of as-deposited films is found to be, at room temperature, of 0.50 $(\Omega\text{-m})^{-1}$ and it is found to be the order of $10^3(\Omega\text{-m})^{-1}$ at around 415K. The conductivity of annealed InSe films increases continuously with increasing temperature Fig. 2(b). This type of variation indicates the semiconducting behavior of the InSe thin films. In extrinsic semiconductors, there will be additional energy levels in the band-gap, a slight thermal excitation is sufficient to donate or accept electrons and, thereby increase the electrical conductivity in the film. Conductivity of annealed InSe is also found to be the order of $10^3(\Omega\text{-m})^{-1}$. The continuous variation of conductivity with temperature can be attributed to thermal excitation of charge carriers from grain boundaries to the neutral region of grains.

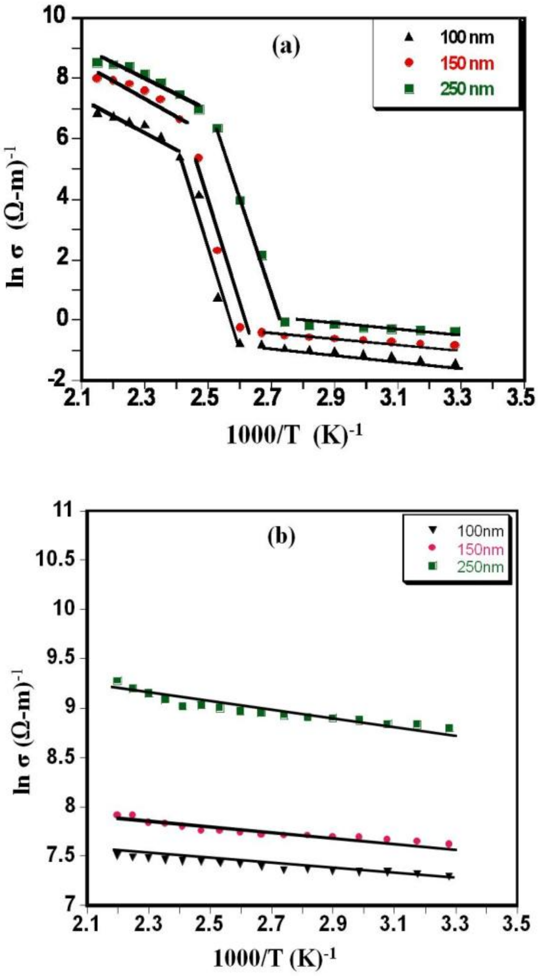

Fig. 2. Variation of ln (σ) versus 1000/T of (a) as-deposited and (b) annealed InSe thin films of different thicknesses

The activation energy is related to the film conductivity and given by the relation:

$$\sigma = \sigma_0 \exp(-\Delta E/2K_B T) \quad (1)$$

where ΔE is the activation energy, σ_0 is the conductivity at 0^0C and K_B is the Boltzmann constant and T is the absolute temperature. The activation energies of the films have been calculated from the slopes of the curves. The values of activation energies of three temperature regions are given in Table 1.

3.3 Optical Study

The optical spectra of transmittance *T* (%) and reflectance R (%) have been measured at wavelength ranges 400 ≤ λ ≤ 1100nm using a "UV-Visible SHIMADZU double beam spectrophotometer". Figure 3 shows the variation of transmittance *T* (%) with wavelength for the as-deposited and annealed InSe thin films of thicknesses 100, 150 & 250 nm. From these Figures it is seen that for both the as-deposited and annealed films transmittance is high in the infrared (IR) region and it decreases with decreasing wavelength in the visible region. In visible and nearly ultraviolet region photons are highly absorbed by the films. It is also seen that for both the cases InSe thin films show good transparency in the IR region.

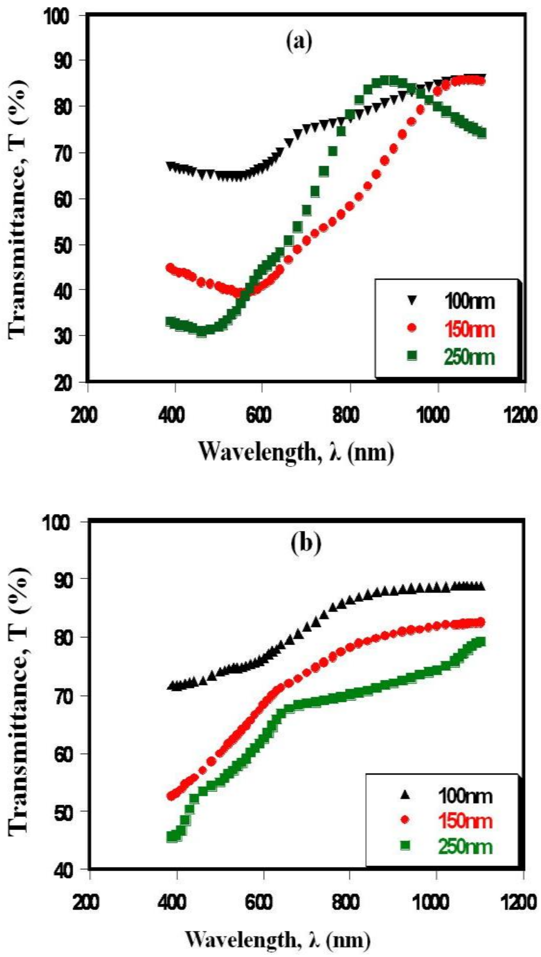

Fig. 3. Spectral variation of transmittance of (a) as-deposited and (b) annealed InSe thin films of different thicknesses

The absorption coefficient (α) was calculated from the transmittance (*T*) measurement, using the relation:

$$\alpha = (1/t) \ln(1/T) \quad (2)$$

where t is film thickness in nm and *T* is the transmittance. Figure 4 shows the absorption coefficient α as a function of photon energy for as-deposited and annealed InSe films. Absorption coefficient α is found to be the order of 10^6 m^{-1} which well agreed with the value reported by earlier work [2] and it increases with increasing photon energy hν.

Table 1
The Value of Activation Energies of InSe Films of Different Thicknesses

Thickness (nm)	Activation energies, ΔE in (eV)			
	As-deposited InSe films			Annealed InSe films
	Temperature ranges			
	300-385 (K)	385-415 (K)	415-465 (K)	
	ΔE	ΔE	ΔE	ΔE
100	0.18	6.27	0.88	0.04
150	0.16	5.75	1.19	0.05
250	0.15	5.31	0.91	0.09

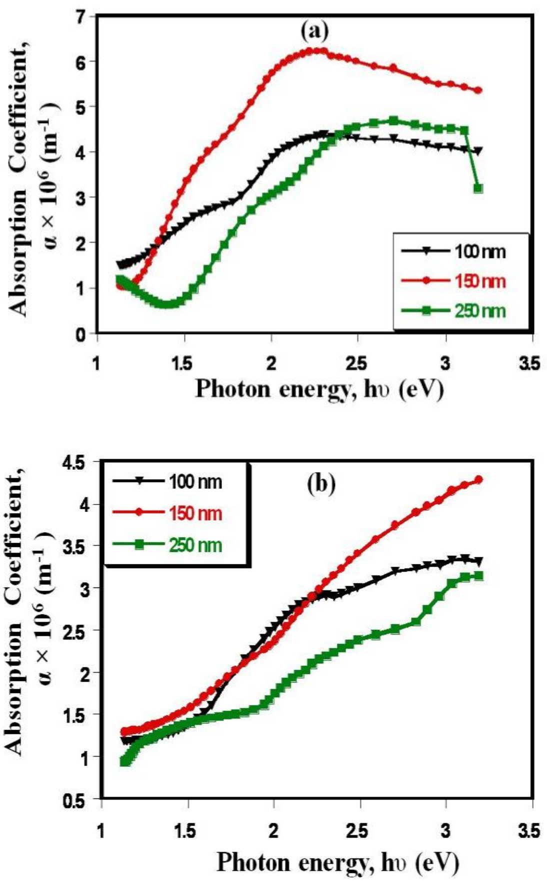

Fig. 4. Absorption coefficient (α) vs. photon energy (hυ) of (a) as-deposited and (b) annealed InSe thin films of different thicknesses

As InSe is a direct band gap semiconductor, absorption coefficient follows the relation:

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^{1/2} \qquad (4)$$

where E_g is the band gap, hυ is the energy of the incident photon, and A is a constant depending on the transition. Figure 5 shows plots of $(\alpha h\upsilon)^2$ with photon energy hυ for for the as-deposited and annealed InSe thin films of thicknesse 100nm. Extrapolation of the linear portion of the curve to $(\alpha h\upsilon)^2 = 0$ gives the band gap energy which is 1.79 eV and 1.56 eV for as-deposited and annealed films, respectively, which agrees well with early reports [4,14]. It is noted that the band gap is found to decrease in the annealed films.

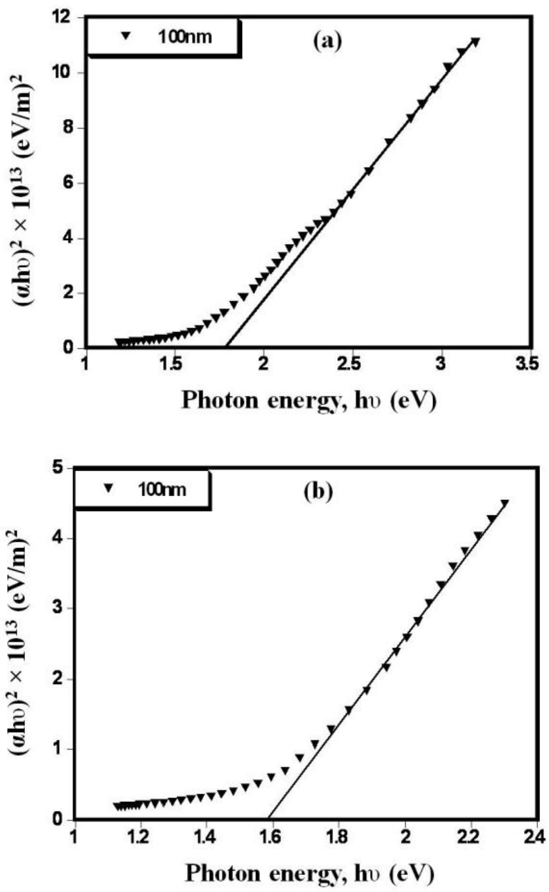

Fig. 5. Plots of $(\alpha h\upsilon)^2$ vs. Photon energy (hυ) of (a) as-deposited and (b) annealed InSe thin films of 100nm thicknesses

IV. CONCLUSION

InSe films were successfully prepared on to glass substrate by e-beam evaporation technique. Annealing shows the improvement of the quality of the as-deposited InSe films because of the appearance of grain boundaries. The presence of grain boundaries in the annealed films may be attributed to the polycrystalline nature of the films. The electrical conductivity varies smoothly in case of annealed films showing semiconducting nature. While the presence of three different slopes in the conductivity *vs* temperature curves most probably suggest the presence of three types of conduction mechanisms in as-deposited InSe films. Further investigation is needed on this issue to reveal the actual picture. Optical analysis revealed that prepared InSe thin films indicating direct band gap transition. High absorption coefficient (of the order of 10^6 m^{-1}) of both cases of films can become promising for photovoltaic applications.

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