ON THE ELECTRICAL CHARACTERISTICS OF VACUUM EVAPORATED INDIUM SELENIDE THIN FILMS

C. Viswanathan, G. G. Rusu[a], S. Gopal, D. Mangalaraj[*], Sa. K. Narayandass

Thin film laboratory, Department of Physics, Bharathiar University, Coimbatore, India
[a]Solid State Department, "Al. L. Cuza" University, Romania

The electrical conductivity, σ, of Indium Selenide (InSe) semiconducting thin films prepared by vacuum evaporation technique onto glass substrates maintained at different temperatures (303-573K) was investigated. For the film deposited onto unheated substrate, the conductivity was 5.64×10^{-4} $\Omega^{-1}m^{-1}$ and after first heating-cooling process and second heating-cooling process the values were 18.36 $\Omega^{-1}m^{-1}$ and 361.4 $\Omega^{-1}m^{-1}$, respectively. For the films deposited at the substrate temperature 573 K before and after heat treatment the values were 2.07×10^{-7} $\Omega^{-1}m^{-1}$, 6.82 $\Omega^{-1}m^{-1}$, respectively. The effects of substrate temperature and post deposition heat treatment on the temperature dependence of the electrical conductivity of the films were studied. Before heating-cooling process the band gap values and refractive index for the above films were calculated. The results were discussed in detail in relation with film recrystallization during the heating-cooling process.

1. Introduction

The transport properties of indium selenide (InSe) along the layers have been widely investigated in the past years [1, 2]. The near band –edge optical and electrical properties of strongly anisotropic crystals are a subject of considerable technical interest. The InSe single crystals are made of a fourfold stacking of selenium-indium-indium-selenium atoms sheets which characterized all M_2X_2 molecular-like crystals. The semiconducting III-VI compounds as InSe, GaSe and GaS have gained attention in recent years for their interesting optoelectronic properties [3]. Being layer-type semiconductors, their two-dimensional structure and their resulting anisotropic properties are of particular interest. In these materials inter-layer interactions are very weak compared to those in a single layer. It is known that semiconductor applications are strongly influenced by the presence in the forbidden gap of the energy levels arising from impurities and structural defects [4]. Furthermore, the numbers of defects present in the amorphous structure, changes due to post deposition heat treatment [5]. Hence, systematic studies on the dependences of the InSe thin films properties onto substrate temperature during the deposition process and post-deposition heat treatment must be made.

In this paper, the electrical and optical properties of InSe films, prepared by a vacuum evaporation technique onto heated and unheated substrates, are studied. The influence of the substrates temperature and of the post deposition heat treatment on the electrical conductivity and the absorbance of the films was investigated. A correlation between the temperature dependence of the electrical conductivity and the structural characteristic of the films was established.
The structural properties were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX).

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[*] Corresponding author: dmraj800@yahoo.com

2. Experimental

InSe powder (99.99% purity from Alfa Aesear) was evaporated from a resistive heated molybdenum boat onto glass substrates held at room temperature and also onto heated substrate (573 K) using a conventional vacuum coating unit (12A4).The pressure inside the chamber was lower than 10^{-5} Torr. The thickness of films was measured by using Multiple Beam Interference (MBI) technique. The crystalline structure of the films is analyzed using a Philips (PW1830) X-ray diffractometer (CuK$_\alpha$). For the present SEM investigation was employing a DSI 30 dual scan scanning electron microscope with a beam of very small diameter ~10 nm, produced by electron gun and electron lenses. The composition was confirmed using Energy Dispersive Analysis by X-Ray (EDAX). The optical transmittance was recorded using a UV-VIS-Spectrophotometer in the wavelength range 500-1200 nm. For the electrical measurements, samples with planar geometry have been used [6]. A Keithley 6517A electrometer was used for resistance measurement in the temperature range of 290-555 K. The DC conductivity was determined according to the relation $\sigma = l/(Rdb)$, where l = 2 mm is the distance between the electrodes, b =1 cm was the width of the film and R represents the measured electrical resistance of the film. The film temperature was monitored during the measurement of the electrical resistance using a chromel - alumel thermocouple.

3. Results and discussion

3.1. Structural characteristics of the films

Fig. 1 shows the XRD patterns of InSe films grown at different substrate temperature. The films exhibit a diffraction pattern typical for a polycrystalline structure [7]. The strong diffraction peak at 2θ =21.05° corresponds to diffraction from the (004) planes while the other peaks at 2θ =10.8° and 27.5° are the result of diffraction from the (002) and (101) planes, respectively. According to XRD results, the InSe films are polycrystalline (hexagonal system) [7,8].
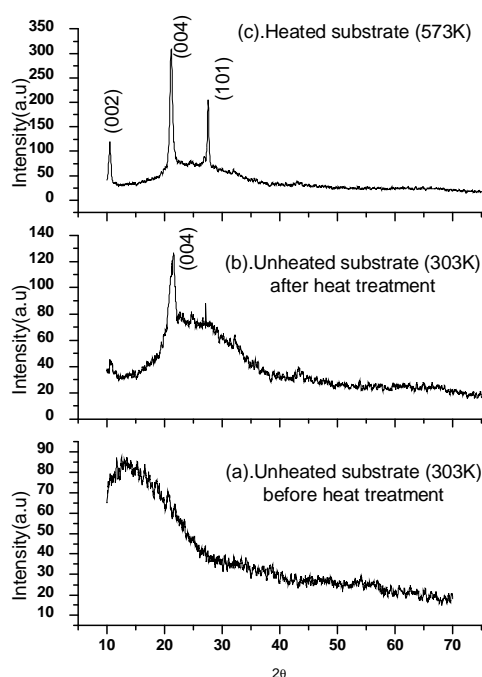

Fig. 1. Influence of the substrate temperature and heat treatment on the XRD spectra for InSe thin films: unheated substrate before (a) and after (b) heat treatment; heated substrate (c).

From the XRD profiles, the mean crystallite size (D) of the films was calculated from the Debye Scherrer's formula from the full-width at half-maximum (FWHM) β for the (004) plane. The strain ε is calculated from the slope of $\beta \cos \theta$ versus $\sin \theta$ plot using the relation

$$\beta = \frac{\lambda}{D \cos \theta} - \varepsilon \tan \theta \qquad (1)$$

The dislocation density (δ), defined as the length of dislocation lines per unit volume of the crystal, has been calculated by using the formula $\delta = 1/D^2$. For the films prepared at T_{sb}= 573 K, the grain size, lattice spacing (d), dislocation density (δ) and strain (ε) were calculated as 17.58 nm, 4.23 Å, 3.235×10^{15} lines / m^2 and 3.158×10^{-3} lines^{-2} m^{-4} respectively.

3.2 Composition analysis

The surface analysis of the layers has been studied by scanning electron microscopy. The SEM observation shows that the room temperature deposited films have amorphous structure but the films deposited onto heated substrate are polycrystalline with small grains (Fig. 2). These results were confirmed by XRD.
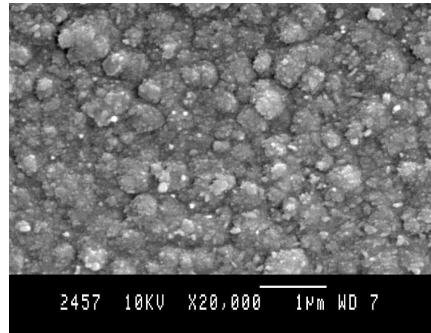

Fig. 2. SEM micrograph of the surface for InSe films deposited onto heated substrates (573 K).

The Energy Dispersive Analysis by X-Ray (EDAX) revealed that the InSe thin films prepared onto unheated substrate contains In = 47.24 %, and Se =52.76 % (Fig. 3) and the films deposited onto heated substrates (T_{sb} =573 K) contains In = 50.08 %, and Se =49.92 %, respectively (Fig. 4).
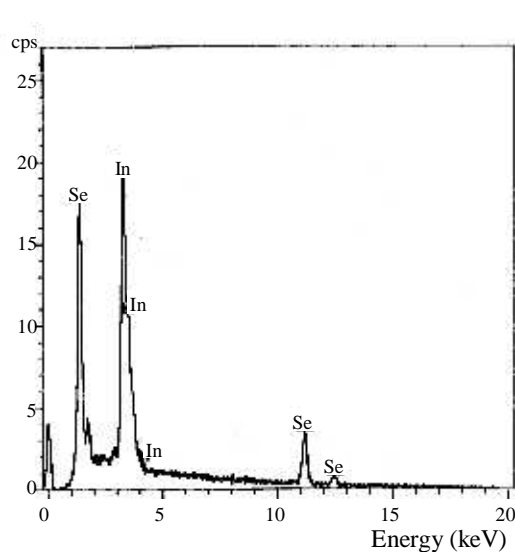

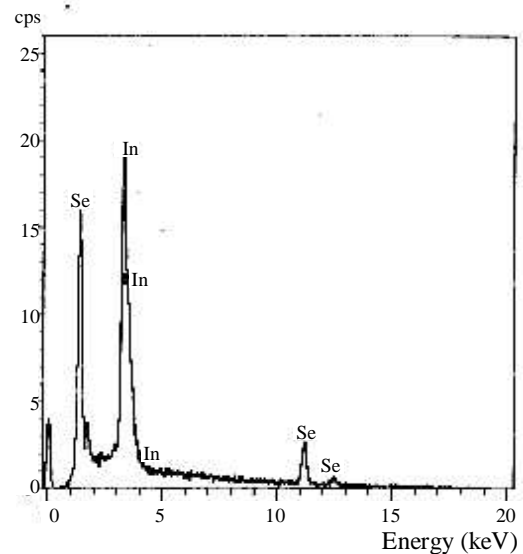Fig. 3. EDAX spectra for sample deposited at room temperature.

Fig. 4. EDAX spectra for sample deposited at substrate temperature of 573 K.

3.3. Optical properties

The band gap energy (E_g) was estimated on the basis of the recorded optical spectra using the following relation:

$$\alpha\hbar\omega = A\left(\hbar\omega - E_g^{opt}\right)^n \tag{2}$$

where A is a constant, α is the absorption coefficient, $h\nu$ is the photon energy, and n depends on the nature of the transition. For direct transition $n = 1/2$ or $3/2$, while for the indirect case $n = 2$ or 3, depending on whether they are allowed or forbidden respectively.
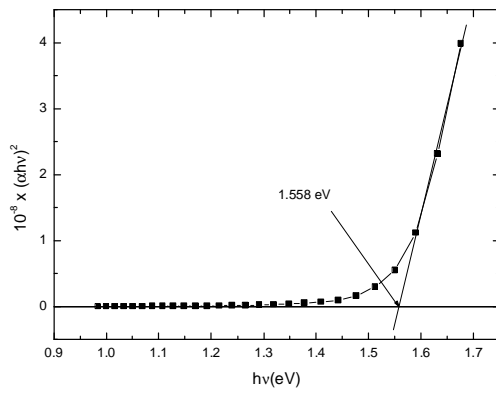
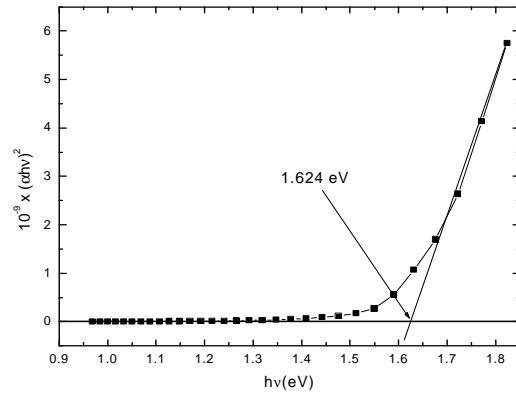Fig. 5. Plot of $\alpha h\nu$ vs. $h\nu$ for InSe thin fims deposited onto unheated substrates.

Fig. 6. Plot of $\alpha h\nu$ vs. $h\nu$ for InSe thin fims deposited onto heated substrates (573 K).

The best fit to the experimental data was obtained for $n = 1/2$. This is in agreement with the literature data according to which InSe is a semiconducting material with a direct band gap. The relation $(\alpha h\nu)^{1/2}$ vs. $h\nu$ yields to a straight line (Figs. 5 and 6) which means that the fundamental absorption edge can be described by the direct–allowed transition. It has been found that the optical energy gap values for films deposited onto unheated and heated substrates are 1.55 eV and 1.62 eV respectively. This result is in agreement with early reported data [10-12].

The observed change of the as deposited and heated substrates deposited films can be partially explained – as done for amorphous InSe thin films [13] – on the basis of the model of the density of states in amorphous solids proposed by Mott and Davis [14]. According to this model, the width of the localized states near the mobility edges depends on the level of disorder and defects present in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds (like native bonds [15]) are produced as a result of non-stoichiometry of the components in the amorphous films [16]. The unsaturated bonds are responsible for the formation of some defects in the films. Such defects produce localized states in the amorphous solids. The presence of a high concentration of localized states in the band structure is responsible for the low value of E_g^{opt} in the case of room temperature deposited amorphous films. In the process of heated 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 [17, 18].

In Fig. 7, the calculated values of refractive index (n) for the InSe films are plotted as a function of wavelength (700-1300 nm). At lower wavelength region, the refractive index increases and remains constant at higher wavelength region. The increase of refractive index in the lower wavelength region may be due to the strong effect of surface and volume imperfections on the microscopic scale [19].
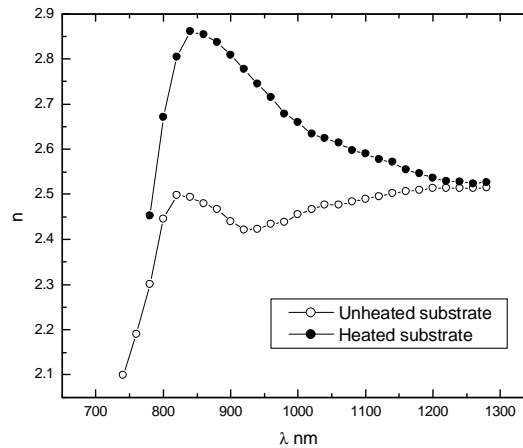
Fig. 7. Dependence of refractive index on the wavelength for In Se thin films deposited onto unheated and heated (573 K) substrates.

3.4. Electrical properties

The electrical conductivity of InSe thin films largely depends on the substrate temperature. The films deposited at higher substrate temperature have an electrical conductivity, which is one or two orders of magnitude higher than those deposited at lower substrate temperatures. The substrate temperature is a significant factor, who influence the structural characteristics of the films and hence their electrical properties. To facilitate comparison, the electrical characteristics of InSe thin films deposited by the same procedure but on the heated and unheated substrates have been analyzed. It is known that the study of the temperature dependence of the electrical conductivity of semiconducting thin films offers a lot of information about the correlation between the structure and the electrical properties of the films [20]. Moreover, when this study is carried out during successive heating and cooling cycles, it may reveal possible changes in the film structure during the annealing process [10, 21, 22]. The temperature dependence of conductivity during successive heating-cooling cycles has been studied for the films deposited at substrate temperatures of 303 K and 573 K.

Fig. 8 shows the temperature dependence of the conductivity for the InSe films prepared under unheated substrate condition. It is seen that the electrical conductivity before heat treatment shows a lower value (5.64×10^{-4} $\Omega^{-1} m^{-1}$) and after first heating/cooling cycle, the electrical conductivity increases strongly at 18.36 $\Omega^{-1} m^{-1}$. After second heating/cooling cycle, the electrical conductivity increases by an order of magnitude and reaches 361.4 $\Omega^{-1} m^{-1}$. The curve shows an upward trend during first heating process and a constant during the cooling process and again an upward trend for second heating process and remains almost the same for the second cooling process. The irreversible temperature dependence of the electrical conductivity shows the changes in the film structure during heating cooling process and the improvement in the crystallinity of the film.

Fig. 9 shows the temperature dependence of the conductivity for the InSe films prepared unto heated substrates. The curve shows an upward trend before heat treatment and the conductivity value is 2.07×10^{-7} $\Omega^{-1} m^{-1}$. During first heating cooling and second heating/cooling process the film shows almost reversible nature of temperature dependence of electrical conductivity and the electrical conductivity value becomes 6.82 $\Omega^{-1} m^{-1}$. This also shows a better improvement in the crystallinity of the film than the film prepared unto heated substrate condition.
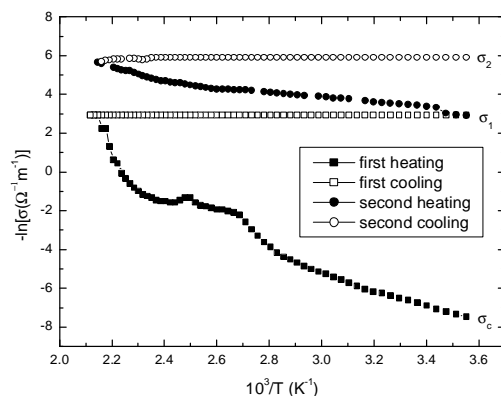
Fig. 8. Temperature dependence of electrical conductivity for In Se thin films deposited
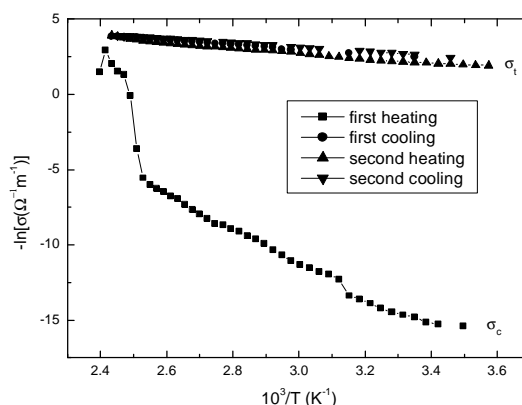onto unheated substrates.

Fig. 9. Temperature dependence of electrical conductivity for In Se thin films deposited
onto heated (573 K) substrates.

This improvement in the crystallinity is also confirmed by the typical XRD pattern for InSe films prepared under unheated substrate condition and heated substrate condition before and after heating – cooling process. The Fig. 1(a) shows that the structure of the film prepared under unheated substrate condition is amorphous, but after heating – cooling cycles this structure is improved due to the recrystallization process during the annealing of the film (Fig. 1(b)). Fig. 1(c) shows the structural characteristics for the film prepared under heated substrate condition. The structure of theses films is stable and is not affected much by the annealing process. This may explain the reversible temperature dependence of the electrical conductivity of such film. Many facts may determine an irreversible dependence of the film conductivity with temperature for the films prepared under unheated substrate condition, particularly an irreversible variation of the carrier density or their mobility during film annealing. From the analysis, we conclude that the observed irreversible dependence of conductivity is caused primarily by the film recrystallization during the annealing process. For the films deposited onto unheated substrates, the structural defects such as the stacking faults will be more numerous, determining the amorphous structure. The heating/cooling process of such films leads to an improvement of the arrangement of indium and selenium atoms in the film crystallites.

4. Conclusions

The XRD pattern revealed an amorphous nature for the films prepared under unheated substrate condition and polycrystalline nature for films deposited onto heated substrate. Optical studies show that direct band gap values of InSe film are higher for films deposited onto heated substrate compared to films obtained onto unheated substrate.

The influence of deposition condition was investigated on the electrical conductivity and on its dependence on the substrate temperature. The obtained results revealed that the structural and the electrical conductivity of the films are strongly influenced by the substrate temperatures during deposition process. The films deposited under unheated substrate condition have an amorphous structure and an irreversible dependence of their electrical conductivity observed during heating/cooling process. The film prepared on heated substrate shows reversible nature of electrical conductivity during heating/cooling process.

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