Study The Effect of Annealing on Structural and Optical Properties of Indium Selenide (InSe) Thin Films Prepared by Vacuum Thermal Evaporation Technique

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Abstract. In this work, InSe thin films were deposited on glass substrates by thermal evaporation technique with a deposit rate of (2.5±0.2) nm/sec. The thickness of the films was around (300±10) nm, and the thin films were annealed at (100, 200 and 300) °C. The structural, morphology, and optical properties of Indium selenide thin films were studied using X-ray diffraction, Scanning Electron Microscope and UV–Visible spectrometry respectively. X-ray diffraction analyses showed that the as deposited thin films have amorphous structure. At annealing temperature of 100 °C and 200 °C, the films show enhanced crystalline nature, but at 300 °C the film shows a polycrystalline structure with Rhombohedral phase with crystallites size of 17.459 nm. The results of the UV–Visible spectrometry in the wavelength range (300 – 1100) nm showed that the band gap energy of the thin films increased with increasing annealing temperature.

Keywords: InSe, Thin Film, annealing, Optical, structural, Vacuum Thermal Evaporation

1. Introduction

Numerous studies have been focused on Indium monoselenide (InSe) as a semiconducting layered compound since it exhibits a good photoelectric property and can be used as an active media for the generation of visible and near-infrared radiation[1]. InSe thin films are used as high energy radiation detectors owing to its high stability towards ionizing radiation [2]. Also, it used as solar cells due to its optical energy gap between (1 and 2) eV[3]. The problem of the preparation of high quality thin InSe films is still unsolved due to the existence of several In–Se phases [4]. Therefore, it is considered of complicated stoichiometries due to the existence of InSe, In₂Se₃, In₃Se₅, In₄Se₃, and In₆Se₇ phases [5]. Moreover, (InSe) exhibits at least three modified crystalline phases of (2H-β) (two-layer hexagonal, 2H) and (2H-γ) or (3R-δ) (three-layer rhombohedral, 3R) [6,7]. There are five relatively known phases of In₂Se₃ compound α (hexagonal), β (rhombohedral), γ (hexagonal), δ, as well as the recently discovered k phase (anisotropic structure)[7,8]. Indium selenide has two crystalline surfaces showing very different physical properties. The cleaving surface perpendicular to the z-axis consists of Se atom bounded together with covalent bonds. The other surface parallel to the z-axis is made up of Se atoms of adjacent layers being bounded by Van der Waal forces [8,9]. Depending on the deposition technique and deposition conditions, one of the crystalline forms of InSe is produced. Each form has a unique range...
of structural, optical and electronic properties [10] and thin-film growth method on substrates [11]. So far, many techniques are used to prepare InSe thin films such as chemical bath deposition [12], Spray pyrolysis [13], sol gel method [14] and thermal evaporation [15]. In this work, we firstly prepared InSe alloy at (In:Sn = 50\%:50\%), and the InSn thin films were thermally evaporated on glass substrates. The structural, Topographical and optical properties of Indium Selenide thin films were studied as a function of different annealing temperatures.

2. Experimental
In this work, InSe compound was prepared from Indium (99.99\% purity) and selenium (99.99\% purity) elements mixed into a sealed and evacuated quartz tube at (5 \times 10^{-2} \text{ mbar}), and then the quartz tube was heated at 900 °C for 1 h in a furnace followed by ice water quenching. The tube was broken to extract the substance that was grounded to be used for depositing the thin films using thermal evaporation technique under a vacuum of (3 \times 10^{-5} \text{ mbar}). Glass substrates were cleaned by detergent with ethanol and rinsed ultrasonically in deionized water. The glass slides are placed on a shaped semi ball-holder inside the thermal evaporation chamber, and the InSe compound was evaporated using Mo boat. The Indium Selenide thin films were evaporated at room temperature onto cleaned glass substrates. The thickness of the films was determined by using weighing method to be (300 ± 10) nm, and the thin films were annealed at (100, 200 and 300) °C. (XRD) patterns were obtained using a (SHIMADZU Japan -XRD600) with a CuKα source of λ=1.54059 Å to study the crystal structure of the thin films. (VEGA3-TESCAN model, USA) scanning electron microscope (SEM) was used to study the surface morphology. (UV-visible 1800 spectra photometer) in the wavelength range (300 – 1100) nm was used to study the optical properties of thin films.

3. Results and Discussion
3.1. The XRD diffraction analysis
Fig. (1) shows the XRD diffraction analysis of the InSe alloy. This result indicates the appearance of InSe, In$_2$Se$_3$ in different phases. In addition, the highest peak of (006) plane is related to the Rhombohedral structure of InSe. A few weak peaks with mixed indices indicating that in addition to the trend along c- axis (0012) and (0018), there are also some other crystalline features along (110), (116) and (119). By comparing the results with the standard cards for ICDD λ of different (InSe, In$_2$Se$_3$ , In$_3$Se$_3$, In$_5$Se$_5$, In$_7$Se$_7$…) structures, we observe the emergence of different peaks corresponding to the phases (InSe-M, InSe-R, InSe-H). Also, some peaks have compatible Miller indices, for example (116) and (114) related to the phases InSe-R and InSe-H, respectively. The peaks with incompatible Miller indices, such as (201) and (103) are related to the Monoclinic and Rhombohedral phases respectively. This is because the Rhombohedral is a special case of hexagonal structure. Similarly is applied to the In$_2$Se$_3$ structure, and Table (1) shows XRD results for the alloy.
Figure 1. XRD diffraction analysis of the InSe alloy. R means rhombohedral InSe; M means Monoclinic and H means hexagonal.

Table 1. shows XRD results for alloy

| JCPDS card No. | Phase      | 2θ abs | 2θ stand. | d-abs | d-stand. | hkl | FWHM   |
|---------------|------------|--------|-----------|-------|----------|-----|--------|
| 1-70-2541     | InSe-R     | 21.468 | 21.35     | 4.13585 | 4.1583   | 006 | 0.2077 |
| 0-34-1431     | InSe-H     | 25.66  | 25.6887   | -     | 3.465    | 100 | -      |
| 1-72-1470     | In₃Se₃-R   | 27.86  | 27.8868   | -     | 3.1966   | 009 | -      |
| 0-34-1431     | InSe-H     | 30.38  | 30.3775   | -     | 2.94     | 103 | -      |
| 1-80-2272     | InSe-M     | 32.4046| 32.4998   | 2.76064 | 2.7527   | 400 | 0.27   |
| 1-80-2272     | InSe-M     | 41.8203| 41.7474   | 2.15829 | 2.1618   | 002 | 0.2272 |
| 1-70-2541     | InSe-R     | 43.668 | 43.4989   | 2.07115 | 2.0792   | 0012| 0.2958 |
| 1-70-2541     | InSe-R     | 45.26  | 45.3049   | -     | 2        | 110 | -      |
| 1-70-2541     | InSe-R     | 50.56  | 50.6016   | -     | 1.3861   | 116 | -      |
| 1-72-1470     | In₃Se₃-R   | 51.44  | 51.4981   | -     | 1.7731   | 0114| -      |
| 0-34-1431     | InSe-H     | 56.6   | 56.667    | -     | 1.623    | 116 | -      |
| 1-71-250      | In₃Se₃-H   | 62.1   | 62.0331   | -     | 1.4949   | 227 | -      |
| 1-71-250      | In₃Se₃-H   | 63.26  | 63.3042   | -     | 1.4679   | 1112| -      |
| 0-34-1431     | InSe-H     | 67.562 | 67.5258   | =     | 1.386    | 0012| =      |
| 1-71-250      | In₃Se₃-H   | 67.8685| 67.865    | 1.37987 | 1.3799   | 233 | 0.2612 |
| 1-70-2541     | InSe-R     | 73.88  | 73.9022   | -     | 1.2814   | 214 | -      |

The XRD patterns for the as-deposited and annealed InSe thin films with 300 nm show that the as-deposited thin films are amorphous in nature. After annealing at 100°C and 200°C, the films show enhanced crystalline nature, and the film annealed at 300°C shows a polycrystalline structure. These results are in good agreement with those in reference [15]. The transformation to polycrystalline structure is due to the recrystallization process during the annealing of the thin film.Annealing process led to the cancellation of some levels presented after the growth and rearrangement of the crystalline grains within...
the lattice after taking a sufficient energy to grow and arrange [16]. This result indicates the appearance of InSe- Rhombohedral phases with the orientations of (006), (101), (104), (110), (116) and (021). The preferred orientation was along (101) R plane. The spectrum also contains two weak peaks correspond to the Se- Monoclinic phases. Table (2) Shows XRD results for InSe thin films annealed at 300 °C.

![Figure 2. X-ray diffraction analysis of thin film: R means rhombohedral of InSe thin films; M means Monoclinic of Se](image)

| JCPDS No. | Phase | 2θ abs | 2θ stand. | d-abs | d-stand. | hkl |
|-----------|-------|--------|-----------|-------|----------|-----|
| 00-042-0919 | InSe-R | 21.35 | 21.353 | 4.15 | 4.1583 | 006 |
|           | InSe-R | 26    | 25.933 | 3.423 | 3.432   | 101 |
|           | InSe-R | 29.018 | 29.432 | 3.074 | 3.029   | 104 |
|           | InSe-R | 45.29 | 45.281 | 2     | 2       | 110 |
|           | InSe-R | 50.60 | 50.581 | 1.802 | 1.8     | 116 |
|           | InSe-R | 53.08 | 52.918 | 1.72  | 1.728   | 021 |

The crystallite size was estimated from the (β) value of the preferential orientation along (101)R plane using the Scherrer relation [17]:

\[
C.s = k \frac{\lambda}{\beta \cos \theta}
\]

where C.s is the crystallite size, k ≈ 0.9, \(\lambda\) is the wavelength of X – ray radiation, \(\theta\) is the Bragg’s angle of the(101) peak in degrees, and \(\beta\) is the peak width of the diffraction peak profile at half maximum. The calculated crystallite size of the thin films was found to be 10.157 nm.

The dislocation density (δ) was estimated from relation (2) [18].

\[
\delta = \frac{1}{C.s^2}
\]
The micro strain (ε) is one of the important factors in lattice dynamics calculated from relation (3) [19].

\[ \varepsilon = \beta \frac{\cos \theta}{4} \]  
(3)

The number of crystallites per unit surface area (N₀) was calculated using relation (4) [20].

\[ N_0 = \frac{t}{C_s S^3} \]  
(4)

where \( t \) is the thickness of the thin film

The calculated Crystallite size, dislocation density, micro strain and the number of crystallites per unit surface area for the preferred orientation along (101)R plane of InSe thin film annealed at 300 °C were listed in Table 3.

Table 3. Crystallite size, dislocation density, micro strain and the number of crystallites per unit surface area for InSe thin film annealed at 300 °C.

| 2Ø (degree) | hkl | β(deg) | β (rad) | C.s(nm) | δ (nm)^2 | ε   | N₀ (nm)^2 |
|-------------|-----|--------|---------|---------|----------|------|-----------|
| 26          | 101 | 0.839  | 0.0146  | 10.157  | 0.0097   | 0.0035 | 0.286     |

Due to the convergent change in the structural properties of the annealed films at temperatures of (100 and 200) °C, we will ignore the morphology and optical properties of the film annealed at 200°C.

3.2 Morphology

Scanning electron microscope (SEM) was used to study the thin film surfaces. Morphological information of these thin films is shown in figures (3, 4 and 5).

The as deposited film shows a particle size of (50nm). While the films annealed at 100 °C and 300 °C show particle sizes of (300nm) and (280nm) respectively.

![Figure 3. SEM images of as deposited InSe thin film at different resolution.](image)
3.3 Optical Properties

The absorbance spectra of as deposited and annealed (InSe) thin films are shown in figure (6). It is observed that the maximum absorption at a wavelength range of (300 -700) nm is suitable for the solar cell applications in this region.
Figure 6. Absorption of InSe thin films as a function of annealing temperature: at (as-prepared, 100 and 300)°C.

Figure (7) shows the transmittance spectra of InSe thin films at different annealing temperature. We noticed that the maximum transmittance at a wavelength range of (1000 -1100) nm at (as-prepared, 100 and 300)°C. The annealing temperature plays an important role in the transmission spectrum by increasing transmission. On the other hand, the film annealed at 300 °C shows improved transmission compared to that annealed at 100 °C. This tuning of transmission by annealing indicates their utility as various technological applications. The film deposited with higher annealing temperatures shows a higher transmittance. These results agreed well with [16].
Figure 7. The transmittance of InSe thin films as a function annealing temperature: at (as-prepared, 100, and 300) °C.

The absorption coefficient ($\alpha$) behaves as absorption behavior, and ($\alpha$) was determined by equation 5) [21]:

$$\alpha = 2.303 \frac{A}{l}$$

(5)

A is the absorption
Figure 8. The variation of the absorption coefficient with energy for InSe thin films as a function of annealing temperature: (as-prepared, 100 and 300 °C).

The extinction coefficient \( (K) \) of InSe thin films were determined by equation (6) [22,23].

\[
k = \frac{\alpha \lambda}{4\pi} \tag{6}
\]

Figure 9. Extinction coefficient Vs Wavelength of InSe thin films: as a function of annealing temperature at (as-prepared, 100 and 300) °C
The optical band gap was calculated by Tauc’s extrapolation method [24].

\[ \alpha h\nu = B(h\nu - E_g)^r \]  

(7)

where : (h) Planck’s constant, (v) frequency of the photon, (B) Constant and r is constant depends on the nature of transitions, r =1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively.

Compared to the plot of \((\alpha h\nu)^2\) variation with \(h\nu\) for the determination of direct band gap \(E_g\) which is shown in Figure 10. The optical band gap values are showed in Table 4.

![Figure 10](image)

**Figure 10.** Plot of \((\alpha h\nu)^2\) versus \((h\nu)\) for InSe thin films as a function of annealing temperature (as-prepared, 100 and 300 °C)

The band gap energy increases with increasing annealed temperature. The optical band gap values changes from 1.55 to 1.75 eV. The value of \(E_g\) is in good agreement with the reported values (1 – 2 eV) for InSe films. Table 4 shows the values of band gap energy for annealed InSe thin films.

The reduction in the number of unsaturated defects decreases the density of localized states in the band structure, consequently increasing the band gap [25].

**Table 4.** Bandgap variation of InSe with different annealing temperatures.

| Temp. °C     | Eg(eV) |
|--------------|--------|
| as-prepared 27 | 1.55   |
| 100          | 1.65   |
| 300          | 1.75   |

4. Conclusion

In_{50}Se_{50} bulk samples are prepared by melt quenching technique and thin films of powdered alloys are deposited using thermal evaporation technique. The XRD pattern revealed that the as deposited films are amorphous in nature and annealed at 300°C films exhibit polycrystalline nature. It was found that the physical properties of the films are heavily affected by annealing temperature. The absorption
edge and optical band gap depended on the crystalline structure. This tuning of transmission and band gap on annealing temperature indicates their utility in various technological applications.

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