Composition dependent structural phase transition and optical band gap tuning in InSe thin films

Harpreet Singh a,b, Palwinder Singh a,b, Randhir Singh c, Jeewan Sharma c, A.P. Singh d, Akshay Kumar e, Anup Thakur b,*

a Department of Physics, Punjabi University, Patiala, 147 002, Punjab, India
b Advanced Materials Research Lab, Department of Basic and Applied Sciences, Punjabi University, Patiala, 147 002, Punjab, India
c Department of Nanotechnology, Sri Guru Granth Sahib World University, Fatehgarh Sahib, Punjab, 140 407, India
d Department of Physics, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar, Punjab, 144 011, India

* Corresponding author.
E-mail address: dranupthakur@gmail.com (A. Thakur).

ABSTRACT

Bulk alloys of In$_x$Se$_{100-x}$ (x = 5, 10, 20, 30, 40 and 50) are prepared using melt quenching technique. Thin films having thickness ~750 nm of these prepared bulk alloys are fabricated using thermal evaporation technique on glass substrate. The as-deposited In$_x$Se$_{100-x}$ thin films with x ≤ 40 are amorphous and In$_{50}$Se$_{50}$ thin film is crystalline in nature verified from X-ray diffraction (XRD). The change in morphology of deposited thin films with indium content also verifies structural phase transition and found that the phase transition started with x = 40 which is not detected in XRD pattern. The drastic change in transmission is found with 50% indium content. In$_{50}$Se$_{50}$ thin film has less than 30% transmission whereas other films are highly transparent. Optical band gap is calculated using Tauc’s plot and decrease in optical band gap is observed with indium content. The variation of optical band gap from 1.88 eV to 1.12 eV is achieved with induction of 5%–50%. The structural transition and change in optical band gap depict that InSe thin films are potential candidates in various technological applications.

1. Introduction

Chalcogenide alloys, consisting of chalcogen elements (S, Se and Te) or these elements as major constituents, are gathering attention from researchers and technological world because of their wide range of applications. Chalcogenide alloys are important materials for technologically important devices, such as optical data storage [1, 2], phase change random access memory [3, 4], near-infrared transmission window [5, 6], electrical switching [7, 8], optical fiber [9], solar cell [10], xerography [11] etc.

Indium selenide (InSe) is an important material and it belongs to a special semiconductor alloys group III-VI. The structural, optical [12, 13, 14], electronic [15, 16] and electrical [17, 18, 19] properties of InSe have been studied by various researchers. It is a layered semiconductor made of stacked layers of Se–In–In–Se atoms [20]. InSe is a potential material for solar cell [21, 22, 23, 24, 25], diode [25], electrical switching [26], nonlinear optics [27], photodetector [28, 29, 30], photoinduced structural transformations [14], strain engineering [31] and microelectronics [18]. InSe thin films have been deposited using various physical and chemical methods [13, 14, 32, 33].

The property contrast accompanied by phase transition is an important aspect of chalcogenide materials for various applications. The flexible structure of chalcogenide is responsible for this phase transition. The phase transition in chalcogenide thin films is achieved by vacuum annealing [34], pressure [35] etc. Such phase transition can also be achieved by incorporation of suitable dopant with proper content in chalcogenide alloys [36].

In the present research work, effect of indium content in InSe thin films is investigated in reference to structural and optical properties. Bulk alloys and thin films of In$_x$Se$_{100-x}$ (x = 5, 10, 20, 30, 40 and 50) have been prepared using melt quenching and thermal evaporation, respectively. The structural properties of as-prepared In$_x$Se$_{100-x}$ thin films are investigated using X-ray diffraction. The morphology of as-prepared thin films is studied using field emission scanning electron microscope. The transmission spectrum is analyzed and the optical band gap is calculated. Some physical parameters have also been calculated and an effort has been made to correlate these parameters with structural properties.
2. Experimental details

Bulk alloys of In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and $50$) are prepared using melt quenching method [37, 38]. Here, $x$ denotes the atomic-weight percentage of elements. Highly pure (5N) elements are purchased from Sigma-Aldrich. For each stoichiometry, elements are weighed according to atomic weight percentage and poured into the quartz ampoules. These ampoules are sealed using torch equipped with oxygen and liquefied petroleum gas under the base pressure of $\sim 5 \times 10^{-6}$ mbar to remove the possibility of any reaction of alloy with oxygen at elevated temperature. The sealed ampoules are heated in the increasing order of the melting point of constituent elements and after that rocking is performed to ensure the homogeneity of the mixture. Heated and rocked ampoules are quenched in ice-water after 24 h. The ingot is powdered using mortal pestle. Thin films of In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and $50$) prepared alloys are deposited on pre-cleaned glass substrates using thermal evaporation method [11, 37] using the Hind High Vacuum system (Model: BC-300) under a base pressure better than $6 \times 10^{-6}$ mbar. Thickness of deposited thin films is monitored in-situ using a digital thickness monitor (Hind High Vacuum, DTM-101). The structural properties of deposited thin films are checked by X-ray diffraction (XRD) using X-ray diffractometer (XPERT PRO PANalytical) with radiation of Cu K$_{\alpha}$ ($\lambda = 1.5406$ Å). For morphological study, field emission scanning electron microscope (FE-SEM) images are obtained using Hitachi-SU8010 and the composition of as-deposited thin films is measured by double beam UV-visible-NIR spectrophotometer (Varian Cary-S000) in the wavelength range of 500–1200 nm.

3. Results and discussion

3.1. Physical parameters

In chalcogenide alloys, the variation in mean coordination number ($<m>$) is due to the change in local structure. The value of $<m>$ can be calculated using Eq. (1) for In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and $50$) binary alloys.

$$<m> = \frac{aN_{In} + bN_{Se}}{a+b}$$

where $a$ and $b$ denote the values of atomic percentages of indium and selenium, respectively. Here $N_{In}$ and $N_{Se}$ are the coordination number of indium and selenium, respectively. The values of average coordination number of In$_x$Se$_{100-x}$ alloys are listed in Table 1. It is found that the value of $<m>$ increases with indium content in In$_x$Se$_{100-x}$ binary alloy. In covalent solids, there are two main neighbor bonding configurations; one is the bond stretching and other is the bond bending. These bonding configurations can be related to the value of $<m>$. $n_a$ number of bond stretching constraint, is related with $<m>$ as $<m>/2$, and $n_b$ bond bending constraint, is related with $<m>$ as $2 <m> - 3$. It is found that the values for $n_a$ and $n_b$ increases with indium content and are listed in Table 1.

Chalcogenide alloys exhibit floppy or rigid region depending upon the value of $<m>$. The amount of floppy modes can be calculated using Eq. (2).

$$f = 2 - \frac{5}{6} <m>$$

(2)

The calculated values for the amount of floppy modes are tabulated in Table 1. It is observed that the value of $f$ decreases with indium content. Chalcogenide alloys exhibit structural relaxation due to the presence of lone pair of electrons. The number of lone pair of electrons is correlated with the vitreous state of chalcogenide alloys by Zhenhua [39]. Number of lone pair of electrons can be calculated using relation $L = V - <m>$, here $L$ and $V$ are the number of lone pairs of electron and valence electrons, respectively. The calculated number of lone pair of electrons is tabulated in Table 1. It is found that the number of lone pair of electrons decreased as indium content is increased in In$_x$Se$_{100-x}$ alloy.

The increase in the values of $<m>$, $n_a$, $n_b$ and decrease in $f$ and $L$ is also found with the incorporation of small amount of antimony in selenium [40]. The changes in physical parameters have also been observed in other chalcogenides with doping [41, 42].

3.2. Structural and morphological study

XRD patterns of as-prepared In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and $50$) thin films are shown in figure 1. It is clear from this figure that there is no sharp peak in XRD patterns of films with $x \leq 40$. This suggests that as-prepared In$_x$Se$_{100-x}$ films with $x \leq 40$ are amorphous in nature. On the other hand, XRD pattern of In$_5$Se$_5$ film has a sharp peak at 33.6° which matches with the monochinic phase [43, 44, 45] of InSe with space group P21. So, structural transition from the amorphous phase to crystalline

### Table 1. Values of $<m>$, $n_a$, $n_b$, $f$, $V$ and $L$ for In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and $50$) thin films.

| $x$ | $<m>$ | $n_a$ | $n_b$ | $f$ | $V$ | $L$ |
|-----|-------|-------|-------|-----|-----|-----|
| 5   | 2.05  | 1.03  | 1.1   | 0.292 | 5.95 | 3.9 |
| 10  | 2.10  | 1.05  | 1.2   | 0.250 | 5.90 | 3.8 |
| 20  | 2.20  | 1.10  | 1.4   | 0.167 | 5.80 | 3.6 |
| 30  | 2.30  | 1.15  | 1.6   | 0.083 | 5.70 | 3.4 |
| 40  | 2.40  | 1.20  | 1.8   | 0     | 5.60 | 3.2 |
| 50  | 2.50  | 1.25  | 2.0   | -0.083 | 5.50 | 3.0 |
phase is achieved with higher indium content in In$_x$Se$_{100-x}$. The change in structure from amorphous to the crystalline phase of In$_x$Se$_{100-x}$ thin films with indium content can be understood from change in the physical parameters (Table 1).

Figure 2 (a–c) show the morphology of as-deposited In$_x$Se$_{100-x}$ ($x = 5, 40$ and $50$) thin films. In$_5$Se$_{95}$ thin film has uniform and smooth morphology without any growth of crystallites. This also confirms the amorphous nature of thin film. The change in morphology is observed with higher indium content ($x = 40$). FE-SEM micrographs show that phase transition starts at $x = 40$, which is not detected through XRD. In$_{50}$Se$_{50}$ thin film has large crystallites compared to In$_{50}$Se$_{50}$. The drastic change in morphology confirms the phase transition from amorphous to crystalline phase in InSe thin films. Figure 2(d–f) show EDS spectra of as-deposited In$_x$Se$_{100-x}$ ($x = 5, 40$ and $50$) thin films, presence of indium and selenium X-ray peaks confirm the local composition of films.

### 3.3. Optical study

The optical transmission of as-deposited In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and $50$) thin films in the wavelength range of $500–1200$ nm is shown in figure 3. The appearance of interference fringes are the signature of smooth and uniform films [46,47]. Thin films with indium content $x \leq 40$ are highly transparent with transmission more than $50\%$. But the drastic change in transmission is observed in In$_{50}$Se$_{50}$ film. In$_{50}$Se$_{50}$ film has transmission less than $30\%$. The decrease in transmission also confirms the phase transition in In$_{50}$Se$_{50}$ film. The decrease in transmission may be due to increase in scattering with In addition [48].

The optical transmission of In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and $50$) thin films shows a strong absorption edge in the wavelength region of $550–650$ nm, but for In$_{50}$Se$_{50}$ it is around $800$ nm. The strong absorption in the material normally occurs because of the band transitions of carriers. It is observed from figure 3 that the absorption edges show red shift.
with indium addition. The absorption coefficient ($\alpha$) is inherent property of material which helps to derive other optical properties. It is calculated using the following relation [49]:

$$\alpha = \frac{1}{t} \ln \frac{1}{T}$$

(3)

where $T$ is optical transmission and $t$ is the thickness of film. The estimated thickness measured using DTM of as-prepared films is ~750 nm. The optical band gap can be calculated using the relation given by Eq. (4) known as Tauc’s relation [50]:

$$a\nu = \beta (\nu - E_g)^n$$

(4)

where $h\nu$, $\beta$ and $E_g$ denotes the photon energy, band tailing parameter and optical band gap, respectively. The parameter $n$ can have different values depending upon the nature of transition. So, $n$ can be 1/2, 2, 3/2 and 3 for direct allowed transition, indirect allowed transition, direct forbidden transition and indirect forbidden transition, respectively. From literature, the value of $n$ is 2 used for InSe thin films [13,51,52]. Figure 4 shows the variation of $(a\nu)^{0.5}$ with energy for the thin films. The value of optical band gap is obtained from figure 4 and found that it changes significantly from 1.88 eV to 1.12 eV as indium content increases.

The values of optical band gap for In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and 50) thin films can also be estimated theoretically [53] using Eq. (5):

$$E_{bg}^b(PQ) = Y E_g(P) + (1 - Y) E_g(Q)$$

(5)

where $Y$ denotes fraction of each element in the stoichiometry. For the stoichiometric alloy PQ, $E_g(P)$, $E_g(Q)$ and $E_{bg}^b(PQ)$ are the values of optical band gap for elements P, Q and alloy PQ, respectively. The values for optical band gap for indium and selenium are used as 0.2 eV and 1.95 eV, respectively. The variation of optical band gap, calculated experimentally and theoretically, is shown in the inset of figure 4. It is clear from inset that experimentally and theoretically calculated values of optical band gap are in close agreement. The optical band gap with indium addition in amorphous thin films can be understood from density of localized states in the forbidden gap. The localized states in the forbidden band gap in chalcogenide alloys have been described through various models [54]. The presence of these localized states indicates the formation of defects, which originate due to valence band formation through lone pairs in chalcogenides. Thus, addition of indium in selenium matrix will give rise to additional absorption over a wide range of energy which leads to band tailing and shrinking of optical energy gap. The decrease in optical band gap in In$_{50}$Se$_{50}$ is because of change in phase from amorphous to crystalline [55].

Figure 3. Transmission spectra of as-deposited In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and 50) thin films.

Figure 4. The variation of $(a\nu)^{0.5}$ with $h\nu$ for In$_x$Se$_{100-x}$ ($x = 5, 10, 20, 30, 40$ and 50) thin films. Inset shows the variation of experimentally observed and theoretically calculated optical band gap with indium content.
4. Conclusions

In$_50$Se$_50$, x = 5, 10, 20, 30, 40 and 50) bulk alloys and thin films (thickness ~750 nm) are prepared using melt quenching and thermal evaporation technique, respectively. X-ray diffraction patterns reveal that In$_50$Se$_{50+x}$ with x ≤ 40 thin films are amorphous in nature and phase transition from amorphous to crystalline has been achieved with x = 50 in In$_20$Se$_{80}$ thin film. The morphology of amorphous thin films is smooth and uniform. The drastic change in morphology is observed with structural transition. FE-SEM micrographs verify that the phase transition in In$_50$Se$_50$ thin films is reversible near-infrared window, Phys. Rev. Appl. 10 (5) (2018), 054070.

Additional interest statement

The authors declare no conflict of interest.

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