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Effects of Additives on Structural and Optical Properties of Selenium Thin Films

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***Abstract*—** Chalcogenide alloys are highly explored due to their various technological applications. In present study, effect of additives on structural and optical properties of a-Se thin films is observed. Bulk samples of a-Se, $In_{50}Se_{50}$ (InSe) and $Sb_{50}Se_{50}$ (SbSe) are prepared using melt quench technique. Thin films of powdered samples have been deposited by thermal evaporation technique. X-ray diffraction study reveals that Se and SbSe thin films are amorphous in nature, whereas InSe thin films are crystalline in nature which indicates about phase change upon In incorporation. The change in morphology due to phase change, studied by field emission scanning electron microscopic image, is also shown. The optical transmission is also found to vary with Sb and In alloying. The optical band gap decreases greatly in SbSe with slight decrease in transmission, whereas in InSe, transmission reduced drastically with decrease in band gap. The decrease in transmission in InSe is attributed to the phase change in InSe thin films. The tuning of band gap and transmission upon In and Sb addition makes them applicable for various technological applications.

***Keywords*—** Chalcogen, melt quenching, thermal evaporation, phase change material, optical transmission.

I. Introduction

Chalcogenide alloys are widely investigated recently due to their utility in various fields such as in photonic devices [1], optical data storage [2,3], reversible phase change optical recording materials [4,5], optical waveguides in infrared biosensors [6] and switching devices [7] and near infrared transmission window [8,9]. The wide range of applicability of chalcogenide alloys is due to their high refractive index [10,11,12], low phonon energy [12] and high nonlinearity [13,14] which makes them attractive for their application in above mentioned fields.

Among chalcogenides, amorphous selenium (a-Se) is widely explored semiconductor having applications in high gain avalanche rising photoconductor video tubes [15], switching memory devices [16], xerographic machines [17] etc. But due to low thermal stability, low sensitivity and ageing effect have put a bar on its utility. Incorporation of metals or metalloids in Se is found to affect its optical properties to a greater extent.

In present study, effect of metal (In) and metalloid (Sb) addition on structural and optical properties of a-Se is studied. Thin films of a-Se, $Sb_{50}Se_{50}$ (SbSe) and $In_{50}Se_{50}$ (InSe) are deposited using thermal evaporation technique. Both additives are seen to affect the structural and optical properties of deposited thin films.

II. Related Work

Singh *et al.* [9] have reported that the interplay of phase change property and optical transmission in chalcogen based thin films. The change in optical transmittivity with change in phase can be used for their utility as reversible NIR window.

In context with additives in Se thin films, Kaur *et al.* [18] have done a systematic study on Sb incorporation in Se thin films. Sb alloying affects the optical transmission greatly by shifting the absorption edge to longer wavelength side. It is further reported that the shift in optical transmission/decrease in band gap is due to increase in electron deep traps with Sb doping. Other research groups have also reported that Sb addition decrease the band gap of the Se thin films with significant red shift in absorption edge [19.20].

Similarly, Qasrawi *et al.* [21] studied the effect of In doping on various properties of Se thin films. In doping induces phase change in Se thin films which further resulted in decrease in band gap.

III. METHODOLOGY AND CHARACTERIZATIONS

Bulk samples of a-Se, $Sb_{50}Se_{50}$ (SbSe) and $In_{50}Se_{50}$ (InSe) were prepared by melt quenching technique [22]. The precursors used were 5N pure (Sigma Aldrich) and were weighed according to their atomic weight percentages. These were sealed in quartz ampoules using LPG torch under base pressure of ~ 5 × 10^{-5} mbar. The sealed ampoules were heated in muffle furnace in increasing order of melting point of constituent elements, which were further heated and rocked in rocking furnace for 24 hours to ensure the homogeneity of alloys. The ampoules were then quenched in liquid nitrogen and the ingots were powdered using mortar and pestle.

Thin films of powdered alloys were deposited on glass substrate using thermal evaporation technique using Hind High Vacuum System (Model: BC-300) under the base pressure of ~ 5 × 10^{-6} mbar. *In-situ* thickness monitoring of deposited films was done with the help of digital thickness monitor (Hind High Vacuum, DTM-101).

The structural property of deposited thin films was studied using X-ray diffraction (XRD) with the help of X-ray diffractometer (X'Pert PRO PANalytical) with Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å). Morphological study was done by field emission scanning electron microscopy (FE-SEM) technique using Hitachi-SU8010. The optical transmission of deposited thin films was measured by double beam UV-visible-NIR spectrophotometer (Varian Cary-5000) in the wavelength range of 400-2400 nm.

IV. RESULTS AND DISCUSSION

A. Structural and morphological study

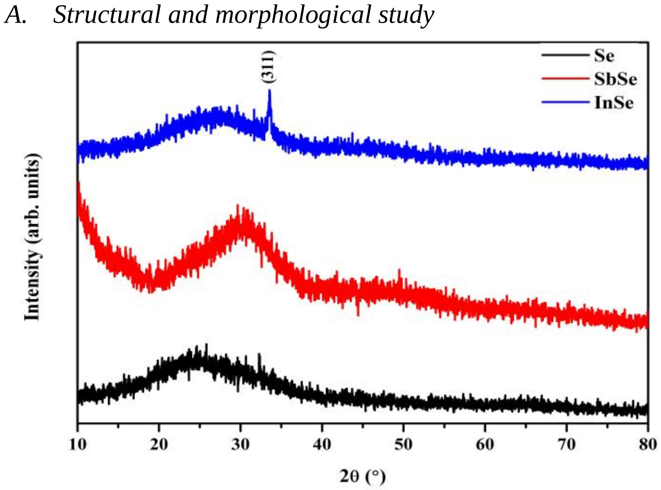

Figure 1. X-ray diffraction patterns of a-Se, SbSe and InSe thin films.

Figure 1 represents the XRD of a-Se, SbSe and InSe thin films. It is clear from the fig. 1 that a-Se is amorphous in nature as there is no sharp diffraction peak in its XRD spectra. Addition of Sb in Se does not affect the crystallinity of sample. The hump appearing at 25° is shifted to higher side (~ 30°) and increased in intensity. The overall alloy is amorphous in nature. On the other hand, addition of In in Se affects the crystallinity of Se thin films significantly. There appears a sharp diffraction peak at 33.6° which matches with monoclinic phase of $In_{50}Se_{50}$ (ICSD 071083). This shows that addition of In produced a phase change in a-Se.

Similarly, additives in a-Se also affect the morphology of thin films. The morphology of a-Se and SbSe is smooth (not shown here), as these films are amorphous in nature. The change in phase of InSe also affects the morphology drastically. Figure 2 is representing FE-SEM micrographs of InSe thin films at different resolutions. The crystallite growth is easily seen with round morphology.

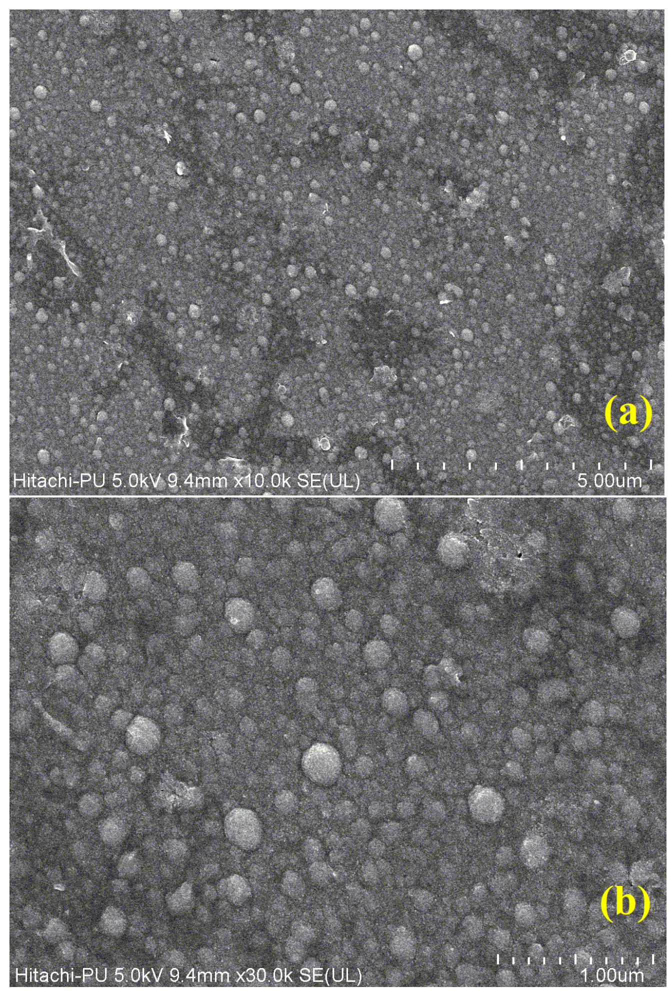

Figure 2. Field emission scanning electron microscopic image of InSe at different resolution scales.

B. Optical study

The optical transmission of a-Se, SbSe and InSe thin films is shown in fig. 3. The absorption edge of a-Se thin films shows a sharp rise at ~ 580 nm due to band transition of charge carriers. On addition of Sb and In, absorption edge shows drastic shift in absorption edge and change in transmission features. The shift in absorption edge indicates about change in optical band gap and decrease (or increase) in transmission indicates about increase (or decrease) in crystallinity. For SbSe, the absorption edge red shifted to ~ 946 nm and the transmission also decreases slightly. Ramandeep *et al.* [17] have reported effect of different concentration of Sb in Se. They stated that red shift in absorption edge, which is due to decrease in optical band gap, is attributed to increase in concentration of electron deep traps. On the other hand, addition of In strongly decreased the transmission of thin films. The decrease in transmission is due to increase in crystallinity of thin films. The red shift in absorption edge (~ 796 nm) is due to decrease in band gap of a-Se on incorporation of In. It is worthy to note here that the band edge of InSe is not as sharp as that of a-Se and SbSe. This is indicating that In additions induced the band tailing which results in leaning of absorption edge. Hence, the effect of additives in a-Se is helpful in optical band gap tuning. This tuning of band gap and transmission by using additives can be used for various potential applications.

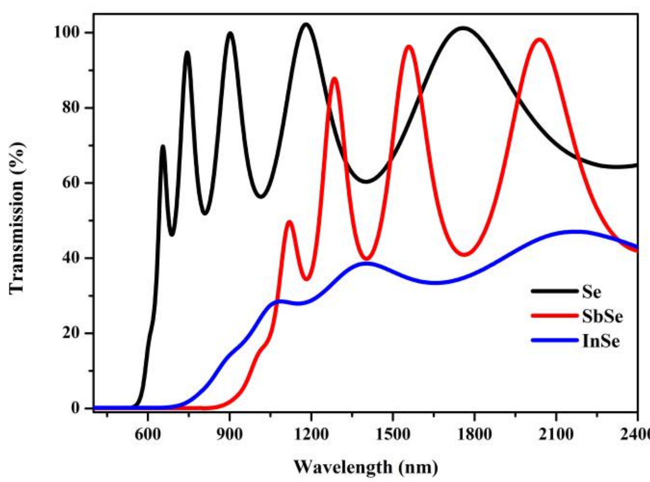

Figure 3. Transmission spectra of a-Se, SbSe and InSe thin films.

V. CONCLUSION

a-Se, $In_{50}Se_{50}$ and $Sb_{50}Se_{50}$ bulk samples are prepared by melt quenching technique and thin films of powdered alloys are deposited using thermal evaporation technique. The addition of In is observed to induce phase change from amorphous phase of Se to monoclinic phase of InSe, whereas Sb addition does not affect the phase of Se. The optical properties are heavily affected by In and Sb addition. Sb addition red shifted the transmission edge due to decrease in band gap but with slight decrease in transmission. On the other hand, In addition causes less red shift as compared to Sb but strongly decreased the transmission. In addition is also observed to cause band tailing in InSe thin films. This tuning of transmission and band gap on Sb and In addition indicates about their utility as various technological applications.

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Authors Profile

Harpreet Singh completed his Master of Science in Applied Physics from Punjabi Univeristy, Patiala in 2014. He is currently pursuing Ph.D. in Punjabi University, Patiala and is awarded fellowship from University Grant Commission, New Delhi. His main research work focuses on phase change chalcogenide materials for various technological applications.

