

STRUCTURAL AND OPTICAL INVESTIGATIONS OF AMORPHOUS TERNARY $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ THIN FILMS

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Amorphous thin films of $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x=0,3,6,9$) have been deposited on chemically cleaned glass substrate by thermal evaporation technique under vacuum. Glassy nature of the films has been verified by X-ray diffraction pattern. The analysis by absorption spectra measured at normal incidence, in the spectral range 400-1100 nm has been used for the optical characterization of thin films under investigation. The optical constants (absorption coefficient (α), extinction coefficient (k) and optical band gap (E_g)) have been studied. It is found that the absorption coefficient (α) increases with increase in incident photon energy and In content. Optical band gap (E_g) has also been calculated and found to decrease with In content in $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x=0,3,6,9$) glassy system. The decrease of optical band gap (E_g) with In concentration has been explained on the basis of Mott and Davis model.

(Received February 25, 2015; Accepted April 10, 2015)

Keywords: Amorphous semiconductor, Thin films, Optical properties, Absorption coefficient, Optical band gap

1. Introduction

Chalcogenide glasses are obtained by mixing of chalcogen elements, viz, S, Se and Te with elements of periodic table such as Ga, Sb, In, Bi, Ag, As, Cd and Zn etc. In these glasses short range inter atomic forces are pre-dominantly covalent: strong in magnitude and highly directional, where as weak Vander Walls forces contribute significantly to the medium range order.

The optical properties of chalcogenide glasses make them candidate materials for a variety of optical applications such as infrared transmission and detection, memory switches, optical fibers, integrated and nonlinear optics, memory storage media, chemical and biosensors etc [1-10]. Chalcogenide glasses have received little attention until recently due to traditional silicon technology. However, the use of silicon as an optoelectronic material is rapidly approaching its physical limitations, making chalcogenide materials to receive attention worldwide. Chalcogenide glass of selenium exhibits reversible transformation property [11] useful in optical memory devices [12-14]. Apart from these applications amorphous selenium has been found to have tremendous potential in xerographic applications and therefore, a lot of attempts have been made to improve its property by alloying [15-17].

Though amorphous selenium has got various device applications, however pure selenium is thermally unstable and less photosensitive to electromagnetic radiations. To overcome these problems, selenium is usually doped with other elements like lead (Pb), antimony (Sb), Tellurium (Te), germanium (Ge), Bismuth (Bi) which improves its crystallization temperature, aging effect and sensitivity [18-20]. In the present work In has been chosen as an additive element in amorphous Se-Te matrix. Addition of a third element to binary selenium alloy expands the glass forming area and also creates compositional and configurational disorder in the material which will be useful in understanding the structural, electrical and optical properties of chalcogenide

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glasses[21-31].The incorporation of third element like In in Se-Te binary alloy is expected to change the optical and electrical properties of host alloy,which play a major role in device preparation. The aim of present paper is to study the effect of In incorporation on the optical properties of Se-Te matrix.The optical absorption spectra of the films of $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0,3,6,9$) are measured in the wavelength range 400-1100nm,by double beam UV-Vis spectrophotometer. The optical constants (absorption coefficient (α)), extinction coefficient(k)) as well as band gap (E_g), which are supposed to be most significant parameters in amorphous semiconducting thin films, have been investigated in the present study.

2. Experimental

The bulk samples of $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x= 0,3,6,9$) were prepared by melt quenching technique.The appropriate amount of high purity of Se,Te and In (5N) in accordance with their atomic percentage were weighted using an electronic balance(LIBROR AGE 120,Japan) with the least count of 10^{-4} gm. This was followed by sealing in quartz ampoule evacuated to 10^{-5} Torr to avoid sample contamination. A high vacuum pumping system (Vacuum Technique Pvt. Ltd. Bangalore, Model: VT-ACG-03) is used for this purpose. The ampoule containing materials were heated to 800°C and were held at that temperature for 12 hours. The temperature of furnace was raised slowly at a rate of $4^\circ\text{C}/\text{minute}$ to avoid unnecessary build up of vapour pressure in the quartz ampoule to obtain homogeneous glassy alloy. During heating process the ampoules were constantly rocked by rotating a certain rod to which the ampoules were tucked away in the furnace. After rocking about 12 hours obtained melt was rapidly quenched in ice cool water.The ampoules were broken to obtain the quenched sample. Thin film of glassy Se-Te-In alloys were prepared by vacuum evaporation technique for which substrate was kept at room temperature at a base pressure of 10^{-6} Torr using a molybdenum boat. The films were kept inside the deposition chamber for 24 hours to achieve the metastable equilibrium[32]. The thickness of the film was measured by using a single crystal thickness monitor. The XRD pattern of the films were recorded with the help of x-ray spectrophotometer (XPRT-PRO) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54\text{\AA}$). The tube was operated at 45kV and 35 mA. The normal incidence absorption spectra of $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0,3,6,9$) thin film have been taken by a double beam UV-VIS computer controlled spectrophotometer (ECIL-Hyderabad, India, Model No. 5704 SS) in the wavelength range 400-1100nm.

3. Result and discussion

3.1 Structural property

The XRD pattern for $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x=0,3,6,9$) has been shown in Fig. 1.The X-ray diffraction patterns indicate that the films are amorphous in nature.

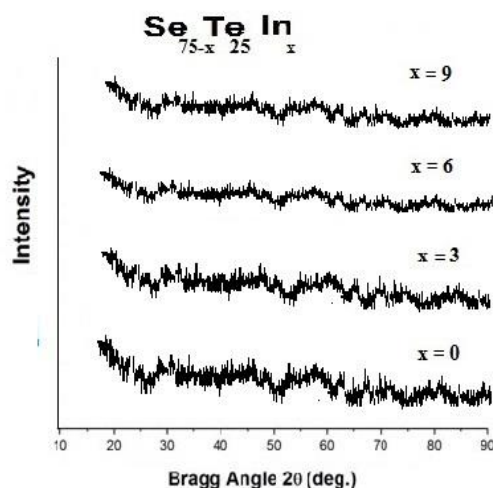


Fig.1XRD pattern of $Se_{75-x}Te_{25}In_x$ ($x = 0, 3, 6, \& 9$) thin films.

3.2 Optical Properties

3.2.1. Absorption coefficient and optical band gap (E_g)

The absorption coefficient of $Se_{75-x}Te_{25}In_x$ ($x = 0, 3, 6, \& 9$) films can be calculated using the well-known relation (1) [33-35].

$$\alpha = \text{optical density} / \text{thickness} \quad (1)$$

A plot of absorption coefficient (α) as a function of photon energy ($h\nu$) is given in Fig. 2, and values are given in Table 1. It has been observed that absorption coefficient (α) increases with increase in photon energy ($h\nu$) as well as Indium concentration, for all the samples of $a-Se_{75-x}Te_{25}In_x$.

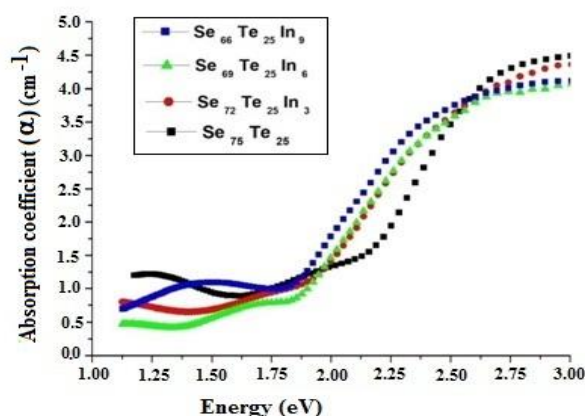


Fig.2 Variation of absorption coefficient (α) with photon energy ($h\nu$) in $Se_{75-x}Te_{25}In_x$ ($x = 0, 3, 6, \& 9$) thin films.

The values for the optical band gap (E_g), absorption coefficient (α) and extinction coefficient (k) for glassy alloys $Se_{75-x}Te_{25}In_x$ ($x = 0, 3, 6 \& 9$) has been shown in the table 1.

Table 1 Optical band gap (E_g), absorption coefficient (α) and extinction coefficient (k) for $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ glassy system

S.No.	Sample	Optical Band Gap (E_g) in eV	Absorption coefficient (α) (cm^{-1})	Extinction coefficient (k) 10^{-4}
1.	$\text{Se}_{75}\text{Te}_{25}$	1.41	2.23777	890.8
2.	$\text{Se}_{72}\text{Te}_{25}\text{In}_3$	1.40	5.94092	2365.0
3.	$\text{Se}_{69}\text{Te}_{25}\text{In}_6$	1.38	6.00163	2775.4
4.	$\text{Se}_{66}\text{Te}_{25}\text{In}_9$	1.36	6.03365	2846.6

The analysis of the absorption coefficient has been carried out to obtain the optical band gap (E_g). The optical band gap has been determined from absorption coefficient data as a function of $(h\nu)$ by using Tauc relation [36-38].

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (2)$$

Where A is the edge width parameter representing the film quality, which is calculated from the linear part of this relation and E_g is the optical band gap of the material. The variation of $(\alpha h\nu)^{1/2}$ with $(h\nu)$ for a- $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ films are shown in Fig 3.

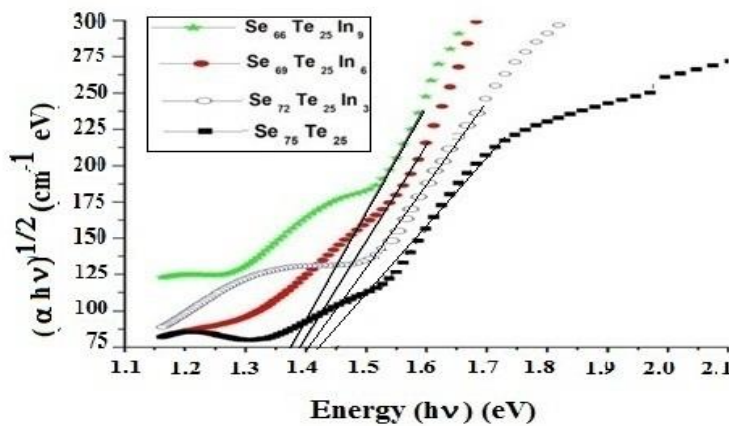


Fig.3 Variation of $(\alpha h\nu)^{1/2}$ with $(h\nu)$ in a- $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ ($x = 0, 3, 6, \& 9$) thin films.

The values of indirect band gap (E_g) have been calculated by taking the intercept on the x-axis. The calculated values of E_g for all glassy samples of a- $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ are given in Table 1. It is evident from the Table 1 that the values of optical band gap (E_g) decreases with increasing In concentration. The decrease in optical band gap E_g indicates an increase in the density of defect states (DOS). The decrease in the optical band gap could also be discussed on the basis of density of state model proposed by Mott and Davis [38]. Chalcogenide thin films always contain a high concentration of unsaturated bonds or defects. These defects are responsible for the presence of localized states in the amorphous band gap.

The decrease in E_g along with the increase in the density of defect states may also be correlated with the electronegativity of the elements involved. The valence band in chalcogenide glasses is constituted by lone pair p-orbital contributed by the chalcogen atoms [39]. These lone pair electrons will have a higher value of energies adjacent to electropositive atom than those of the electronegative atoms. Thus the addition of an electropositive element to the electronegative element may raise the energy of lone pair states, which is further responsible for the broadening of the valence band inside the forbidden gap. The electronegativities of Se, Te and In are 2.4, 2.1 and 1.7 respectively. Since In has lower electronegativity than Se, the substitution of In for Se may

raise the energy of lone pair states, which may be further responsible for the broadening of the valence band. This leads to band tailing and hence shrinking of the band gap. Therefore, E_g decreases with In content.

Variation of (E_g) with In concentration in a- $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ is shown in Fig.4.

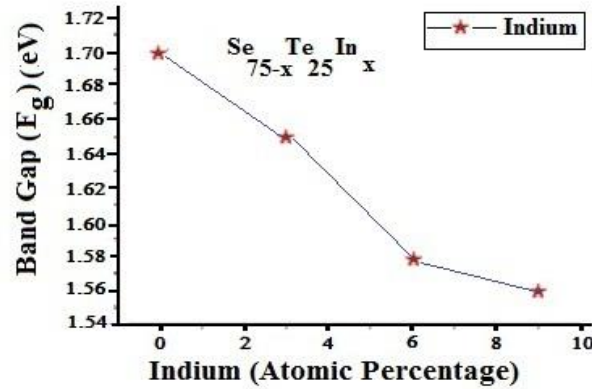


Fig. 4 Variation of optical band gap (E_g) with In concentration in a- $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0, 3, 6, \& 9$) thin films.

3.2.2 Extinction coefficient (k)

The optical behavior of the material has been utilized to determine its extinction coefficient (k). The extinction coefficient (k) has been calculated using the relation

$$k = \alpha \lambda / (4\pi) \quad (3)$$

Where α = optical density / film thickness

Figure 5 shows the spectral dependence of k for a- $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0, 3, 6, \& 9$) thin films. It is clear from the figure that k decreases linearly with an increase in λ for all the samples. This behavior is due to decrease in absorption coefficient with increase in λ . It is also evident from table 1 that k increases with In concentration in a- $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ thin films.

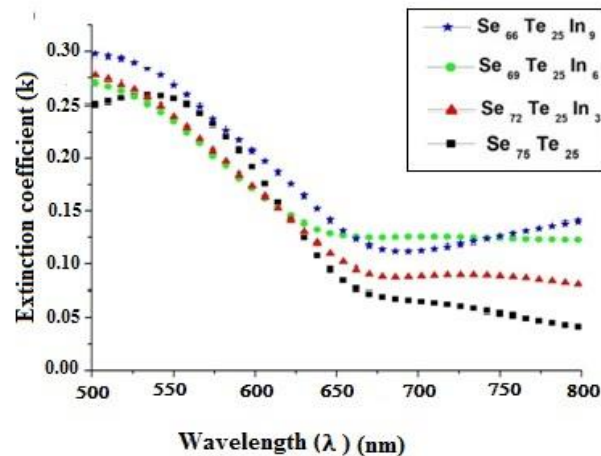


Fig.5 Variation of extinction coefficient (k) with wavelength (λ) in $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ (0,3,6&9) thin films.

4. Conclusion

Thin films of $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0, 3, 6, \& 9$) glassy alloy have been deposited onto a chemically cleaned glass substrate by thermal evaporation technique. The glassy nature of samples was ascertained by x-ray diffraction analysis. The optical absorption spectra of a- Se_{75-x}

$x\text{Te}_{25}\text{In}_x$ ($x = 0, 3, 6, \& 9$) glassy alloy have been studied in the wavelength range of 400-1100 nm by spectrophotometer. The optical parameters like absorption coefficient (α), extinction coefficient (k) and optical band gap (E_g) have been calculated for a- $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0, 3, 6, \& 9$) glassy system. It is observed that extinction coefficient (k) decreases with wavelength (λ) for all the samples. Absorption coefficient (α) is found to increase linearly with incident photon energy ($h\nu$) for all the samples. It has further been observed that both k and α changes with In content for $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0, 3, 6, \& 9$). The decrease in optical band gap with increase in In may be due to the amount of disorder in the materials and increase in the density of states. The decrease in optical band gap for $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0, 3, 6, \& 9$) could also be explained in terms of electronegativity difference between the elements involved in making the a- $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$ ($x = 0, 3, 6, \& 9$) glassy system. Due to the large absorption coefficient and compositional dependence these materials are promising for optical memory devices.

Acknowledgement

The Authors are very much thankful to the University Grants Commission (UGC), New Delhi, India for providing financial assistance in form of major research project F.No. 39-452/2010(SR). The Authors also thank Dr. K. L. Yadav, Department of Physics, IIT Roorkee, for providing the facility for XRD.

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