

EFFECT OF THERMAL ANNEALING ON STRUCTURE AND OPTICAL BAND GAP OF AMORPHOUS $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ THIN FILMS BY VACUUM EVAPORATION TECHNIQUE

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Thin films of $\text{a-Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ were prepared by vacuum evaporation technique in a base pressure of 10^{-6} Torr on to well cleaned glass substrate. $\text{a-Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ thin films were annealed at different temperatures below their crystallization temperatures for 2h. The structural analysis of the films has been investigated using X-ray diffraction technique. The x-ray pattern indicates that the as-prepared films are amorphous in nature but it shows some polycrystalline structure in amorphous phases after annealing. The optical band gap of as prepared and annealed films as a function of photon energy in the wavelength range 400-1100 nm has been studied. It has been found that the optical band gap decreases with increasing annealing temperatures in the present system.

(Received January 18, 2014; Accepted February 28, 2014)

Keywords: Chalcogenide glass, XRD, annealing, crystallization, optical band gap.

1. Introduction

Amorphous chalcogenide thin films have truly emerged as multipurpose materials and have been used to fabricate technologically important devices such as IR detector, electronic and optical switches, electronic resist and optical recording media [1-7]. In recent years efforts have been made to develop chalcogenide based rewritable optical memories. The mechanism of recording memories is an optically, thermally, or electrically induced reversible phase transition between amorphous to crystalline state and vice-versa in thin films [8-9]. Thermal processes are known to be important in inducing crystallization in semiconducting chalcogenide glasses [10-11]. Crystallization of chalcogenide films is accompanied by a change in the optical band gap [12-13]. Separation of different crystalline phases with thermal annealing has been observed in ternary glasses [14-16]. The change in optical energy gap could be determined by identification of the transformed phase. The effect of thermal annealing has been explained on the basis of amorphous-crystalline phase transformation.

The aim of the present work is to investigate the structural and optical properties of thermally annealed Se-Te-Sb thin films. Effective optical band gap during thermal annealing of Se-Te-Sb films have been determined. Chalcogenide glassy materials in particular Se-glasses exhibit unique property of reversible transformation which makes it very useful in optical memory devices [17-19]. Though amorphous Se have got various device applications such as rectifiers, photo cells, vidicons, xerography, switching and memory etc, which makes it attractive but pure Se has disadvantages like short life time and low sensitivity. In order to overcome this difficulty several authors have used alloy of Se with certain additives (Ga, Ge, Bi, Zn etc) for alloying with Se. Alloying gives higher sensitivity, higher crystallization temperature and smaller aging effects[20-22]. We have chosen Sb as an additive material in amorphous Se-Te alloy. The addition of third element (Sb) may create topological and chemical disorder in a Se-Te alloy with respect to binary alloys which will be useful in understanding the structural and optical properties of Se-Te-Sb system. It has been reported that effect of alloying Sb with Se drastically improves the thermal

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stability of Se [23]. The lattice perfection and energy band gap of the material play a major role in the preparation of the device for a particular wavelength, which can be modified by addition of dopants.

2. Experimental Techniques

Glassy alloys of $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ ($x = 0, 3, 6, \& 9$) were prepared by applying melt quenching technique. The exact proportions of high purity (99.999%) Se, Te and Sb elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampule (length ~ 5 cm and internal diameter ~ 8 mm). The ampule containing material was heated to 800°C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of $3 - 4^\circ\text{C} / \text{minute}$. During heating, the ampule was constantly rocked, by rotating a ceramic rod to which the ampule was tucked away in the furnace. This was done to obtain homogeneous glassy alloy. After rocking for about 12 hours, the obtained melt was rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampule. Thin films of glassy alloys of $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ ($x = 0, 3, 6, \& 9$) of thickness 400 nm were prepared by vacuum evaporation technique, in which the 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. The thickness of the film was measured using a single crystal thickness monitor. The XRD patterns of the as prepared and annealed films were recorded with the help of x-ray diffractometer (XPRT-PRO) using $\text{CuK}\alpha$ radiation. The tube was operated at 45 kV and 35 mA. To determine the crystallization temperatures differential scanning calorimetric (DSC) measurements were carried out on powdered samples of $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ under pure N_2 atmosphere using Mettler Toledo Star instrument (Model No. DSC-200PC). Thin films of glassy alloys of $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ were annealed for 2h in a specially designed sample holder under a vacuum of 10^{-2} Pa at three different temperatures (353K, 373K and 393K) which are below the crystallization temperature of the samples. The normal incidence absorption spectra of $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ ($x = 0, 3, 6, \& 9$) thin films have been taken by a double beam UV-Vis-NIR computer controlled spectrophotometer (ECIL-Hyderabad, India, Model No.5704 SS) in the wave length range 400-1100 nm.

3. Result and discussion

3.1. Structure

A typical DSC thermogram of a- $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ at a particular heating rate of 10 Kmin^{-1} is shown in Fig. 1. Similar thermograms were obtained at other heating rates of 5, 15, 20 Kmin^{-1} (not shown here).

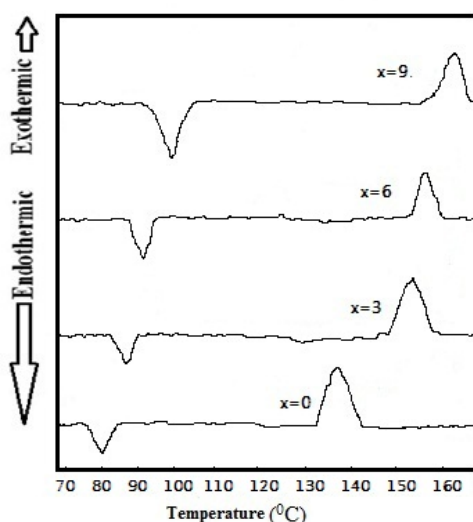


Fig.1 DSC Thermograms for glassy $Se_{75-x}Te_{25}Sb_x$ ($x = 0, 3, 6, 9$) alloys at heating rate of 10 K / min.

It is evident from Fig.1 that the thermogram shows two distinct peaks corresponding to glass transition (T_g) and peak crystallization (T_p) temperatures. Glass transition and peak crystallization temperatures for a- $Se_{75-x}Te_{25}Sb_x$ ($x = 0, 3, 6, 9$) have been determined and listed in table 1.

Table-1 Glass transition and crystallization temperatures for glassy $Se_{75-x}Te_{25}Sb_x$ ($x = 0, 3, 6, 9$) alloys

Sr. No.	Samples	T_g ($^{\circ}C$)	T_c ($^{\circ}C$)
1.	$Se_{75}Te_{25}$	80	135
2.	$Se_{72}Te_{25}Sb_3$	87	152
3.	$Se_{69}Te_{25}Sb_6$	92	156
4.	$Se_{66}Te_{25}Sb_9$	97	162

The glassy nature of the alloys was ascertained by X-ray diffraction (XRD) technique. The XRD patterns of $Se_{72}Te_{25}Sb_3$ alloy in as prepared and annealed form is shown in Fig. 2. Absence of any sharp peak in XRD pattern of as prepared $Se_{72}Te_{25}Sb_3$ alloy confirms the glassy nature of $Se_{72}Te_{25}Sb_3$ alloy. Similar XRD patterns were obtained for the other glassy alloys (not shown here).

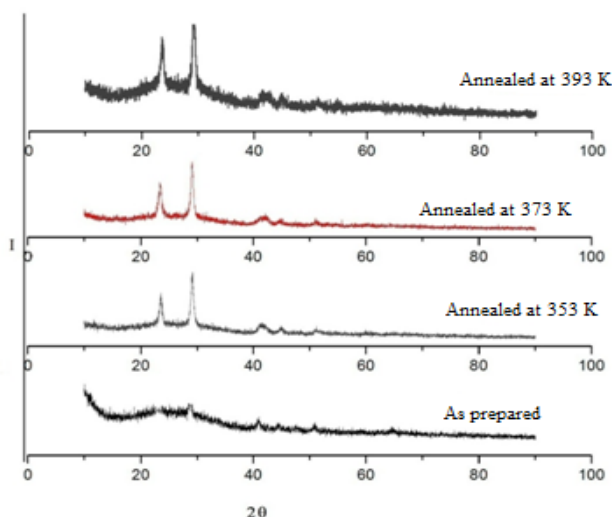


Fig.2 X-ray diffraction curves of the as-prepared and annealed $Se_{72}Te_{25}Sb_3$ sample

X-ray diffraction data reveals that as prepared sample is amorphous in nature. The X-ray peaks continue to grow with increasing value of annealing temperature. It is evident that there is formation of polycrystalline structure in amorphous phases after annealing.

3. 2. Optical properties

3.2.1 Absorption coefficient (α) and optical band gap (E_g)

The spectral dependence of absorbance as a function of wave length of as prepared and annealed films of a- $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$ with different annealing temperatures were studied. Fig.3 shows the absorption coefficient (α) as a function of incident photon energy ($h\nu$) for as prepared and annealed films of a- $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$ with different annealing temperatures of crystallization.

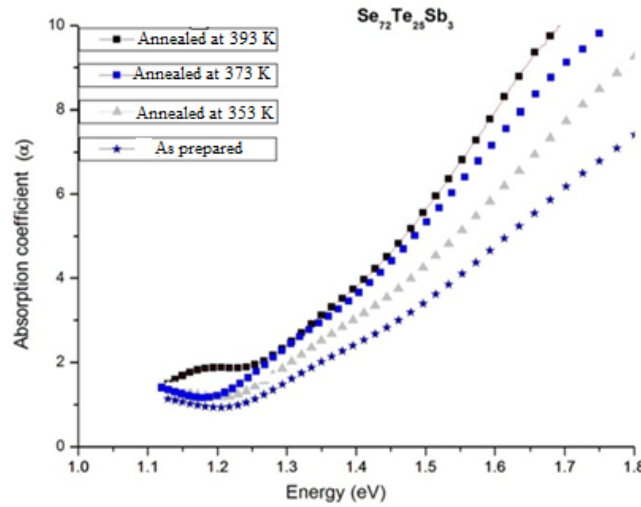


Fig.3 Variation of absorption coefficient (α) as a function of photon energy in as prepared and annealed films of $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$.

The absorption coefficient (α) has been obtained directly from the absorbance against wavelength curve using the relation

$$\alpha = OD/ t \quad (1)$$

where OD is the optical density measured at given layer thickness (t). It has been observed that the value of absorption coefficient (α) increases linearly with the increase in photon energy ($h\nu$) for as-prepared and annealed films as shown in Fig.3. Similar trends have also been observed for other samples of a- $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$, which are not shown here.

In the absorption process, a photon of the known energy excites an electron from lower to higher energy state corresponding to an absorption edge. In chalcogenide glasses, a typical absorbance edge can broadly be ascribed to one of the three processes: residual below gap absorption, Urbach tails and interband absorption.

Chalcogenide glasses have been found to exhibit highly reproducible optical edges, which are relatively insensitive to preparation conditions. The analysis of 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 [24].

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

where A is the edge width parameters 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 photon energy ($h\nu$) for as prepared and annealed films of $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$ are shown in Fig.4.

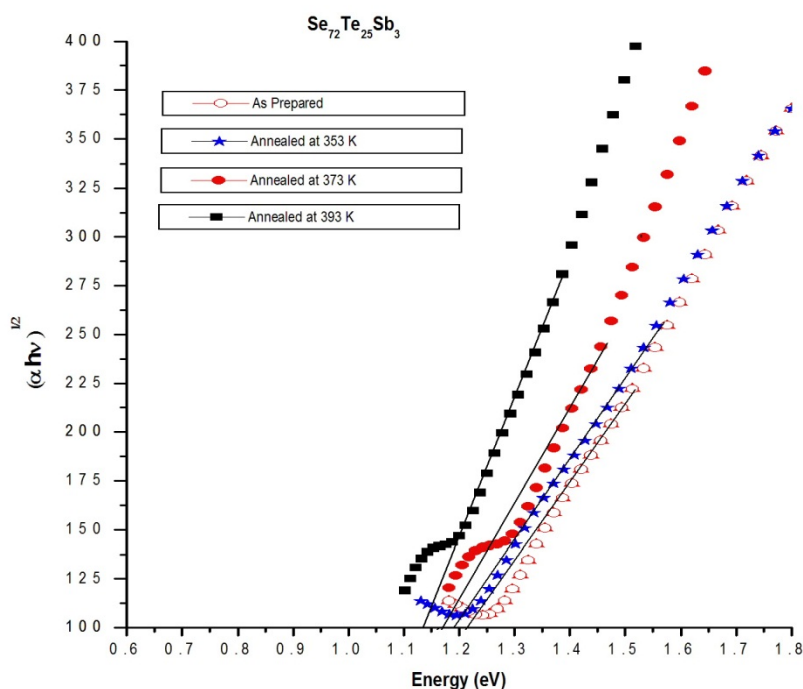


Fig.4 Variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) in as prepared and annealed films of $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$.

The value of optical band gap (E_g) has been calculated by taking the intercept on the x-axis. The calculated value of E_g for all the glassy samples of a- $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$ (as prepared and annealed films) are given in table 2. It has been observed that optical band gap decreases with the increase in the annealing temperature for a- $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$ thin film. Similar trends of decreasing optical band gap with increasing annealing temperature were observed for other samples of a- $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$, which are not shown here.

Table- 2 Optical band gap of $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$ thin films at different annealing temperatures

S.No.	Sample $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$	Optical Band Gap (E_g) in eV
1.	As prepared	1.21
2.	Annealed at 353 K	1.19
3.	Annealed at 373 K	1.16
4.	Annealed at 393 K	1.13

In the present case annealing temperatures have been chosen above glass transition temperature (T_g). Thermal annealing above T_g is known to be important in inducing crystallization in semiconducting chalcogenide glasses [25-27]. During annealing at temperatures higher than T_g , the indirect optical band gap decreases and the width of localized states tails increases with the increase in annealing temperature. These results can be interpreted by assuming the production of surface dangling bonds around crystallites during the process of crystallization [28]. It has been suggested by other workers that nearly ideal amorphous solids crystallize under heat treatment and that in the process of crystallization, dangling bonds are produced around the surface of crystallites

[29]. Further heat treatment causes the crystallites to breakdown [29] into smaller crystals, thereby increasing the number of surface dangling bonds. These dangling bonds are responsible for the formation of some types of defects in the highly polycrystalline solids. As the number of dangling bonds and defects increase with an increase in annealing temperature, the concentration of localized states in the band structure also increases gradually. Hence, the heat treatment of the films causes an increase in the energy width of the localized state thereby reducing the optical energy gap.

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

Fig. 5 shows the spectral dependence of k for a- $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$ thin films (as prepared and annealed).

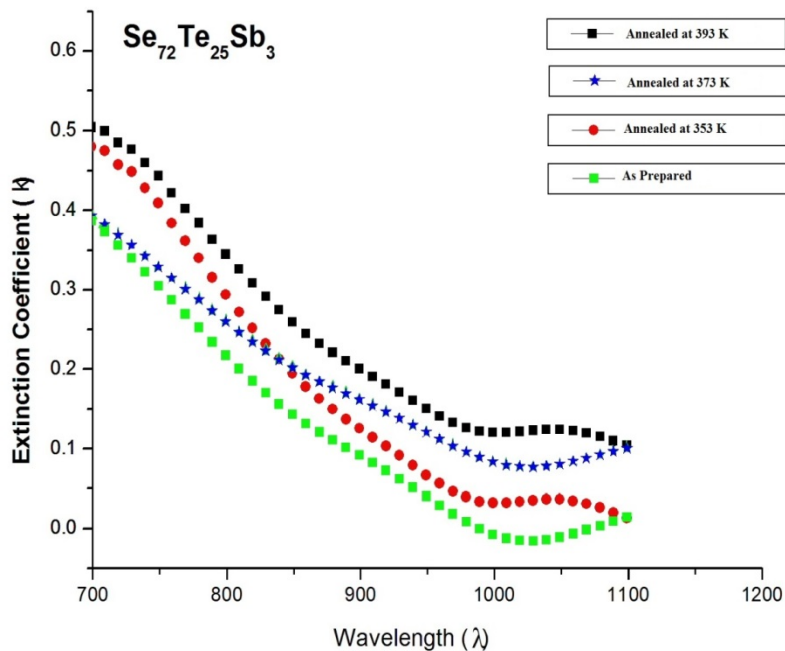


Fig.5 Variation of extinction coefficient (k) with wavelength (λ) in as prepared and annealed films of $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$.

It is clear from the Fig.5 that k decreases linearly with an increase in λ for as prepared and annealed films. This behavior is due to decrease in absorption coefficient with increase in λ . Similar trends have also been observed from other samples of a- $\text{Se}_{75-x}\text{Te}_{25}\text{Sb}_x$, which are not shown here. The absorption coefficient (α) and extinction coefficient (k) for as prepared and annealed film of a- $\text{Se}_{72}\text{Te}_{25}\text{Sb}_3$ have been calculated and listed in table 3.

Table- 3 Absorption and extinction coefficient of $Se_{72}Te_{25}Sb_3$ thin films at different annealing temperatures

S.No.	Sample $Se_{72}Te_{25}Sb_3$	Absorption Coefficient (cm^{-1})	Extinction Coefficient (k) 10^{-4}
1.	As prepared	8.19759	3616.0
2.	Annealed on 353 K	10.67052	4247.2
3.	Annealed on 373 K	10.67082	4247.6
4.	Annealed on 393 K	10.67093	4247.8

4. Conclusion

Amorphous thin films of $Se_{75-x}Te_{25}Sb_x$ were obtained by thermal evaporation technique on glass substrates. The obtained films are found to be of amorphous nature. The X-ray diffraction patterns indicate that the films are amorphous and their nature changes from amorphous to crystalline with increasing value of annealing temperature. The optical absorption measurements on the a- $Se_{75-x}Te_{25}Sb_x$ films during crystallization indicate that absorption occurs due to indirect transition. Crystallization of chalcogenide films is accompanied by a change in the optical band gap. The effect of thermal annealing is interpreted on the basis of amorphous-crystalline transformation. It has been found that optical band gap decreases on increasing annealing temperature. Absorption coefficient and extinction coefficient have also been studied for as-prepared and annealed films. It has been observed that both absorption coefficient and extinction coefficient increases with increase in annealing temperature. $Se_{75-x}Te_{25}Sb_x$ thin films provide a promising alternative for phase-change memory applications.

Acknowledgement

The Authors are very much grateful 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 thanks Prof. K.L. Yadav, Department of Physics, I.I.T., Roorkee and Prof. M.Zulfiquar, Department of Physics, Jamia Millia Islamia, New Delhi for providing the facility for XRD and optical measurements respectively.

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