Structural and Optical Investigations of Amorphous Se$_{75-x}$Te$_{25}$Sbx Thin Films

D. K. Dwivedi$^{1,*}$, H. P. Pathak$^{1}$, R. K. Shukla$^{2}$, A. Kumar$^{2}$

$^1$Department of Physics, Amorphous Semiconductor Research Lab, M.M.M. Engineering College, Gorakhpur, India
$^2$Department of Physics, H.B.T.I., Kanpur, India

*Corresponding author: dwivedidkphys@rediffmail.com

Abstract Thin films of Se$_{75-x}$Te$_{25}$Sbx (x = 0, 3, 6, & 9) glassy alloys have been deposited onto a chemically cleaned glass substrate by thermal evaporation technique under vacuum. Glassy nature of the films has been ascertained 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 has been found that extinction coefficient (k) decreases with increase in wavelength (λ). The absorption coefficient (α) is found to increase with incident photon energy. Optical band gap (E$_g$) has also been calculated and found to decrease with Sb content in Se$_{75-x}$Te$_{25}$Sbx (x = 0, 3, 6, & 9) glassy system. The decrease of optical band gap (E$_g$) with Sb concentration has been explained on the basis of Mott and Davis model.

Keywords: chalcogenide glasses, amorphous semiconductors, thin films, optical properties, optical band gap


1. Introduction

Chalcogenide glasses have recently attracted great deal of interest because of their potential applications in solid state devices [1-9]. These materials in particular Se glasses exhibit unique properties of reversible transformation [10]. This property makes these glasses very useful in optical memory devices [11,12,13]. Se based chalcogenide glasses have high transparency in the broad middle and for IR region and have strong nonlinear properties [14]. Apart from this application, amorphous selenium has been found to have tremendous potential in xeroxing applications and therefore a lot of attempts have been made to improve its properties by alloying [15,16]. Though amorphous selenium have got various device applications such as rectifiers, photocells, vidicons, xerography, switching and memory etc which make it attractive but pure selenium has disadvantages like short life time and low sensitivity. This problem can be overcome by alloying Se with some impurity atoms, which gives higher sensitivity, higher crystallization temperature and smaller aging effect [17,18,19]. In the present work Sb has been chosen as an additive element in amorphous Se-Te alloys. The third element behaves as chemical modifier as it is reported to expand the glass forming region and also creates compositional as well as configurational disorder in the material with respect to binary alloys which will be useful in understanding the structural, electrical and optical properties of chalcogenide glasses [20-30]. The incorporation of a third element like Sb 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. It has been reported that effect of alloying Sb with Se drastically improves the thermal stability of Se [31]. The optical constants (absorption coefficient (α), extinction coefficient (k)) as well as band gap (E$_g$) are the most significant parameters in the amorphous semiconducting thin films. The optical behavior of a material is utilized to determine its optical constant. Therefore an accurate measurement of optical constants is extremely important. The aim of present paper is to study the effect of Sb incorporation on the optical properties of Se-Te matrix. The optical absorption spectra of the films of Se$_{75-x}$Te$_{25}$Sbx (x = 0, 3, 6, & 9) are measured in the wavelength range 400-1100 nm, by double beam UV-VIS spectrophotometer. Optical parameters like absorption coefficient (α), extinction coefficient (k) and optical band gap (E$_g$) have been calculated for a-Se$_{75-x}$Te$_{25}$Sbx glassy system.

2. Experimental

Glassy alloys of Se$_{75-x}$Te$_{25}$Sbx (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 $10^{-5}$ gm. The material was then sealed in evacuated (~10$^{-3}$ Torr) quartz ampoule.
(length ~ 5cm and internal diameter ~ 8mm). The ampoule 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°C/minute. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule 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 ampoule. Thin films of glassy alloys of a Se75-xTe25Sbx (x = 0, 3, 6, & 9) 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 as suggested by Abkowitz [32]. The thickness of the film was measured using a single crystal thickness monitor. The XRD patterns of the films were recorded with the help of x-ray diffractometer (XPERT-PRO) using Cu-Kα radiation (λ=1.54 Å). The tube was operated at 45 kV and 35 mA. Normal incidence absorption spectra of Se75-xTe25Sbx (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 400-1100nm.

### 3. Results and Discussion

#### 3.1. Structural Property

The XRD pattern for Se75-xTe25Sbx (x = 0, 3, 6, & 9) has been shown in Figure 1. The X-ray diffraction patterns indicate that the films are amorphous in nature.

![Figure 1. XRD pattern of Se75-xTe25Sbx (x = 0, 3, 6, & 9) thin films](image)

#### 3.2 Optical Properties

##### 3.2.1. Absorption Coefficient (α) and Optical Band Gap (Eg)

The absorption coefficient (α) of the film was calculated using the equation (1). A plot of absorption coefficient (α) as a function of photon energy (hν) is given in Figure 2, and values are given in Table 1. It has been observed that absorption coefficient (α) increases with increase in photon energy (hν) as well as Sb concentration, for all the samples of a-Se75-xTe25Sbx.

![Figure 2. Variation of absorption coefficient (α) with photon energy (hν) in Se75-xTe25Sbx (x = 0, 3, 6, & 9) thin films](image)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Sample</th>
<th>Optical Band Gap (Eg) in eV</th>
<th>Absorption Coefficient (α) (m⁻¹)</th>
<th>Extinction Coefficient (k) 10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Se75Te25</td>
<td>1.41</td>
<td>1.99217</td>
<td>951.7</td>
</tr>
<tr>
<td>2.</td>
<td>Se72Te25Sb3</td>
<td>1.21</td>
<td>8.19759</td>
<td>3616.0</td>
</tr>
<tr>
<td>3.</td>
<td>Se69Te25Sb6</td>
<td>1.17</td>
<td>8.72369</td>
<td>4167.6</td>
</tr>
<tr>
<td>4.</td>
<td>Se66Te25Sb9</td>
<td>1.11</td>
<td>8.86962</td>
<td>4237.1</td>
</tr>
</tbody>
</table>

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

\[ \alpha = OD/t \]  

(1)

Where OD is the optical density measured at a given layer thickness (t).

The analysis of the absorption coefficient has been carried out to obtain the optical band gap (Eg). The optical band gap has been determined from absorption coefficient data as a function of (hν) by using Tauc relation [33,34,35].

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

(2)

Where A is the edge width parameter representing the film quality, which is calculated from the linear part of this relation and Eg is the optical band gap of the material. The variation of \((\alpha h\nu)^{1/2}\) with \((h\nu)\) for a-Se75-xTe25Sbx films are shown in Figure 3.
Figure 3. Variation of $(\alpha h\nu)^{1/2}$ with $(h\nu)$ in Se$_{75-x}$Te$_{25}$Sbx (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-Se$_{75-x}$Te$_{25}$Sbx are given in Table 1. It is evident from the Table 1 that the values of optical band gap ($E_g$) decreases with increasing Sb 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 [35]. 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 [36]. 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 may be further responsible for the broadening of the valence band inside the forbidden gap. The electronegativities of Se, Te and Sb are 2.4, 2.1 and 2.05 respectively. Since Sb has lower electronegativity than Se, the substitution of Sb 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 Sb content.

Variation of $E_g$ with Sb concentration in a-Se$_{75-x}$Te$_{25}$Sbx glassy sample is shown in Figure 4.

Figure 4. Variation of optical band gap ($E_g$) with Sb concentration in Se$_{75-x}$Te$_{25}$Sbx (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

$$K = \alpha \lambda / 4\pi$$

where $\alpha$ = optical density /film thickness.

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

Figure 5. Variation of extinction coefficient ($k$) with wavelength ($\lambda$) in Se$_{75-x}$Te$_{25}$Sbx (x = 0, 3, 6, & 9) thin films

4. Conclusion

Thin films of a-Se$_{75-x}$Te$_{25}$Sbx (x = 0, 3, 6, & 9) glassy alloy have been deposited onto a chemically cleaned glass substrate by thermal evaporation technique. The glassy nature of the samples was ascertained by x-ray diffraction analysis. The optical absorption spectra of a-Se$_{75-x}$Te$_{25}$Sbx glassy alloy has been studied in the wavelength range of 400-1100 nm by spectrophotometer. The optical parameters like absorption coefficient ($\alpha$), extinction coefficient ($k$) and optical band gap ($E_g$) have been calculated for a-Se$_{75-x}$Te$_{25}$Sbx glassy system. It is observed that extinction coefficient ($k$) decreases with wavelength ($\lambda$) for all the samples. Absorption coefficient ($\alpha$) is found to increase linearly with incident photon energy ($h\nu$) for all the samples. It has further been observed that both $k$ and $\alpha$ increases with increasing Sb concentration in a-Se$_{75-x}$Te$_{25}$Sbx glassy alloy. It is also observed that optical band gap decreases with Sb content. The decrease in optical band gap with increase in Sb concentration may be due to the increase in the amount of disorder in the materials and increase in the density of defect states. The decrease in band gap could also be explained in terms of electronegativity difference between the elements involved in making the a-Se$_{75-x}$Te$_{25}$Sbx glassy system. Due to the large absorption coefficient and compositional dependence of absorption these materials may be suitable for optical memory devices.
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.O.N.Srivastava, Department of Physics, B.H.U., Varanasi and Prof. M.Zulfiqar, Department of Physics, Jamia Millia Islamia, New Delhi for providing the facility for XRD and optical measurements respectively.

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