A STUDY OF OPTICAL PARAMETERS OF AMORPHOUS $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ THIN FILMS BEFORE AND AFTER HEAT TREATMENT

V. Pandey, S. K. Tripathia, A. Kumar*

Department of Physics, Harcourt Butler Technological institute, Kanpur-208 002, India
Department of Physics, Panjab University, Chandighrah-160 014, India

Amorphous thin films of $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ (x = 2 & 6) are thermally evaporated onto chemically cleaned glass substrate. Some optical parameters of these films are studied before and after thermal annealing above glass transition temperature of the respective alloys. The calculations of optical parameters have been made in the wavelength range 400-2400 nm by Swanepoel method using optical transmission data. Optical band gap has been determined before and after annealing. Other optical parameters like refractive index (n), extinction coefficient (k), absorption coefficient ($\alpha$), real and imaginary dielectric constant ($\varepsilon'$ & $\varepsilon''$) are also calculated. In both the glassy alloys, $E_g$ is found to increase after thermal annealing of the films above glass transition temperature. $E_g$ is also found to increase with Ag concentration in $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ system.

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1. Introduction

The chalcogenide glassy semiconductors are some of the widely used amorphous semiconductors for a variety of applications in optics, optoelectronics, waveguides, optical memories, optical sensors, infrared lasers etc. There has been an increased interest in the properties of Se-rich chalcogenide glassy alloys due to their current use as photoreceptors in TV vidicon pickup tubes [1] and in digital X-ray imaging [2]. The shortcomings of pure glassy selenium for its practical application include its short lifetime, low sensitivity and low thermal instability. Recently, it has been pointed out that Se-Te alloys have more advantages than a-Se from the technological point of view due to their greater hardness, higher crystallization temperatures, higher photosensitivity and smaller aging effect. Therefore, glassy Se-Te alloys are used to extend the utility of a-Se.

The properties of chalcogenide glassy semiconductors are usually affected by the addition of third element. Experimental results reported by various workers have shown that the addition of impurity atoms in binary Se-Te systems does change the optical properties of chalcogenide glassy semiconductors. Several workers [3-8] have reported the impurity effects in the various chalcogenide glasses. It has also been found that the effect of impurities depends strongly on the composition of the glass, the chemical nature of the impurity and the method of the doping. Impurity concentration obviously is a critical factor in such cases. Several of the physical properties are found to be improved by the addition of certain impurities.

Ag-containing chalcogenide glasses have attracted much interest in glass science and technology for fundamental research of their structure, properties and preparation [9-13]. They have many current and potential applications in optics, optoelectronics, chemistry and biology such as optical elements, gratings, photo doping, optical memories, microlenses, waveguides etc. [14-19].

*Corresponding author: dr.ashok.kumar@yahoo.com
The optical band gap, refractive index and extinction coefficient are the most significant parameters in amorphous semiconducting thin films. The optical behavior of material is utilized to determine its optical constants. Films are ideal specimen for reflectance and transmittance type measurements. Therefore, an accurate measurement of the optical constants is extremely important.

Chalcogenide glasses have been found to exhibit the change in n under the influence of light, which make it possible to use these materials to record not only the magnitude but also the phase of illumination. The latter is especially important in holographic optical data storage and in the fabrication of various integrated components and devices such as selective optical filters, mixers, couplers and modulators [20-22].

In the present work, we have studied optical properties of amorphous thin films in Se70Te30-xAgx system with a view to study the effect of increase in Ag concentration in this glassy system. The effect of annealing on the optical parameters of amorphous Se70Te30-xAgx thin film has also been reported in this paper.

2. Experimental

Glassy alloys of Se70Te30-xAgx (x = 2 & 6) are prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Ag elements, in accordance with their atomic percentages, are weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated (~10^{-5} Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material is heated to 1000 °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 ampoules are constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This is done to obtain homogeneous glassy alloys. After rocking for about 12 hours, the obtained melt was then rapidly quenched in ice-cooled water. The quenched sample is then taken out by breaking the quartz ampoule. The glassy nature of the alloy was ascertained by X-ray diffraction.

Thin films of glassy alloys of a Se70Te30-xAgx are prepared by vacuum evaporation technique, in which the substrate is kept at room temperature at a base pressure of 10^{-6} Torr using a molybdenum boat. The films are kept inside the deposition chamber for 24 hours to achieve the metastable equilibrium. A Double UV/VIS/NIR Computer Controlled Spectrometer (Hitachi-330) is used for measuring optical transmission of Se70Te30-xAgx thin films as a function of wavelength of the incident light.

3. Results and discussion

The optical system under consideration is amorphous, homogeneous and uniform. Optical transmission (T) is a very complex function and is strongly dependent on the absorption coefficient (\(\alpha\)). Fig. 1(a) & 1(b) shows the variation of transmission (T) with wavelength (\(\lambda\)) in Se70Te30-xAgx thin films before and after the heat treatment respectively. According to Swanepoel’s method [23], which is based on Mainfacer [24], the envelope of the interference maxima and minima occurs in the spectrum can be utilized for obtaining optical parameters. The extinction coefficient (k) can be neglected in the region of weak and medium absorption (\(\alpha \neq 0\)). Therefore, this approximation is valid over most spectrums. The presence of maxima and minima of transmission spectrum of the same wavelength position confirmed the optical homogeneity of the deposited film and that no scattering or absorption occurs at long wavelength. The Swanepoel’s method has been used in chalcogenide glasses by various workers [25-27].

3.1 Determination of optical constants

For the method proposed by Swanepoel, the optical constants are deduced from the fringe patterns in the transmittance spectrum. In the transmittance region where the absorption coefficient (\(\alpha = 0\)), the refractive index n is given by
where \( N = \left( \frac{2s}{T_m} \right) - \left( \frac{s^2 + 1}{2} \right) \)

\( T_m \) is the envelope function of the transmittance minima and \( s \) is the refractive index of the substrate.

In the region of weak and medium absorption, where \( \alpha \neq 0 \), the transmittance decreases mainly due to the effect of \( \alpha \) and the refractive index \( n \) is given by

\[ n = \left[ N + \left( N^2 - s^2 \right)^{1/2} \right]^{1/2} \]  

(2)

where \( N = \left( \frac{2s(T_M - T_m)}{T_M T_m} \right) + (s^2 + 1)/2 \) and \( T_M \) is the envelope function of the transmittance maximum.

In the region of strong absorption, the transmittance decreases drastically due almost exclusively to the influence of \( \alpha \) and \( n \) can be estimated by extrapolating the values in the other regions. Because the thickness of our film is uniform, interference give rise to the spectrum as shown in Fig. 1(a) & 1(b). The fringes can be used to calculate the refractive index \( n \) of the film using eqn. (1) and (2) as indicated previously.

**Fig. 1a.** Variation of transmittance (T) with wavelength (\( \lambda \)) in Se\(_{70}\)Te\(_{30-x}\)Ag\(_x\) thin films before the heat treatment.

**Fig. 1b.** Variation of transmittance (T) with wavelength (\( \lambda \)) in Se\(_{70}\)Te\(_{30-x}\)Ag\(_x\) thin films after the heat treatment.
The extinction coefficient \( k \) can be calculated from the relation

\[
k = \frac{\alpha \lambda}{4\pi} = \left(\frac{\lambda}{4\pi d}\right) \ln(1/x)
\]  

where \( x \) is the absorbance and \( d \) is the film thickness.

If \( n_1 \) & \( n_2 \) are the refractive indices at two adjacent maxima or minima at \( \lambda_1 \) & \( \lambda_2 \) then the thickness is given by,

\[
d = \frac{\lambda_1 \lambda_2}{2[\lambda_1 n_2 - \lambda_2 n_1]}
\]  

In the region of weak and medium absorption, using the transmission minima \( T_m \), \( x \) is given by

\[
x = \left[ E_m - \left\{ E_m^2 - (n^2 - 1)^2 (n^2 - s^4)\right\}^{1/2}\right] / \left[ (n - 1)^2 (n - s^2)\right]
\]  

Where \( E_m = \left[ (8n^2s/T_m) - (n^2 - 1)^3 (n^2 - s^4)\right] \)

The spectral distributions of both \( n \) and \( k \) for \( \text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x \) thin films before and after heat treatment respectively are shown in Figs. 2(a & b) and 3(a & b) respectively and the calculated values are also given in Table 2(a) & 2(b).

Fig. 2a. Variation of refractive index (\( n \)) with wavelength (\( \lambda \)) in \( \text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x \) thin films before the heat treatment.

Fig. 2b. Variation of refractive index (\( n \)) with wavelength (\( \lambda \)) in \( \text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x \) thin films after the heat treatment.
3.2 Determination of dielectric constants

The dielectric constant of Se\textsubscript{70}Te\textsubscript{30-x}Ag\textsubscript{x} thin films can be calculated with the help of refractive index n and extinction coefficient k [28]. Real dielectric constant (\(\varepsilon'\)) can be calculated by the following eqn,

\[
\varepsilon' = n^2 - k^2
\]

While the imaginary dielectric constant (\(\varepsilon''\)) dielectric constants can be calculated by the following eqn,

\[
\varepsilon'' = 2nk
\]

The spectral distribution of both real and imaginary dielectric constants for Se\textsubscript{70}Te\textsubscript{30-x}Ag\textsubscript{x} thin films before and after the heat treatment respectively are shown in Figs. 4(a & b) and 5(a & b) respectively and the calculated values are also given in Table 2(a) & 2(b).
Fig. 4a. Variation of real dielectric constant ($\varepsilon'$) with wavelength ($\lambda$) in $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ thin films before the heat treatment.

Fig. 4b. Variation of real dielectric constant ($\varepsilon'$) with wavelength ($\lambda$) in $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ thin films after the heat treatment.

Fig. 5a. Variation of imaginary dielectric constant ($\varepsilon''$) with wavelength ($\lambda$) in $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ thin films before the heat treatment.
3.3 Absorption coefficient and optical band gap

The absorption coefficient $\alpha$ of Se$_{70}$Te$_{30-x}$Ag$_x$ films can be calculated using the well-known relation

$$\alpha = \frac{4\pi k}{\lambda} \tag{9}$$

in which $k$ is substituted by its value obtained from Fig. 3(a) & 3(b).

The spectral distribution of absorption coefficient $\alpha$ for Se$_{70}$Te$_{30-x}$Ag$_x$ thin films before and after the heat treatment respectively are shown in Fig. 6(a) & 6(b) and the calculated values are also given in Table 1(a) & 1(b).

Table 1(a). Optical Parameters before the Heat Treatment.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Optical Band Gap ($E_g$)</th>
<th>Absorption Coefficient ($\alpha$) in M$^{-1}$ at 1400 nm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Se$<em>{70}$Te$</em>{28}$Ag$_2$</td>
<td>0.52</td>
<td>33.83 $\times 10^4$</td>
</tr>
<tr>
<td>2.</td>
<td>Se$<em>{70}$Te$</em>{24}$Ag$_6$</td>
<td>0.61</td>
<td>19.24 $\times 10^4$</td>
</tr>
</tbody>
</table>

Table 1(b). Optical Parameters after the Heat Treatment at 375 k.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Optical Band Gap ($E_g$)</th>
<th>Absorption Coefficient ($\alpha$) in M$^{-1}$ at 1500 nm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Se$<em>{70}$Te$</em>{28}$Ag$_2$</td>
<td>0.56</td>
<td>09.82 $\times 10^4$</td>
</tr>
<tr>
<td>2.</td>
<td>Se$<em>{70}$Te$</em>{24}$Ag$_6$</td>
<td>0.62</td>
<td>14.01 $\times 10^4$</td>
</tr>
</tbody>
</table>
The present system of Se$_{70}$Te$_{30-x}$Ag$_x$ obeys the role of non-direct transition and the relation between the optical band gap, absorption coefficient and energy ($h\nu$) of the incident photon is given by [29-31]:

$$(\alpha h\nu)^{1/2} \propto (h\nu - E_g)$$

(10)

The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for Se$_{70}$Te$_{30-x}$Ag$_x$ thin films before and after the heat treatment respectively are shown in Fig. 7(a) & 7(b). The value of indirect optical band gap $E_g$ has been calculated by taking intercept on x-axis. The values of optical band gap $E_g$ are given in Table 1(a) & 1(b) for each sample.
Table 2(a). Optical Parameters before the Heat Treatment.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Refractive index (n)</th>
<th>Extinction Coefficient (k)</th>
<th>Real Dielectric Constant ($\varepsilon'$)</th>
<th>Imag. Dielectric Constant ($\varepsilon''$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Se$<em>{70}$Te$</em>{30-x}$Ag$_x$</td>
<td>3.02</td>
<td>$4.31 \times 10^{-2}$</td>
<td>9.12</td>
<td>$26.04 \times 10^{-2}$</td>
</tr>
<tr>
<td>2.</td>
<td>Se$<em>{70}$Te$</em>{24}$Ag$_6$</td>
<td>2.73</td>
<td>$2.45 \times 10^{-2}$</td>
<td>6.56</td>
<td>$13.39 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Table 2(b). Optical Parameters after the Heat Treatment at 375 k.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Refractive index (n)</th>
<th>Extinction Coefficient (k)</th>
<th>Real Dielectric Constant ($\varepsilon'$)</th>
<th>Imag. Dielectric Constant ($\varepsilon''$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Se$<em>{70}$Te$</em>{28}$Ag$_2$</td>
<td>2.05</td>
<td>$11.72 \times 10^{-2}$</td>
<td>4.21</td>
<td>$4.81 \times 10^{-2}$</td>
</tr>
<tr>
<td>2.</td>
<td>Se$<em>{70}$Te$</em>{24}$Ag$_6$</td>
<td>2.97</td>
<td>$16.73 \times 10^{-2}$</td>
<td>8.85</td>
<td>$9.95 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

It is evident from the Table 1(a) & 1(b) that optical band gap $E_g$ increases after the heat treatment above glass transition temperature (at 375 K). It is also clear from these tables that optical energy gap ($E_g$) increases with the increase in Ag concentration in Se$_{70}$Te$_{30-x}$Ag$_x$ system. The increase of band gap suggests [32] a decrease in the density of localized states. In Se-Te-Ag system, a decrease in the density of localized states is observed by Singh et. al. [33], on increase in Ag concentration. Following reference [32], the increase in band gap can be related to the decrease in the density of localized states in the present case also.

4. Conclusion

The optical transmission spectra of amorphous thin film of Se$_{70}$Te$_{30-x}$Ag$_x$ ($x = 2$ & 6) are obtained in the wavelength range 400-2400 nm by spectrophotometer before and after the heat treatment in both the glassy alloys. It is observed that optical energy gap ($E_g$) increases with increase in Ag content in Se$_{70}$Te$_{30-x}$Ag$_x$ system. It is also observed that optical band gap $E_g$ increases after the heat treatment above glass transition temperature in both the glassy alloys. It is also found that refractive index (n), extinction coefficient (k), real and imaginary dielectric
constant ($\varepsilon$) and absorption coefficient ($\alpha$) decreases with Ag content. The increase in band gap has been related to the decrease in the density of localized states in the present glassy system.

References