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VARIATION OF OPTICAL CONSTANTS IN $GE_{10}SE_{60}TE_{30}$ THIN FILM

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Thin films of *a*-$Ge_{10}Se_{90-x}Te_x$ ($x = 0, 30$) glassy alloys are prepared by vacuum evaporation technique at ~10^{-5} Torr on glass substrate at room temperature. Optical study is performed to calculate the refractive index (n), extinction coefficient (k), optical conductivity (σ), dielectric constant (real and imaginary), absorption coefficient (α) and optical band gap (E_g^{opt}) using transmission spectra in the wavelength range 400-1200 nm.

Keywords: Chalcogenide glasses, Optical properties, Optical band gap, Defect states, Average bond energy

1. Introduction

Chalcogenide glasses are good candidates for applications in the infrared (IR) region [1,2]. Chalcogenide glasses are vitreous materials having one or more of the chalcogen elements (Group VI): sulfur (S), selenium (Se), and tellurium (Te). The addition of the network formers (Group IV and V) such as silicon (Si), germanium (Ge), tin (Sn), phosphorus (P), arsenic (As), and antimony (Sb) establishes cross-linking between the tetrahedral and pyramidal units which facilitates stable glass formation [3,4]. Depending on the composition, the chalcogenide glasses are stable against crystallization and are chemically inert. They have excellent thermal stability, and are relatively easy to fabricate. In our present work we have taken the *a*-$Ge_{10}Se_{90}$ system and then replace the Se by 30 at. % of Te. The optical properties of the thin films of the prepared samples are calculated using the transmission spectrum in the range 400-1200 nm.

2. Experimental procedure

Glassy alloys of $Ge_{10}Se_{90}$ and $Ge_{10}Se_{60}Te_{30}$ are prepared by well known quenching technique. Materials (5N purity) are weighed according to their atomic percentages and sealed in quartz ampoules in a vacuum ~ 2×10^{-5} Torr. The sealed ampoules are kept inside a furnace where the temperature is increased up to 1000 ^{0}C at a heating rate of 2-3 ^{0}C/min. The ampoules are frequently rocked for 24 hours at the highest temperature to make the melt homogeneous to avoid phase separation. The quenching is done in ice cold water. Thin films are deposited on glass substrates which are first cleaned with soap solution, vapour cleaning and then ultrasonically cleaned by trichloroethylene, acetone followed by methyl alcohol. Finally the substrate is washed by DI water and dried in oven. On the cleaned substrate thin films of the glassy alloys are deposited by vacuum evaporation technique at room temperature and base pressure of ~ 10^{-5} Torr using a molybdenum boat. The normal incidence transmission spectra of thin films of the samples have been measured by a double beam UV/VIS/NIR spectrometer [Hitachi-330], in the transmission range 400- 1200 nm. The spectrometer was set with a suitable slit width of 1 nm in the measured spectral range.

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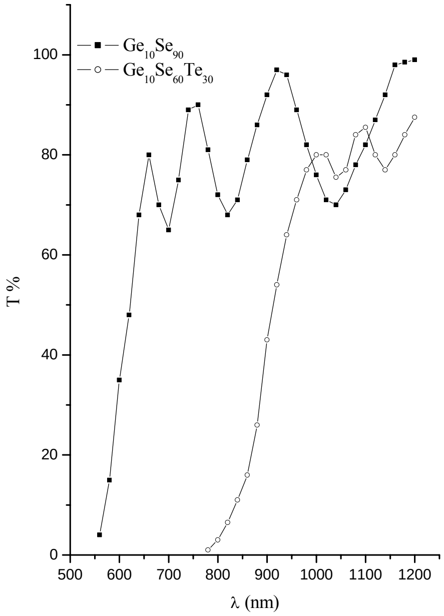

Fig. 1. Variation of Transmittance (T) with wavelength (λ) for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

3. Results and discussion

Optical transmission spectrum of the thin films is observed to be shifted towards higher wavelength with the addition of 30 at. % of Te content. The variation of transmission with wavelength for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films is shown in Fig. 1. Transmission spectrum is used to calculate the refractive index using the envelope method proposed by Swanepoel [5,6]. The refractive index *(n)* has been obtained using the following expressions,

$$n = [M + (M^2 - s^2)^{1/2}]^{1/2} \tag{1}$$

where $M = \dfrac{2s}{T_m} - \dfrac{(s^2+1)}{2}$ for transparent region (2)

and $M = 2s\dfrac{T_M - T_m}{T_M T_m} + \dfrac{(s^2+1)}{2}$ for weak and medium absorption region. (3)

T_M and T_m are the values of maximum and minimum transmission values at a particular wavelength, '*s*' is the refractive index of the substrate. Refractive index can be estimated by extrapolating envelops corresponding to T_M and T_m. As the thickness of film is uniform, interference give rise to the spectrum as shown in Fig. 1. These fringes can be used to calculate the refractive index (*n*) of the thin films using equations (1), (2) & (3). The refractive index corresponding to T_M and T_m for same wavelengths are calculated. The variation of refractive index with energy of incident radiation $(h\nu)$ for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films is shown in Fig. 2. Refractive index found to decrease with the addition of Te. This may be due to the change in crystallite size, stoichiometry and internal strain [7-9] with the addition of Te to the Ge-Se network. The values of refractive indices corresponding to wavelength 1000 nm are given in Table 1.

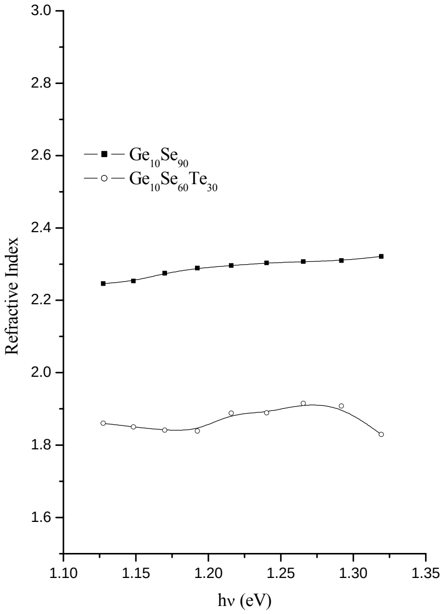

Fig. 2. Variation of Refractive index with *hν* for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

Table 1. Values of refractive index (*n*), extinction coefficient (*k*), optical conductivity (σ), real (ε_r) and imaginary (ε_i) dielectric constant for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ at 1000 nm.

Sample	*n*	*k*	σ	ε_r	ε_i
$Ge_{10}Se_{90}$	2.303	0.02731	1.88×10^{11}	5.303	0.1257
$Ge_{10}Se_{60}Te_{30}$	1.889	0.02221	1.25×10^{11}	3.567	0.0839

The extinction coefficient can be calculated by using the relation [10]

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

where 'α' is the absorption coefficient and is calculated from the relation

$$\alpha = (1/d)\ln(1/T) \tag{5}$$

where '*d'* is the thickness of the film and *'T'* is the transmittance [11]. The thickness of the thin film can be calculated by knowing the values of the refractive indices n_1 and n_2 at two adjacent maxima or minima corresponding to their wavelengths λ_1 and λ_2. Then the thickness is given by

$$d = \lambda_1\lambda_2/2(\lambda_1 n_2 - \lambda_2 n_1) \tag{6}$$

Fig. 3 shows the variation of extinction coefficient with $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films. The value of extinction coefficient increases with the increase in energy of the incident beam. This may be due to the large absorption coefficient for higher energy values.

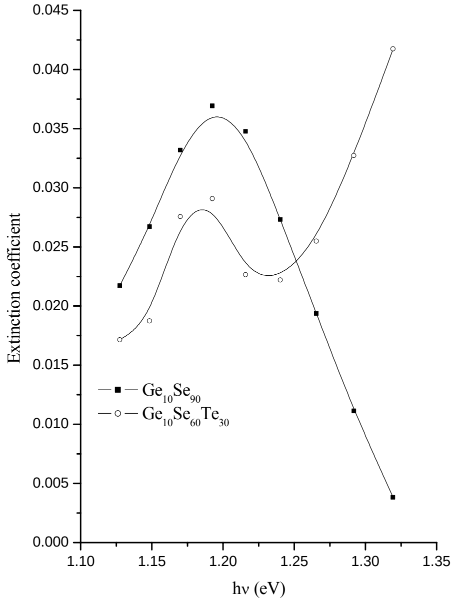

Fig. 3. Variation of Extinction coefficient with *hν* for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

Fig. 4 shows the variation of optical conductivity with the incident photon energy. The optical conductivity is determined using the relation [12]

$$\sigma = \alpha nc/4\pi \tag{7}$$

where *'c'* is the velocity of light. The optical conductivity directly depends on the absorption coefficient and found to increase sharply for higher energy values due to large absorption coefficient for these values.

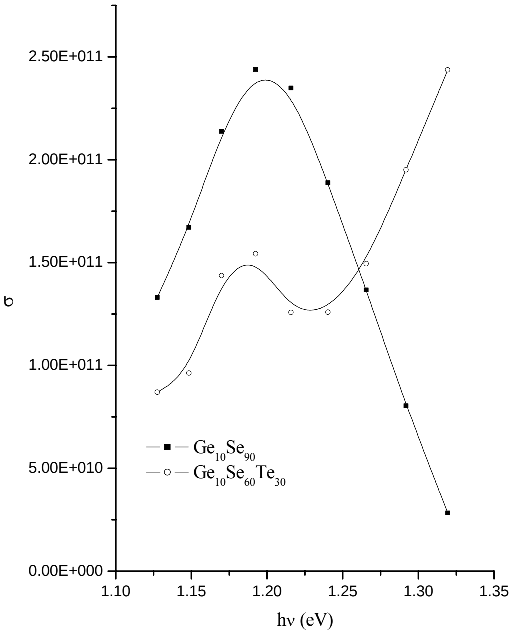

Fig. 4. Variation of Optical conductivity (*σ*) with *hν* for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

Fig. 5 and 6 shows the variation of the real and imaginary dielectric constants for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films. The complex dielectric constant is fundamental intrinsic material property. The real part of it is associated with the term that how much it will slow down the speed of light in the material and imaginary part gives that how a dielectric absorb energy from electric field due to dipole motion. The real and imaginary parts of the dielectric constant were determined using the relation [13],

$$\varepsilon = \varepsilon_r + \varepsilon_i = (n + ik)^2 \tag{8}$$

where 'ε_r' and 'ε_i' are the real and imaginary parts of the dielectric constant respectively and are given by

$$\varepsilon_r = n^2 - k^2 \tag{9}$$

and

$$\varepsilon_i = 2nk \tag{10}$$

The calculated values of ε_r and ε_i corresponding to wavelength 1000 nm are given in Table 1.

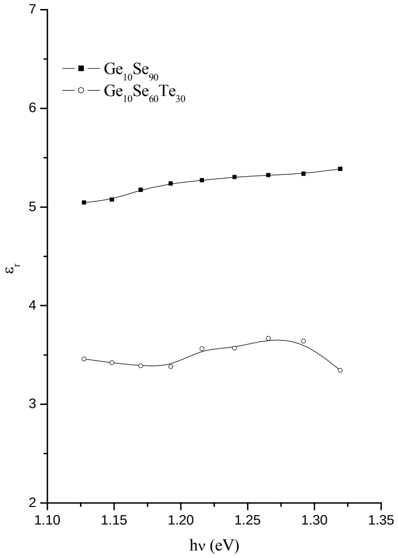

Fig. 5. Variation of real part of dielectric constant (ε_r) with $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

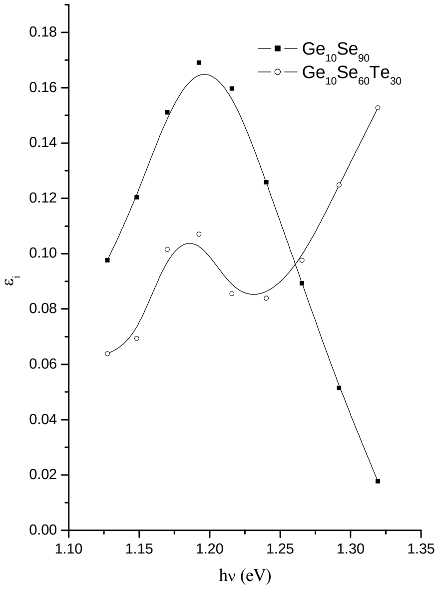

Fig. 6. Variation of imaginary part of dielectric constant (ε_i) with $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

Fig. 7 shows the variation of the absorption coefficient (α) with $h\nu$ for the $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films. The absorption coefficient is calculated by using the equation (5) and the values of α corresponding to wavelength 1000 nm are given in Table 2.

Table 2. Values of absorption coefficient (α) and optical band gap (E_g^{opt}) for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

Sample	α (cm^{-1})	E_g^{opt} (eV)
$Ge_{10}Se_{90}$	0.34×10^4	1.87
$Ge_{10}Se_{60}Te_{30}$	0.27×10^4	1.27

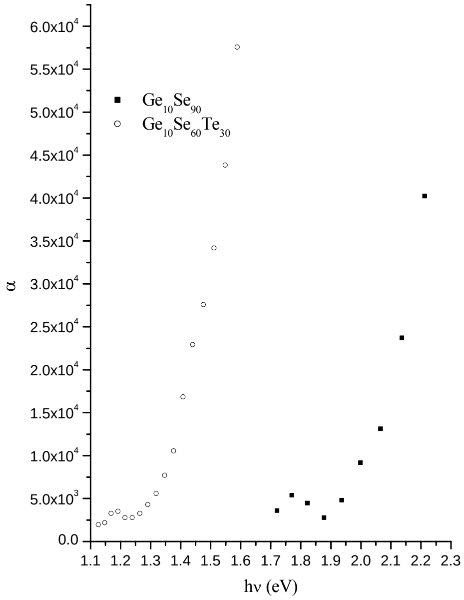

Fig. 7. Variation of absorption coefficient (α) with $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

Fig. 8 shows the variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ which is used to calculate optical band gap (E_g^{opt}). The optical gap is determined by the intercept of the extrapolations to zero with the photon energy axis $(\alpha h\nu)^{1/2} \to 0$, Tauc extrapolation [14]. The optical band gap decreases with the addition of 30 at. % of Te to $Ge_{10}Se_{90}$. The values are given in Table 2. This may be due to the presence of localised states in the forbidden gap. According to Mott and Devis [15] the width of mobility edge depends on the degree of disorder and defects present in the amorphous structure. In amorphous solids unsaturated bonds are responsible for the formation of these defects. Such defects produce localised states in the forbidden gap. The presence of such states is responsible for the decrease of optical band gap. The addition of Te increases the concentration of localised states leading to lowering the optical bad gap. The decrease in optical band gap can also be explained on the basis of average bond energy of the $Ge_{10}Se_{90}$ system. The addition of Te to $Ge_{10}Se_{90}$ system by replacing Se may lead to the formation of Ge-Te bonds (37.4 kcal/bond), Te-Te bonds (33.0 kcal/mol) and Se-Te bonds (40.6 kcal/bond) at the cost of Ge-Se bonds (49.1 kcal/bond) and Se-Se bonds (44.0 kcal/bond) [16]so the average bond energy of the system decreases. As the optical band gap is a bond sensitive property so the decrease in average bond energy of the system leads to decrease in the optical band gap [17].

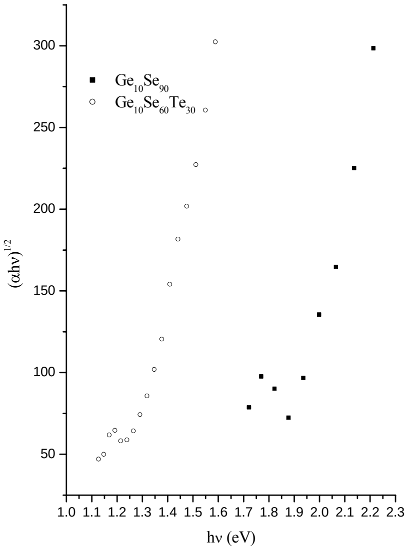

Fig. 8. Variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films.

4. Conclusion

Optical transmission spectrum is used to calculate the optical properties for $Ge_{10}Se_{90-x}Te_x$ $(x = 0, 30)$ thin films. Swanepoel method is used to calculate refractive index and it is found to decrease with the addition of Te. The optical constants *i.e.* extinction coefficient, optical conductivity, real and imaginary parts of dielectric constant, absorption coefficient and optical band gap are calculated. The decrease in optical band is explained on the basis of defect states and the average bond energy of the system.

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