

Calculation of optical constants in $a\text{-Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films

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Thin films of $a\text{-Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) glassy alloys are prepared by vacuum evaporation technique at $\sim 10^{-5}$ Torr on cleaned 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 400-1400 nm.

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1. Introduction

Chalcogenide glasses exhibit many attractive optical properties, including a high refractive index, large nonlinearities and excellent transmission in infrared (IR) region. So chalcogenide glasses are considered good candidates for their potential applications in the IR region like ultra fast all-optical switching, integrated optics, optical imaging, optical data storage and infrared optics [1-8]. 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 [9,10]. 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 $a\text{-Ge}_{10}\text{Se}_{90}$ system and then replace the Se by 30 at. % & 40 at. % of Te. The optical properties i.e. refractive index, extinction coefficient, optical conductivity, real and imaginary parts of dielectric constants, absorption coefficient and optical band gap of the thin films are calculated using the transmission spectrum.

2. Experimental procedure

Glassy alloys of $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) 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 $\sim 2 \times 10^{-5}$ Torr. The sealed ampoules are kept inside a furnace where the temperature is increased up to 1000 °C at a heating rate of 2-3 °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 were 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, dried in oven at about 110°C then subjected to deposition chamber. On the cleaned substrate thin films of the glassy alloys are deposited by vacuum evaporation technique at room temperature and base pressure of $\sim 10^{-5}$ 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 spectrophotometer [Hitachi-330], in the transmission range 400-1400 nm. The spectrometer was set with a suitable slit width of 1 nm in the measured spectral range. The amorphous nature of the deposited thin films is confirmed by X-ray diffraction technique as no sharp peak is observed. All the measurements are taken at room temperature.

3. Results and discussion

Optical transmission spectrum of the thin films is observed to be shifted towards higher wavelength with the addition of Te content. The variation of transmission with wavelength for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films is shown in Fig. (1). Transmission spectrum is used to calculate the refractive index using the envelope method proposed by Swanepoel [11]. The refractive index (n) has been obtained using the following expressions,

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

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

$$\text{and } M = 2s \frac{T_M - T_m}{T_M T_m} + \frac{(s^2 + 1)}{2} \text{ for weak and}$$

medium absorption region. (3)

TM and Tm 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 envelopes corresponding to TM and Tm. Taking the thickness of film as 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 TM and Tm for same wavelengths are calculated. The variation of refractive index with energy of incident radiation ($h\nu$) for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films is shown in Fig. 2. Refractive index found to decrease with the addition of 30 at. % Te and found to increase with 40 at. % of Te corresponding to same wavelength. This may be due to the change in crystallite size, stoichiometry and internal strain [12-14] with the addition of Te to the Ge-Se network. The values of refractive indices corresponding to wavelength 1100 nm are given in Table 1.

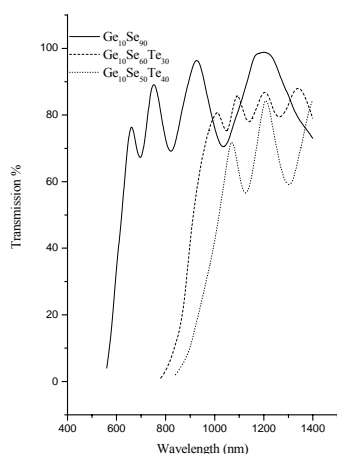


Fig. 1. Transmission spectrum for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

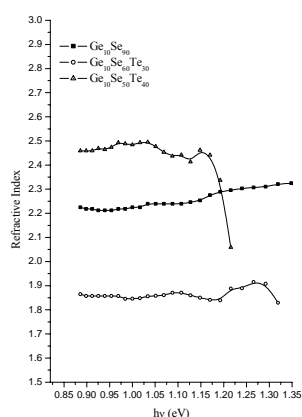


Fig. 2. Variation of Refractive index with $h\nu$ for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

Table 1. Values of refractive index (n), extinction coefficient (k), optical conductivity (σ), real (ϵ_r), imaginary (ϵ_i) dielectric constant and thickness (d) for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films at 1100 nm.

x	n	k	σ	ϵ_r	ϵ_i	d (nm)
0	2.246	0.02173	1.330×10^{13}	5.044	0.09761	798
30	1.860	0.01715	0.869×10^{13}	3.459	0.06379	749
40	2.413	0.05233	3.443×10^{13}	5.819	0.25254	813

The extinction coefficient can be calculated by using the relation [15]

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

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

$$\alpha = (1/d)\ln(1/T) \quad (5)$$

where 'd' is the thickness of the film and 'T' is the transmittance [16].

Fig. 3 shows the variation of extinction coefficient with $h\nu$ for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

The value of extinction coefficient decreases for 30 at. % addition of Te whereas it found to increase for 40 at. % of Te to $\text{Ge}_{10}\text{Se}_{90}$ at 1100 nm, Table 1. Extinction coefficient is a measure of fraction of light lost due to scattering and absorption per unit distance. Hence the fraction of light lost due to scattering and absorption per unit distance in a participating medium increases on the 30 at. % addition of Te in $\text{Ge}_{10}\text{Se}_{90}$ whereas it decreases on 40 at. % addition of Te to $\text{Ge}_{10}\text{Se}_{90}$.

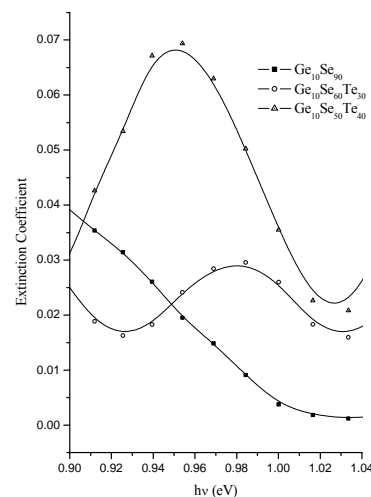


Fig. 3. Variation of Extinction coefficient with $h\nu$ for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

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

$$d = \lambda_1 \lambda_2 / 2(\lambda_1 n_2 - \lambda_2 n_1) \quad (6)$$

The values of thickness are given in Table 1 for the $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

Fig. 4 shows the variation of optical conductivity with the incident photon energy. The optical conductivity is determined using the relation [17]

$$\sigma = anc/4\pi \quad (7)$$

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 with 30 and 40 at. % addition of Te content to $\text{Ge}_{10}\text{Se}_{90}$ due to corresponding large absorption coefficient values. The optical conductivity found to be of the order of 10^{13} . The values of optical conductivity corresponding to wavelength 1100 nm are given in Table 1.

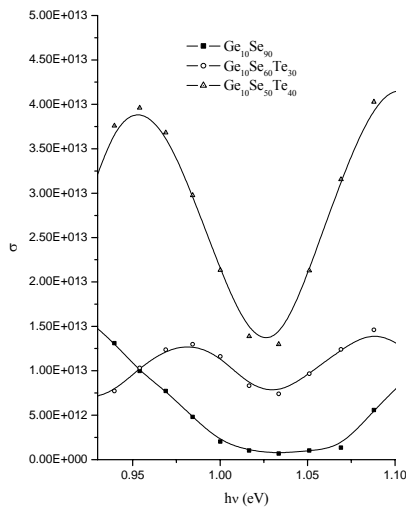


Fig. 4. Variation of Optical conductivity (σ) with $h\nu$ for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

Fig. 5 and 6 shows the variation of the real and imaginary dielectric constants for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) 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 knowledge of real and imaginary part dielectric constants provides information about the loss factor which is the ratio of imaginary part of dielectric constant to real part of dielectric constant i.e. larger the imaginary part of dielectric constant larger the loss factor or smaller the real part of dielectric constant smaller the loss factor. The real and imaginary parts of the

dielectric constant were determined using the relation [18],

$$\varepsilon = \varepsilon_r - i \varepsilon_i = (n - ik)^2 \quad (8)$$

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

$$\varepsilon_r = n^2 - k^2 \quad (9)$$

and

$$\varepsilon_i = 2nk \quad (10)$$

The calculated values of ε_r and ε_i corresponding to wavelength 1100 nm are given in Table 1.

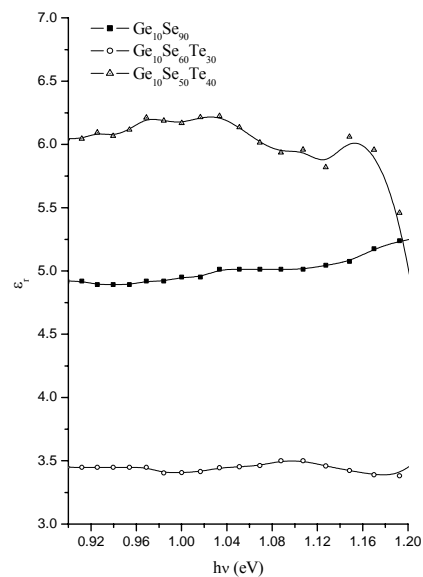


Fig. 5. Variation of real part of dielectric constant (ε_r) with $h\nu$ for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

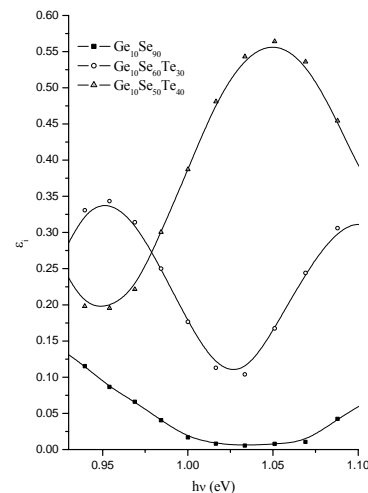


Fig. 6. Variation of imaginary part of dielectric constant (ε_i) with $h\nu$ for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

Fig. 7 shows the variation of the absorption coefficient (α) with $h\nu$ for the $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films. The absorption coefficient is calculated by using the equation (5) and the values of α corresponding to wavelength 1100 nm are given in Table 2.

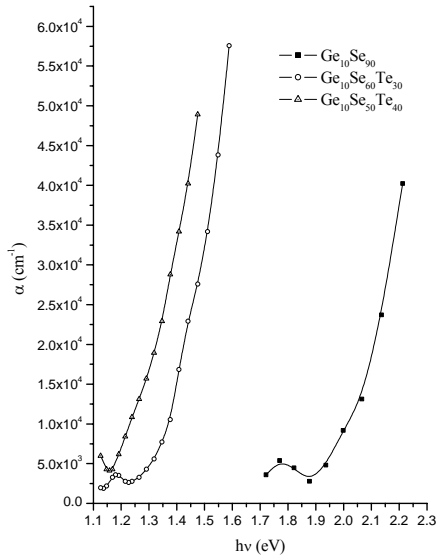


Fig. 7. Variation of absorption coefficient (α) with $h\nu$ for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

Table 2. Values of absorption coefficient (α) at 1100 nm and optical band gap for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

x	α (cm^{-1}) at 1100 nm	E_g^{opt} (eV)
0	0.34×10^4	1.87
30	0.27×10^4	1.27
40	1.08×10^4	1.12

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 $(\alpha h\nu)^{1/2} \rightarrow 0$, Tauc extrapolation [19]. The optical band gap decreases with the addition Te to $\text{Ge}_{10}\text{Se}_{90}$. 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 [20] 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 $\text{Ge}_{10}\text{Se}_{90}$ system. The addition of Te to $\text{Ge}_{10}\text{Se}_{90}$ 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) [21]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 [22].

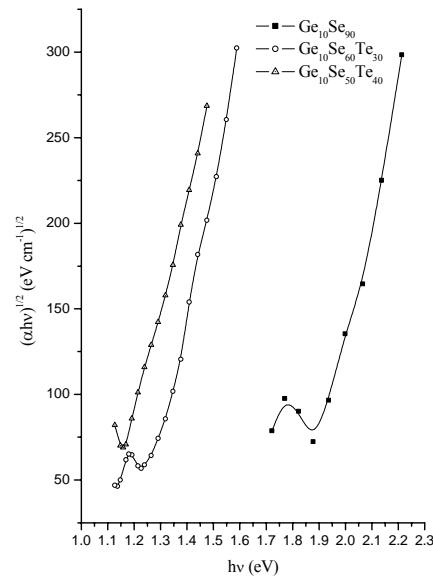


Fig. 8. Variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30, 40$) thin films.

4. Conclusion

Optical transmission spectrum is used to calculate the optical properties for $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x = 0, 30$) thin films. Swanepoel method is used to calculate refractive index. 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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