Optical band gap and refractive index dispersion

Parameters of In-Se-Te amorphous films

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Abstract:

Different compositions of the $In_x(Se_{0.75}Te_{0.25})_{100-x}$ (where $0 \leq x \leq 10$ at. %) chalcogenide thin films were prepared by using thermal evaporation method. A double beam spectrophotometer was used in order to measuring the film transmittance $(T(\lambda))$ at normal incidence in the wavelength range 400-2500 nm for these films. Applying the well known Swanepoel's method helps us in order to drive the film thickness and the real (n) and imaginary (k) parts of complex refractive index. Increasing the In content affect both the refractive index and the extinction coefficient for $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films. Optical absorption measurements show that the fundamental absorption edge is a function of composition. With increasing In content the refractive index increases while the optical band gap decreases. The obtained results well discussed in terms of the chemical bond approach and the cohesive energy.

Keywords: Chalcogenide glasses, thin films, Optical constants.

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1. Introduction

Chalcogenide Semiconducting glasses have particular interest due to their wide range of applications as solid state devices both in scientific and technological fields. Se - In and Se- Te binary alloys has got several advantages over pure and amorphous Se [1, 2]. The binary In-Se glassy alloys have drawn great attention because of their potential use in solar cells [3, 4].

The ternary Se–Te-In chalcogeinde glasses are widely used for various applications in many fields, such as optical recording media because of their excellent laser writer sensitivity, xerography, electrographic applications such as photoreceptors in photocopying and laser printing, infrared spectroscopy and laser fibre techniques [5–7]. There are number of papers [8- 13] found in the literature deals the effect of addition of In into Se-Te glasses on the physical properties such as electrical-, photoelectrical- properties and optical properties. The optical properties of these glasses in the form of thin films are important from an application point of view. The present work study in detail the effect of the additions of In content at the expense of Se and Te content on the optical constants (real and imaginary parts of the refractive index) by using only their transmittance spectra.

2. Theoretical background

Consider a thin homogeneous film of uniform thickness d, complex refractive index n_c = n - ik and absorption coefficient α on a transparent substrate with refractive index s. The substrate is considered to be perfectly smooth, but thick enough so that in practice the planes are not perfectly parallel so that all interference effects arising from the substrate are destroyed. The system is surrounded by air with refractive index n_o = 1. Taking all the multiple reflections at the three interfaces into account, it can be shown that in the case $k^2 << n^2$, the transmission T at normal incidence is given by [14-16]

$$T = \frac{Ax}{B - Cx\cos(\phi) + Dx^2} \tag{1}$$

where

$$A = 16n^2s \tag{2-a}$$

$$B = (n + 1)^3(n + s^2) \tag{2-b}$$

$$C = 2(n^2 - 1)(n^2 - s^2) \tag{2-c}$$

$$D = (n - 1)^3(n - s^2) \tag{2-d}$$

$$\phi = 4\pi n d/\lambda \tag{2-e}$$

$$x = \exp(-\alpha d) \tag{2-f}$$

Moreover, the values of the transmission at the maxima and minima of the interference fringes can be obtained from Eq. (1) by setting the interference condition $\cos\phi = +1$ for maxima (T_M) and $\cos\phi = -1$ for minima (T_m), i.e. the transmission at the maxima and minima of the interference fringes can be written as

$$T_M = \frac{Ax}{B - Cx + Dx^2} \tag{3}$$

$$T_m = \frac{Ax}{B + Cx + Dx^2} \tag{4}$$

From these two new formulae, many of the equations that provide the basis of the method in use are easily derived [14].

3. Experimental Details

Different compositions of bulk $In_x(Se_{0.75}Te_{0.25})_{100-x}$ (where x = 0, 2, 4, 6, 8 and 10 at. %) chalcogenide glasses were prepared from their components of high purity (99.999 %) by the usual melt quenching technique. The elements were heated together in an evacuated silica ampoule up to 750 K, and then the ampoule temperature kept constant for about 20 h. During the course of heating, the ampoule was shaken several times to maintain the uniformity of the melt. Finally, the ampoule was quenched into ice cooled water to avoid crystallization.

The amorphous thin films were deposited by evaporating the glasses from a resistance-heat quartz glass crucible onto clean glass substrates kept at room temperature and a vacuum of about 2×10^{-6} Torr using a conventional coating unit (Denton Vacuum DV 502 A). The evaporation rate as well as the film thickness was controlled using a quartz crystal DTM 100 monitor. Mechanical rotation of the substrate holder ($\approx$ 30 rpm) during deposition produced homogeneous film. The temperature rise of the substrate due to radiant heating from crucible was negligible. Fluctuations in the measured transmittance of the films were very small ($\approx$ 1.0%), confirming their good homogeneity.

The amorphous nature of the as-deposited films was checked using an Philips X-ray diffractometer (1710). The chemical compositions of the as-deposited films were measured using energy dispersive X-ray spectroscopy (Link analytical EDS).

The compositions so determined agreed with those of the starting materials to within± 0.35 at %. The optical transmittance at normal incidence was measured in the wavelength range 200–2500 nm using a double-beam computer-controlled spectrophotometer (Shimadzu UV-2101 combined with PC). The spectrophotometer was set with a slit-width of 1 nm and as this was much smaller than the line widths it was unnecessary to make slit-width corrections. The line width is simply taken to be the separation of two adjacent interference maxima and minima. Without a glass substrate in the reference beam, the measured transmittance spectra were used to calculate the optical constants. In the present work, the envelope method suggested by Swanepoel [14] has been applied.

4. Results and Discussion

Fig.1. represent the XRD patterns for $In_x(Se_{0.75}Te_{0.25})_{100-x}$ ($0\leq x \geq 10$) thin films as shown in this figure that the, films did not reveal discrete or any sharp peaks, but the characteristic broad humps of the amorphous materials.

4.1 Calculation of the refractive index and film thickness

Fig.2(a) shows the measured transmittance (T) spectra for different compositions of $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films. From this figure one can note that, the addition of In content at the expense of Se and Te content shifts the optical transmittance to the lower energies (i. e, red shift of the optical absorption edge). Fig. 2(b) as a comparative example, shows the measured transmittance (T), the created envelopes, T_M, and, T_m, (both the envelopes being computer-generated using the Origin Lab version 7 program), and the geometric mean, $T_\alpha = \sqrt{T_M T_m}$, in the spectral region with interference fringes [17]) for $Se_{75}Te_{25}$ thin film.

According to Swanepoel's method based on the idea of Manifacier et al. [18] the first approximate value of the refractive index of the film, n_1, in the spectral region of medium and weak absorption can be calculated as well as detailed here [17]. Using the values of, n_1, and taking into account the basic equation for the interference fringes:

$$2nd = m_o \lambda \tag{5}$$

where the order number, m_o, is an integer for maxima and a half-integer for minima the first approximate value of the film thickness, d_1, can be expressed as:

$$d_1 = \frac{\lambda_1 . \lambda_2}{2(n_{c2}\lambda_1 - n_{c1}.\lambda_2)} \qquad (6)$$

where, n_{c1}, and, n_{c2}, are the refractive indices at two adjacent maxima (or minima) at, λ_1, and, λ_2. The last value deviates considerably from the other values and must consequently be rejected. The average value ($\overline{d_1}$) of d_1 (ignoring the last value), can now be used, along with, n_1, to calculate, m_o, for the different maxima and minima using Eq. (5). The accuracy of the film thickness can now be significantly increased by taking the corresponding exact integer or half-integer values of, m_o, associated with each extreme point (see Fig. 2(b)) and deriving a new thickness, d_2, using Eq. (1), again using the values of, n_1, The values of the thickness in this way have a smaller dispersion. It should be emphasized that the accuracy of the final thickness, $\overline{d_2}$, is better than 1% as well as reported elsewhere [17]. The deduced values of, $\overline{d_1}$, m_1 and $\overline{d_2}$ are listed in Table 1 for different compositions of $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films.

With the accurate values of m_o and ($d = \overline{d_2}$) expression (1) can then be solved for, n, at each, λ, and, thus, the final values of the refractive index, n_2, are obtained. These values of, n_2, can be fitted to a reasonable function such as the two-term Cauchy dispersion relationship [17]:

$$n(\lambda) = a + b/\lambda^2 \qquad (7)$$

where a and b are constants, then, Eq. 7 can be used to extrapolate the wavelength dependence beyond the range of measurement. Fig. 3 illustrates the dependence of the refractive index, n, on wavelength for different compositions of the amorphous $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films. The relative error in n, $\Delta n/n$, does not exceed the precision of the measurements $\Delta T/T$ (±1%). The least-squares fit of n_2 values (solid lines of Fig.3) for the different samples, yields n = 2.26 + (1.19 x 10^5/ λ^2), n = 2.344 + (1.94 x 10^5/ λ^2), n = 2.444 + (1.95 x 10^5 / λ^2), n = 2.644 + (1.97 x 10^5 / λ^2), n = 2.694 + (1.97 x 10^5 / λ^2), and n = 2.77 + (2.39 x 10^5 / λ^2) for x = 0, 2, 4, 6, 8 and 10 at. %., respectively. As shown in Fig. 3 the refractive index, n, is decreases with increasing wavelength of the incident photon, while at higher wavelengths the refractive index, n, tends to be constant for all compositions under study. Here the values of refractive index for all compositions can be fitted according to the Wemple-DiDomenico (WDD) dispersion relationship [19];

$$n^2(h\nu) = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \tag{8}$$

where E_0 is the single-oscillator energy and E_d is the dispersion energy or single-oscillator strength where, the refractive index factor $(n^2-1)^{-1}$ can be plotted as a function of $(h\nu)^2$ and fitting straight lines as shown in Fig.4, the values of the E_0 and E_d can be determined from the intercept E_0/E_d and the slope $(E_0 E_d)^{-1}$. As well as mentioned before by Tanaka [20] that, the oscillator energy (E_0) is an average energy gap, and to a good approximation, scales with the optical band gap (E_g), $E_0 \approx 2E_g$ as shown in Table 2.

Fig. 4 also shows the values of the refractive index $n(0)$ at $h\nu = 0$ of the $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films. The obtained values of E_o, E_d and $n(0)$ are listed in Table 2. It was observed that, the single oscillator energy E_0 decreases while, both the dispersion energy E_d and $n(0)$ increases with the increase of In content. An important achievement of the WDD model is that it relates the dispersion energy, E_d, to other physical parameters of the material through the following empirical relationship [19]

$$E_d = \beta \, N_c \, Z_a \, N_e \quad (eV) \tag{9}$$

Where N_c is the effective coordination number of the cation nearest-neighbor to the anion, Z_a is the formal chemical valency of the anion, N_e is the effective number of valence electrons per anion and β is a two-valued constant with either an ionic or a covalent value ($\beta_i = 0.26 \pm 0.03$ eV and $\beta_c = 0.37 \pm 0.04$ eV, respectively). Therefore, in order to account for the compositional trended of E_d it is suggested that, the observed decrease in E_d with increasing In content is primarily due to the change in the ionicities (homopolar Se–Se bonds are introduced together with extra Se atoms), which decreases with increasing the In content (see Table.2). The values of the single-oscillator energy, the dispersion energy, the static refractive index and the excess of Se-Se homopolar bonds for the $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films are listed in Table 2.

4.2 Determination of the extinction coefficient and optical band gap

Since the values of the refractive index, n, are already known over the whole spectral range 400-2500 nm, the absorbance $x_a(\lambda)$ can be calculated using the interference-free transmission spectrum T_α (see Fig. 2(b)), using the well-known equation suggested by Connell and Lewis [21]:

$$X_a = \frac{P + [P^2 + 2QT_\alpha \sqrt{(1-R_2R_3)}]}{Q} \qquad (10)$$

where $P = (R_1 - 1)(R_2 - 1)(R_3 - 1)$ and $Q = 2T_\alpha (R_1R_2 - R_1R_3 - 2R_1R_2R_3)$, R_1 is the reflectance of the air–film interface ($R_1 = [(1 - n)/(1 + n)]^2$), R_2 is the reflectance of film–substrate interface ($R_2 = [(n - s)/(n + s)]^2$) and R_3 is the reflectance of the substrate–air interface ($R_3 = [(s - 1)/(s + 1)]^2$). Moreover, since d is known, the relation $x_a = \exp(-\alpha d)$ can then be solved for the values of the absorption coefficient, α. In order to complete the calculation of the optical constants, the extinction coefficient, k, is calculated using the values of, α, and, λ, through the already mentioned formula, $k = \alpha\lambda/4\pi$. Fig.5 illustrates the dependence of, extinction coefficient, k, on the wavelength for $In_x(Se_{0.75}Te_{0.25})_{100-x}$ ($0 \le x \le 10$ at. %) thin films. For $\alpha \le 10^5$ cm^{-1}, the imaginary part of the complex index of refraction is much less than, n, so that the previous expressions used to calculate the reflectance is valid. In the region of strong absorption, the interference fringes disappear; in other words, for very large, α, the three curves T_M, T_α and T_m converge to a single curve. According to Tauc's relation [22, 23] for allowed non-direct transitions, the photon energy dependence of the absorption coefficient can be described by

$$(\alpha h\nu)^{1/2} = B^{1/2} (h\nu - E_g) \qquad (11)$$

where B is a parameter that depends on the transition probability and E_g is the optical energy gap. Fig.6(a) shows the absorption coefficient in the form of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films. The intercepts of the straight lines with the photon energy axis yield values of the optical band gap, E_g as shown in Fig6(b).

The bond energies $D(A - B)$ for hetero-nuclear bonds have been calculated by using the empirical relation proposed by Pauling [24] as

$$D(A - B) = [D(A - A).D(B - B)]^{1/2} + 30(\chi_A - \chi_B)^2 \qquad (12)$$

where $D(A - A)$ and $D(B - B)$ are the energies of the homo-nuclear bonds (in units kcal mol^{-1}) [25], χ_A and χ_B are the electronegativity values for the involved atoms [26]. Bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied [27].In the present compositions, the In-Se bonds with the highest possible energy (54.321 kcal mol^{-1}) are expected to occur first followed by the Se-Te bonds (44.19 kcal mol^{-1}) to saturate all available valence of Se. There are still unsatisfied as which must be satisfied by Se-Se defect

homo-polar bonds. Based on the chemical bond approach, the bond energies are assumed to be additive. Thus, the cohesive energies were estimated by summing the bond energies over all the bonds expected in the material. Calculated values of the cohesive energies for all compositions are presented in Table 2. These results indicate that, the cohesive energies of these glasses show an increase with increasing the In content. According to the chemical bond approach we can say that the highest Se-Se band gap 1.95 eV [28] are replaced by the lowest band gap such as Se-Te and In-Se [29] bonds that can be interpreted the decrease of the Eg with increasing the In content.

5- Conclusion

The addition of In at the expense in Se or Te of $In_x(Se_{0.75}Te_{0.25})_{100-x}$ ((x = 0, 2, 4, 6, 8 and 10 at. %) glasses result in , the increase of refractive index with increasing In content while the optical band gap were found to decreases. The obtained results well discussed in terms of the chemical bond approach, and the cohesive energy CE.

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Figure Captions

Fig.1 represent the XRD patterns for the as prepared $In_x(Se_{0.75}Te_{0.25})_{100-x}$ ($0 \leq x \geq 10$) thin films.

Fig. 2(a) the compositional dependence (red shift of the optical absorption edge) of the measured transmittance (T) spectra for different compositions of $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films.

Fig. 2(b) The measured transmittance (T), the created envelopes, T_M, and, T_m, (both the envelopes being computer-generated using the Origin Lab version 7 program), and the geometric mean, $T_\alpha = \sqrt{T_M T_m}$, in the spectral region with interference fringes [17]) for $Se_{75}Te_{25}$ thin film.

Fig.3 the dependence of the refractive index, n, on wavelength and the indium content for different compositions of the amorphous $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films.

Fig.4 The refractive index factor $(n^2-1)^{-1}$ as a function of $(hv)^2$ for amorphous $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films.

Fig.5 The dependence of, extinction coefficient, k, on the wavelength for $In_x(Se_{0.75}Te_{0.25})_{100-x}$ ($0 \leq x \leq 10$ at. %) thin films.

Fig.6(a) shows the absorption coefficient in the form of $(\alpha hv)^{1/2}$ versus hv for the $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films.

Fig.6(b) The optical band gap as a function of the In content for $In_x(Se_{0.75}Te_{0.25})_{100-x}$ thin films.

Table Headings

Table 1: Table 1. Values of λ, T_s, T_M, T_m, n_1, d_1, m_o, m d_2 and n_2 for $In_x(Se_{0.75}Te_{0.25})_{100-x}$ (where x = 0, 2, 4, 6, 8 and 10 at%) thin films from transmission spectra. The underlined values of transmittance are those given in the transmittance spectra of figure 2(b) and the others are calculated by the envelope method.

Table 2: Some physical parameters as a function of In content for $In_x(Se_{0.75}Te_{0.25})_{100-x}$ (where x = 0, 2, 4, 6, 8 and 10 at%) thin films.