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Abstract

$Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films of different thicknesses were prepared by a thermal evaporation technique. Transmittance and reflectance data are measured for the films obtained, in the wavelength range 400–2500 nm. The optical constants, the refractive index n and the absorption index k, are calculated by an accurate method using Murmann's exact equations. It is found that values of n at any wavelength for $Se_{70}Te_{30}$ films are larger than that for $Se_{70}Te_{20}Cd_{10}$ films. From the analysis of the optical constants it was found that the optical energy gap (E_g^{opt}) and the width of the tails of the localized states in the gap region (E_e) increase while the high frequency dielectric constant decreases with the addition of Cd.

1. Introduction

Amorphous semiconductors, in particular selenium alloys, exhibit the unique property of reversible transformations, which is useful in optical memory devices [1]. These glasses are of tremendous interest because of their wide range of transparency in the far-infrared region [2]. SeTe alloys have created extreme interest due to their greater hardness, higher photosensitivity, higher crystallization temperature and lower ageing effect as compared with amorphous Se [3, 4]. It was found that substitution of Te for Se in Se–Te glasses breaks up the Se_8 ring structure and increases the chain fraction but reduces the chain structure in the Te structure [5–7].

Several authors have investigated the physical properties of SeTe glasses and the effect of Cd on these properties [1, 8–12] for the bulk form. However few studies are available for these compositions for the thin film form [13–15]. It has been reported [16] that Cd impurity increases the conductivity by orders of magnitude for amorphous As_2SeTe_2. It is therefore interesting to study the effect of such metallic addition on the properties of other glassy systems. Predeep *et al* [10] found that Cd addition to Se–Te alloys makes bonds with Se and Te which are probably dissolved in the Se chains. Thus the number of Se_8 rings decreases while the number

of long Se–Te polymeric chains and Se–Te mixed rings decreases. This affects the values of optical constants and hence the energy gap of the material.

In this paper, optical properties were studied at room temperature for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films deposited on glass substrates with different thicknesses (211–492 nm) at room temperature, using optical transmittance and reflectance data for the spectral region (400–2500 nm). The transmittance and reflectance data were analysed to determine the optical constants (refractive index n; absorption index k and absorption coefficient a). An analysis of the refractive index has been carried out to obtain the high frequency dielectric constant and other related parameters. Analysis of the absorption coefficient has been carried out to obtain the optical band gap and determine the nature of transitions involved. Our results are compared with those obtained previously.

2. Experimental techniques

Glass alloys of $Se_{70}Te_{30-x}Cd_x$ ($x = 0, 10$) were prepared by a quenching technique. Materials (99.999% pure) were weighted according to their atomic percentages and were sealed in quartz ampoules (length 15 cm, internal diameter 12 mm) in a vacuum where the temperature was raised to the maximum temperature (1173 K) at a rate of 3–4 K min^{-1} to 1173 K. The ampoule was rocked frequently for a period of 10 h at the maximum temperature to make the melt homogeneous. The quenching was done in icy water to obtain the synthesized material in an amorphous state. Thin films with different thicknesses of the glasses investigated (211–492 nm) were deposited under vacuum of 10^{-5} Torr, by a thermal evaporation technique using molybdenum boats at a constant rate on dry clean glass substrates, using a coating unit (Edward 306 A). The substrate temperature was held at that of the room during deposition. The film thickness was measured by Tolansky's interferometric method [17]. X-ray diffraction reveals the amorphous nature of the film compositions investigated. The optical transmittance and reflectance of the samples were measured at room temperature using unpolarized light at normal incidence in the wavelength range 400–2500 nm using a dual-beam spectrophotometer (UV-3101 PC Shimadzu). All measurements reported here were carried out at room temperature.

3. Results and discussion

3.1. Determination of optical constants

Figures 1 and 2 represented the spectral distribution curves $T(\lambda)$ and $R(\lambda)$ obtained for the spectral range (400–2500 nm) for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films with different thicknesses in the range 211–492 nm. It is clear that at longer wavelengths, films become transparent ($T + R = 1$) and no light is absorbed ($k = 0$).

In order to obtain the optical constants n and k for the films under test, Murmann's [18] exact equations have been applied in conjunction with a special iterative computer program. This method requires approximate values of n and k. The approximate values n_a and k_a were obtained using the Swanepoel method [19]. Using the experimental values of the transmittance (T) and reflectance (R), it is easy to solve Murmann's exact equations simultaneously to obtain the accurate values of n and k using the iterative technique through initial approximations for n and k obtained by the Swanepoel method. Figures 3 and 4 show the spectral distributions of n and k for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films obtained using Murman's method. The discrepancy in the results obtained lies within the range of the experimental error ($\pm 6\%$ for (n) and $\pm 3\%$ for (k)). Accordingly both n and k are independent of the film thickness in the range investigated
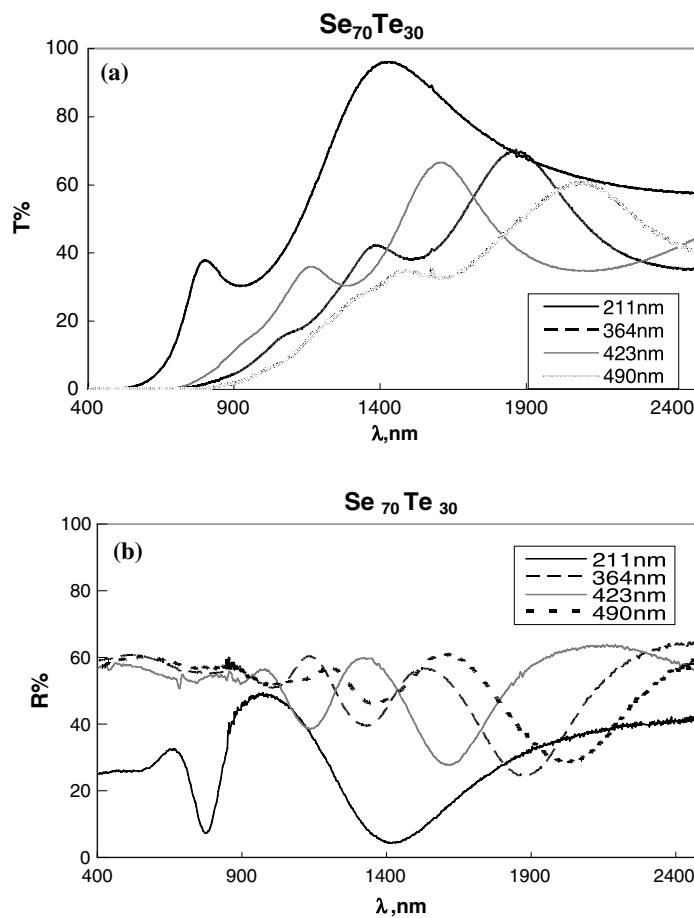
Figure 1. ((a), (b)) Spectral distributions of the transmittance $T(\lambda)$ and reflectance $R(\lambda)$ for $Se_{70}Te_{30}$ films of different thicknesses.

for the compositions under test. It clearly evident from figure 3 that the values of n at any wavelength for $Se_{70}Te_{30}$ films are larger than that for $Se_{70}Te_{20}Cd_{10}$ films.

3.2. Analysis of refractive index n data

The data obtained for the refractive index n can be analysed to obtain the high frequency dielectric constant via two procedures [20]. The first procedure describes the contribution of free carriers and the lattice-vibrational modes of dispersion. The second procedure, on the other hand, is based upon the dispersion arising from the bound carriers in an empty lattice. To obtain a reliable value for the high frequency dielectric constant we employed both procedures. In the first procedure, the square of the refractive index n^2 is plotted versus λ^2 as shown in figure 5(a) for both $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films. It is observed that the dependence of n^2 on λ^2 is linear at longer wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives a value of ε_∞ for both $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$. These values are given in table 1. In the second procedure and at high frequencies, the properties of $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films could be treated as that of a single oscillator at wavelength λ_o.
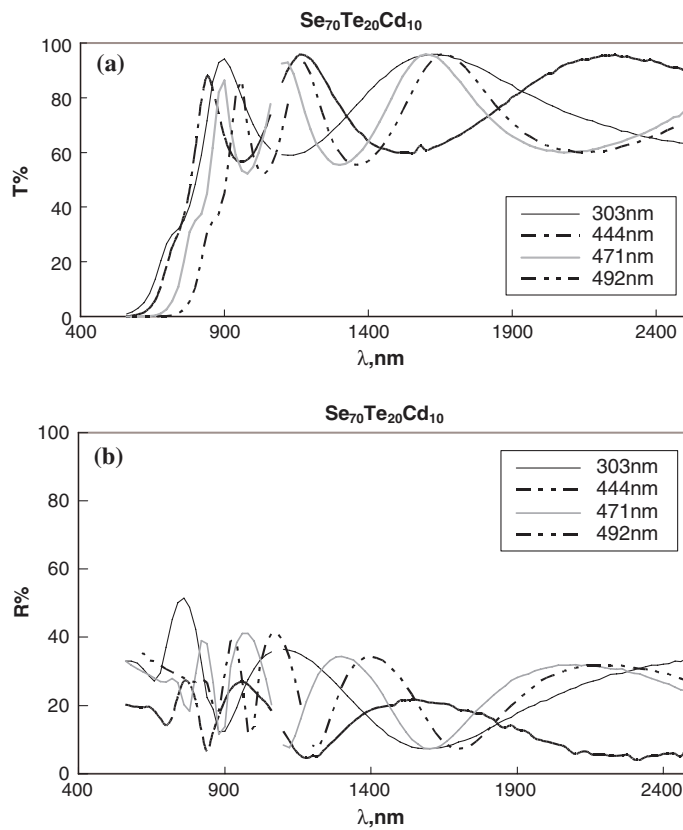
Figure 2. ((a), (b)) Spectral distributions of the transmittance $T(\lambda)$ and reflectance $R(\lambda)$ for Se$_{70}$Te$_{20}$Cd$_{10}$ films of different thicknesses.
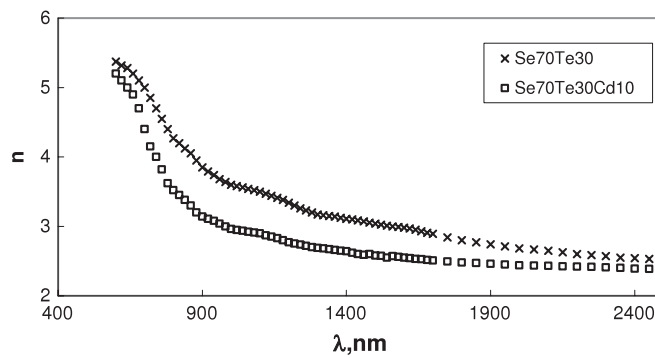

Figure 3. Dependence of the refractive index n on the wavelength λ for Se$_{70}$Te$_{30}$ and Se$_{70}$Te$_{20}$Cd$_{10}$ thin films.

The high frequency dielectric constant can be calculated using the following simple classical dispersion [20]. If n_o is the refractive index of an empty lattice at infinite wavelength, the index will vary as

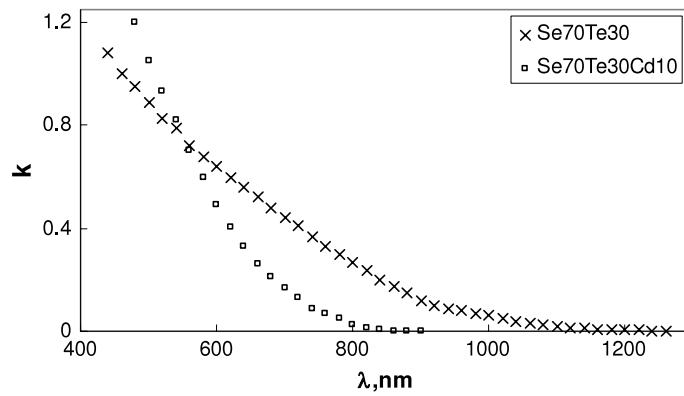$$(n_o^2 - 1)/(n^2 - 1) = 1 - (\lambda_o/\lambda)^2, \tag{1}$$

Figure 4. Dependence of the absorption index k on the wavelength λ for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ thin films.
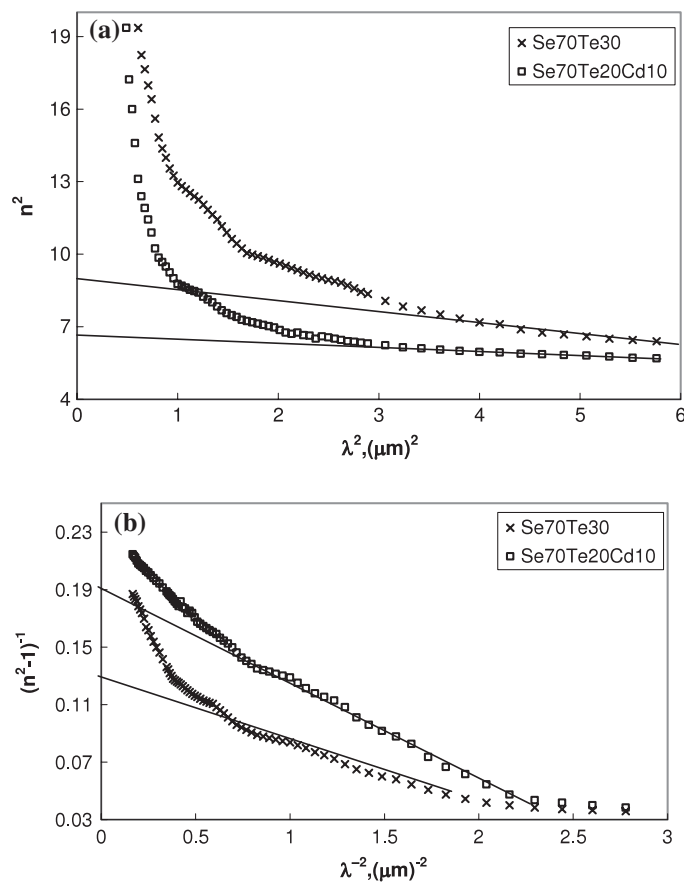
Figure 5. (a) Plot of n^2 against λ^2 for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ thin films. (b) Plots of $(n^2-1)^{-1}$ against λ^{-2} for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ thin films.

where λ_o and n_o are evaluated from plots of $(n^2-1)^{-1}$ against λ^{-2}, as shown in figure 5 (b) for both $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ thin films; the values of $n_o^2 = \varepsilon_\infty$ and λ_o are given in table 1.

Table 1. Parameters derived from the refractive index n for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films.

Parameter	$Se_{70}Te_{30}$ films	$Se_{70}Te_{20}Cd_{10}$ films
$\varepsilon_\infty(1)$	8.92	6.61
$\varepsilon_\infty(2)$	8.69	6.21
λ_o (nm)	645	334
S_o (m^{-2})	3×10^{13}	2×10^{13}
E_s (eV$_s$)	2.6	3.1
E_s/S_o (eV m^2)	8.6×10^{-14}	6.4×10^{-14}
E_d (eV)	15.3	24.3
N/m^* (m^{-3} kg^{-1})	2.7×10^{50}	1.6×10^{50}

Values of ε_∞ obtained by the two procedures are in good agreement with each other within 2.6% in the case of $Se_{70}Te_{30}$ films and 6.2% in the case of $Se_{70}Te_{20}Cd_{10}$ films respectively. The reason for this agreement, despite the difference in procedures used, is that the lattice-vibrational and plasma frequencies are well separated from the absorption band-edge frequency.

Equation (1) can also be expressed as [21]

$$(n^2 - 1) = (S_o\lambda_o^2)/[1 - (\lambda_o/\lambda^2)], \tag{2}$$

where λ_o is the average oscillator wavelength and $S_o = (n_o^2 - 1)/\lambda_o^2$ is the average oscillator strength. Wimple and Didomenico [22, 23] analysed refractive index data below the interband absorption edge using a single-effective-oscillator equation [22–24]

$$(n^2 - 1) = E_d E_s/[E_s^2 - (h\nu)^2], \tag{3}$$

where $h\nu$ is the photon energy, E_s is the single-oscillator energy, and E_d is the dispersion energy.

Values of the parameters E_s and E_d were evaluated by plotting $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ and fitting it to a straight line for both $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films. The values obtained for the single-oscillator parameters E_s and E_d for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films are given in table 1. The values of S_o and E_s obtained are used to calculate the respective index dispersion parameters E_s/S_o for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films which are given also in table 1. This value is of the same order as that obtained before by Didomenico and Wemple [24] for a number of materials ($E_s/S_o = 6.0 \pm 0.5 \times 10^{-14}$ eV m^2).

The real part of dielectric constant can be given in the form

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - \left(\frac{e^2 N}{4\pi^2 c^2 \varepsilon_o m^*}\right)\lambda^2, \tag{4}$$

where ε_∞ is the high frequency dielectric constant calculated according to the first procedure, N is the free charge carrier concentration, ε_o is the permittivity of free space (8.854×10^{-12} F m^{-1}), m^* is the effective mass of the charge carriers and c is the velocity of light. The values of ε_1 obtained are plotted as a function of λ^2 as shown in figure 6. It is observed that the dependence of ε_1 on λ^2 is linear at longer wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives the value of ε_∞ and from the slopes of these lines, values of N/m^* for the compositions investigated were calculated according to equation (4). The values of N/m^* obtained are given also in table 1.

3.3. Analysis of absorption index k data

At different values of the wavelength (λ) in the spectrum considered and using the corresponding values of (k), the absorption coefficient (α) is calculated for $Se_{70}Te_{30}$ and
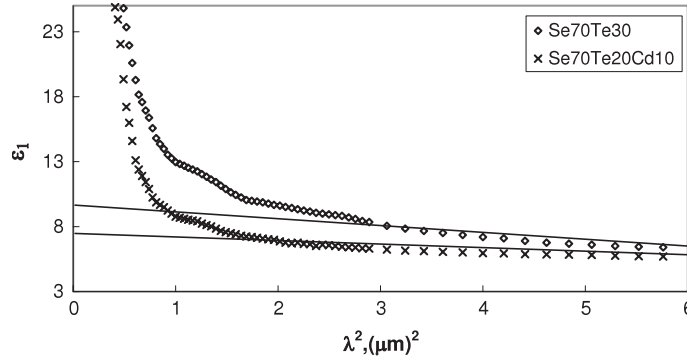
Figure 6. Plots of ε_1 as a function of λ^2 for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ thin films.

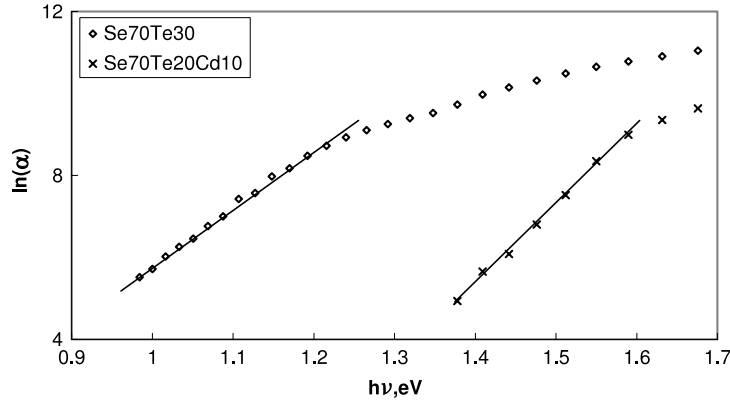**Figure 7.** Dependence of $\ln(\alpha)$ on the photon energy $h\nu$ for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ thin films.

$Se_{70}Te_{20}Cd_{10}$ films using the well known equation $\alpha = 4\pi k/\lambda$. The spectral distribution of the absorption coefficient can be divided into two regions.

(i) For absorption coefficient $\alpha(\nu) \leqslant 10^4$ cm^{-1} there is usually an Urbach [25] tail where $\alpha(\nu)$ depends exponentially on the photon energy $(h\nu)$ as

$$\alpha(\nu) = \alpha_o \exp(h\nu/E_e),$$

where ν is the frequency of the radiation, α_o is constant and E_e is often interpreted as the width of the tails of the localized states in the gap region and in general represents the degree of disorder in an amorphous semiconductor [26]. Therefore, plotting $\ln \alpha$ as a function of $h\nu$ as in figure 7, both values of α_o and E_e for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films are given in table 2.

(ii) For higher values of the absorption coefficient $\alpha(\nu) > 10^4$ cm^{-1}, the variation of the absorption coefficient for indirect transitions obeys the relation [27]

$$\alpha h\nu = A(h\nu - E_g^{opt})^{1/2},$$

where A is the edge width parameter representing the film quality, which is calculated from the linear part of this relation, E_g^{opt} is the optical energy gap of the material. The usual method for the determination of the value of E_g^{opt} involves a plotting of $(\alpha h\nu)^{1/2}$ against $h\nu$ for both $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films. Figure 8 shows that $(\alpha h\nu)^{1/2}$ versus $h\nu$ is a linear function for both compositions. This linearity indicates the existence of the allowed indirect transitions.
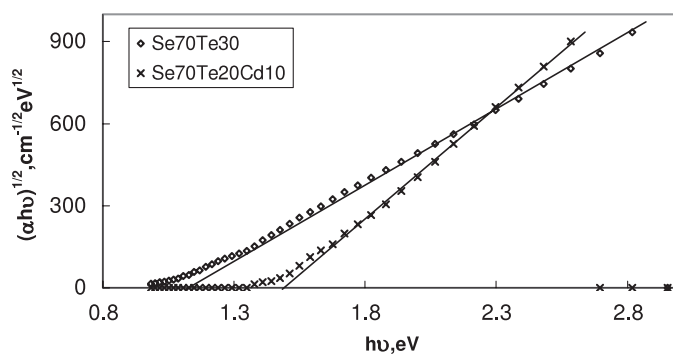
Figure 8. Dependence of $(\alpha h\nu)^{1/2}$ on the photon energy $h\nu$ for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ thin films.

Table 2. Parameters derived from absorption index k for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films.

Parameter	$Se_{70}Te_{30}$ films	$Se_{70}Te_{20}Cd_{10}$ films
E_e (eV)	0.051	0.072
α_o (cm^{-1})	7.49×10^{-5}	6.22×10^{-11}
E_g^{opt} (eV)	1.12	1.48
A (cm^{-1} eV^{-1})	3.09×10^5	4.04×10^5

This result agrees with the data of Fayek *et al* [2] for $Se_{70}Te_{30}$ films in their study of the optical properties of $Se_{70-x}Te_{30}Cd_x$ films; however they give a smaller value of E_g^{opt} (1 eV). This is probably due to the approximate method that they used to calculate the absorption coefficient. The indirect band gap is also obtained by Mendoza *et al* [28] in their study of optical properties of Se_xTe_{1-x} films. They showed that the energy gap increases from 1 eV for $x = 0.32$ to 1.88 eV for $x = 1$. The value of the energy gap E_g^{opt} is determined from the intercept of the extrapolation to zero absorption with the photon energy axis. Accordingly, values of the optical band gap E_g^{opt} and A are given also in table 2. It is indicated that E_g^{opt} increases on addition of Cd. Glasses containing Se are known to consist of a mixture of polymeric chains and Se_8 rings. Also Te enters as copolymer chains and tends to reduce the number of Se_8 rings [29]. Simultaneously, it increases the number of Se and Te atoms in the chain structure. The addition of Cd makes bonds with Se and Te atoms, producing Se–Cd bonds [30] of higher strength than other bonds in the network structure. This leads to a decrease in the number of polymeric chains in the structure. Thus the addition of Cd to the composition investigated results in an increase in the density of bonds between Se (the host element) and the Cd metal stronger than other bonds present in the compositions under investigation, because for the strong bonds between Se and Cd the values of the optical energy gap and the tail width for $Se_{70}Te_{30}$ films are less than those for $Se_{70}Te_{20}Cd_{10}$ films.

4. Conclusions

Transmittance and reflectance data are measured for $Se_{70}Te_{30}$ and $Se_{70}Te_{20}Cd_{10}$ films in the wavelength range 400–2500 nm. The optical constants n and k of have been determined by an accurate method using Murmann's exact equations. Both n and k are practically independent of the film thickness in the range 211–492 nm. The values of n at any wavelength for $Se_{70}Te_{30}$ films are found to be larger than that for $Se_{70}Te_{20}Cd_{10}$ films. Analysis of refractive index data

yields the values of the high frequency dielectric constant, ε_∞ and other important parameters. The optical absorption measurements indicate that the absorption mechanism is due to allowed indirect transitions for both compositions. The increase of the optical energy gap (E_g^{opt}) and the width of the tails of the localized states in the gap region (E_e) with the addition of Cd is explained by the formation of Se–Cd strong bonds because of the addition of Cd to $Se_{70}Te_{30}$ films.

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