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Optical properties of GeSeTl thin films

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Abstract

Using the usual melt-quenching technique, glasses with composition $Ge_{14}Se_{86-x}Tl_x$ ($x = 20\%$, 22%, 23.5%, 25%, 26.5% and 28%) have been obtained to prepare thin films with different thicknesses ($d = 15, 30, 60, 90, 120$ and 180 nm) using electron-beam evaporation. The optical gap E_g was found to decrease with increasing thallium content, x. It is found also that thicker films are accompanied with larger optical gaps. The refractive index n was found to increase with increasing Tl ratio and to decrease with increasing thickness of the films.

1. Introduction

Chalcogenide glasses have been intensively investigated because of their technologically important electrical properties. Electrical transport in amorphous materials has attracted much attention for many years [1–4]. The system Ge–Se–Tl is among the new generation of chalcogenide glasses, so, a lot of work has been done on impurity effects on conductivity and optical properties [5–7]. The change in transport properties of some chalcogenides such as As–Se–Tl is attributed to a corresponding change in thallium content [8–14]. The addition of thallium to chalcogenide glasses causes a marked change in their structural properties, so, it has an apparent application in acousto-optical devices [15, 16]. Both the electrical conductivity and Seebeck coefficients were found to increase with increasing content of thallium [17]. Afifi *et al* [18] reported that the activation energy decreases on increasing the thallium content. Abd El-Raheem *et al* [19] found that the optical gap decreases with increasing thallium contents.

The purpose of this work was to study the effect of thickness and composition on the optical properties of thin films of $Ge_{14}Se_{86-x}Tl_x$.

2. Experimental technique

99.999 purity Ge, Se and Tl were used with their appropriate mole percentages to prepare bulk samples of $Ge_{14}Se_{86-x}Tl_x$ using the melt-quenching technique [19]. Thin films of the prepared compositions were deposited at room temperature by electron-beam evaporation at a pressure of 1.333×10^{-3} Pa using an Edwards high-vacuum coating unit model E306A. The

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rate of deposition was 1–2 nm s^{-1}. Ultrasonically cleaned Corning glass was used as substrate. The film thickness was controlled by means of an Edward's TM200 Maxtek high-vacuum film thickness monitor.

The microstructure analysis was carried out using x-ray diffractometer type Philips model PW1710.

A Jasco model V-570 (UV–visible–NIR) double beam spectrophotometer (with photometric accuracy of ±0.002–0.004 absorbance and ±0.3% transmittance) was employed to record the transmission T and reflection R spectra over the wavelength range from 200 to 2500 nm at normal incidence.

3. Results

The absorption coefficient $\alpha(\omega)$ of the optical absorption near the band edge show an exponential dependence on photon energy $\hbar\omega$ and obey Urbach's empirical formula [20]

$$\alpha(\omega) = \alpha_o \exp(\hbar\omega/E_e)$$

where α_o is a constant and E_e is the width of the band tails of the localized states in the band gap; $\alpha(\omega)$ can be determined directly from the spectrophotometer readings using the formula [21]

$$\alpha = \frac{2.303}{d} \log_{10}\left(\frac{1-R}{T}\right) \tag{1}$$

where d is the film thickness, T is the transmittance and R is the reflectance of the film.

The optical energy gap was estimated from the optical measurements by analysing the optical data with the expression for the optical absorbance, and the photon energy, $h\nu$ using the following equation:

$$(\alpha h\nu)^{2/3} = A(h\nu - E_g) \tag{2}$$

where α represents the absorption coefficient, h is Plank's constant, A is a constant and E_g is the optical energy band gap, which was obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^{3/2}$ versus $h\nu$ to $\alpha = 0$.

The refractive index n was calculated from the following equation:

$$n = \frac{1+R}{1-R} \pm \left[\left(\frac{R+1}{R-1}\right)^2 - (1+k^2)\right]^{1/2} \tag{3}$$

where $k = \alpha\lambda/4\pi$ is the extinction coefficient and λ is the incident light wavelength.

Using Drude's theory of the dielectrics, the real part (ε_1) of the complex dielectric function ε can be written as [22]

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - \frac{e^2}{\pi c^2}\frac{N}{m^*}\lambda^2 \tag{4}$$

where ε_∞ is the residual dielectric constant, c is the velocity of light, N is the free carrier concentration, m^* is the electron effective mass, which was chosen based on the observed data of other works, and e is the electronic charge.

The x-ray diffractograms proved that the structure of all the films of the composition $Ge_{14}Se_{86-x}Tl_x$ used is mainly amorphous.

Figure 1 shows the spectral variation of absorbance, A, and transmittance, T, with λ for equithickness films ($d = 30$ nm) of the different compositions of $Ge_{14}Se_{86-x}Tl_x$ ($x = 20\%$, 22%, 23.5%, 25%, 26.5% and 28%). The spectral variation of absorbance, A, and

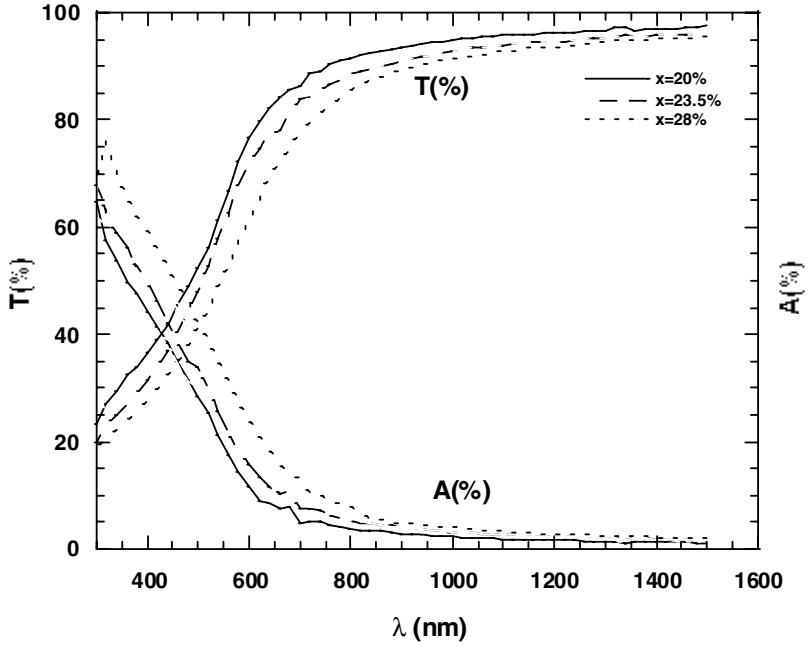

Figure 1. Spectral dependence of both absorbance and transmittance for different compositions.

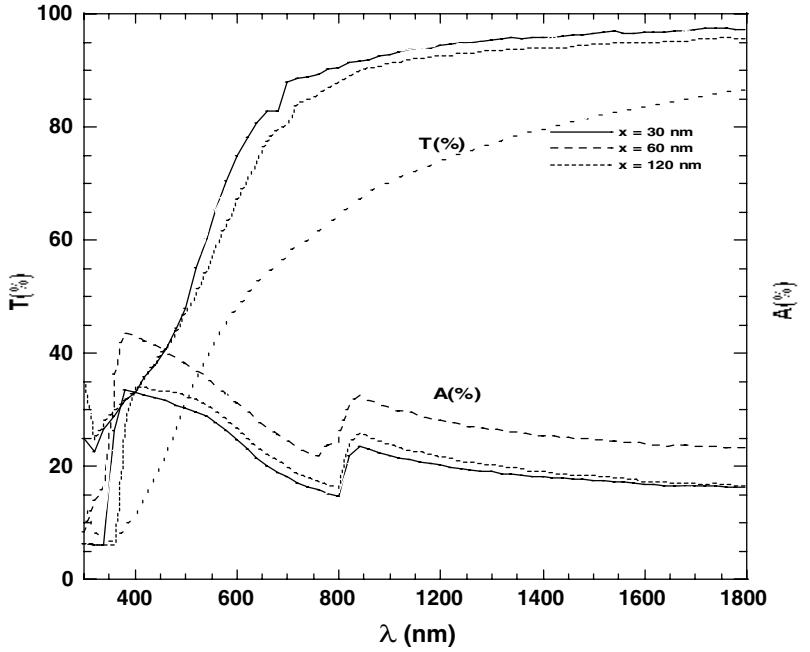

Figure 2. Spectral dependence of both absorbance and transmittance for different thickness.

transmittance, T, with λ for the composition $Ge_{14}Se_{64}Tl_{22}$ for different thicknesses ($d = 15$, 30, 60, 90, 120 and 180 nm) is shown in figure 2.

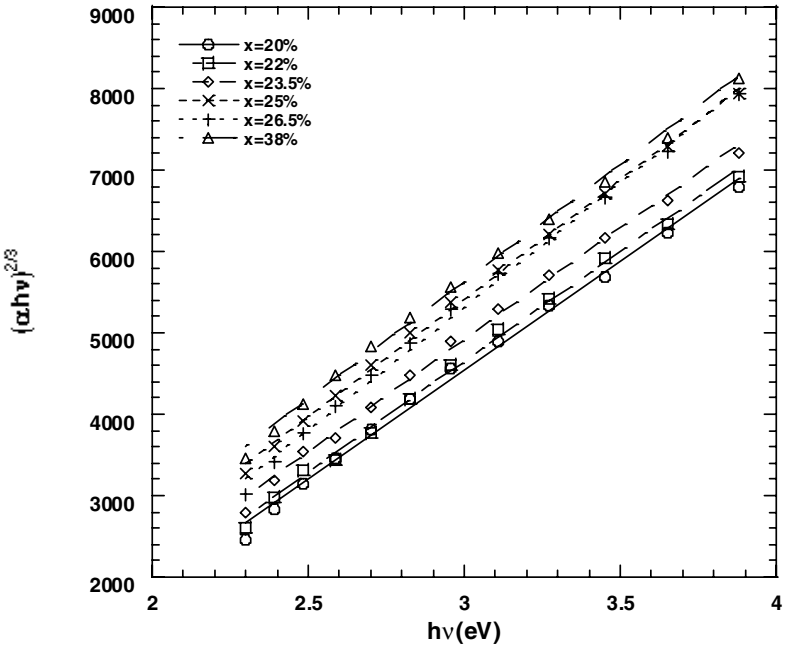

Figure 3. $(\alpha h\nu)^{2/3}$ versus $h\nu$ for different compositions having the same thicknesses.

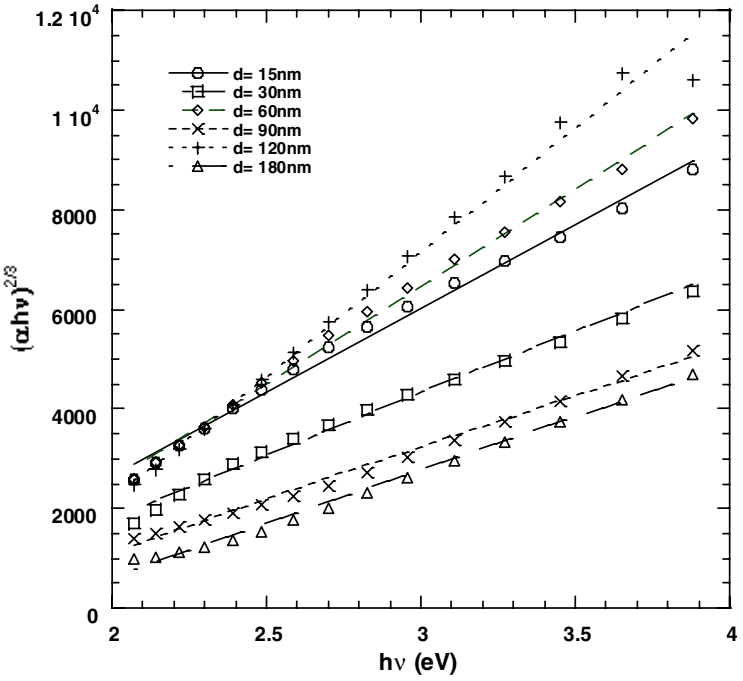

Figure 4. $(\alpha h\nu)^{2/3}$ versus $h\nu$ relations for different thicknesses of the same composition.

The plots of $(\alpha h\nu)^{2/3}$ versus $\hbar\omega$ for different x and d in the range of energies from 2.64 to 3.65 eV were found to be straight lines, as shown in figures 3 and 4, respectively. The

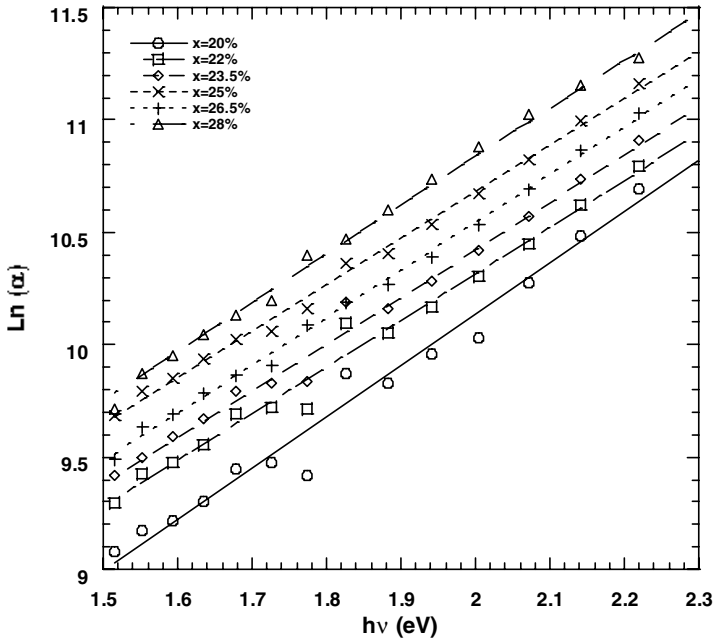

Figure 5. Plot of Ln(α) versus $h\nu$ for different compositions at the same thickness.

Table 1. Variations of E_{op} (eV) and E_e (eV) for $Ge_{14}Se_{86-x}Tl_x$ films with composition and thickness.

	x (%)						d (nm)					
	20	22	23.5	25	26.5	28	15	30	60	90	120	180
E_{op}	1.305	1.289	1.219	1.136	1.245	1.048	1.213	1.274	1.356	1.469	1.551	1.708
E_e	0.472	0.475	0.507	0.512	0.518	0.522	0.502	0.504	0.511	0.53	1.099	1.289
A	1.671	1.683	1.702	1.766	1.816	1.751	1.947	1.589	2.157	1.417	2.513	1.434

optical gap E_{op} was then calculated. The Ln α versus $\hbar\omega$ relations for different compositions and thicknesses in the range of energies from 1.8 to 2.3 eV were studied and were found to be straight lines, as shown in figure 5, from which E_e can be calculated. The dependence of both E_{op} and E_e on composition x and thickness d can be studied using table 1.

From table 1 it is clear that E_{op} decreases with x but increases with d, while E_e is nearly constant for both x and d with the exception of $d = 120$ and 180 nm, where E_e rises steeply. Table 1 also reveals that A increases with increasing x, but does not show continuous increase or decrease with increasing d.

Using equation (3), the refractive index n was calculated, and then its variation with both x (at $d = 30$ nm) and d (at $x = 22\%$) at certain photon energies 1.941, 2.142, 2.588, 3.269, 4.141 and 5.647 were taken in consideration, as recorded in table 2.

From the values in table 2 it can be seen that the refractive index n goes through a maximum for all values of x and d at about 3.269 eV.

Plotting the relation between ε_1 and λ^2 for different compositions revealed straight lines, verifying equation (4), as shown in figure 6; plots relating to different thicknesses also showed

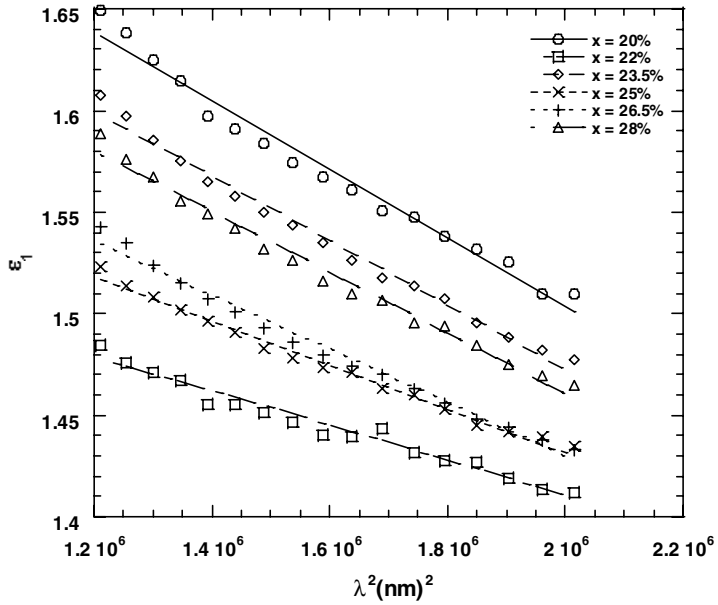

Figure 6. Plots of ε_1 versus λ^2 for different compositions at the same thickness.

Table 2. Variation of n with x and d at certain photon energies.

	x (%)/n						d (nm)/n					
$\hbar\omega$	20	22	23.5	25	26.5	28	15	30	60	90	120	180
1.941	1.244	1.250	1.309	1.322	1.324	1.355	1.573	1.3337	1.272	1.243	1.211	1.211
2.142	1.304	1.309	1.395	1.384	1.403	1.412	1.733	1.406	1.339	1.310	1.244	1.245
2.588	1.356	1.402	1.436	1.474	1.475	1.537	1.940	1.511	1.399	1.375	1.331	1.300
3.269	1.390	1.419	1.342	1.459	1.500	1.553	2.102	1.596	1.428	1.417	1.347	1.315
4.141	1.060	1.051	1.062	1.075	1.052	1.075	1.127	1.087	1.065	1.065	1.057	1.042
5.647	1.109	1.057	1.000	1.094	1.068	1.084	1.253	1.170	1.119	1.122	1.116	1.024

Table 3. Variations of N and ε_∞ for $Ge_{14}Se_{86-x}Tl_x$ films with composition and thickness.

x (%)	d (nm)	20	22	23.5	25	26.5	28	15	30	60	90	120	180
$N \times 10^{21}$ m^{-3}		0.892	1.194	1.479	1.672	1.659	1.876	6.218	6.581	6.720	6.923	8.609	10.150
ε_∞		1.579	1.646	1.694	1.789	1.758	1.840	1.368	1.462	1.555	1.64	1.78	1.858

the same behaviour. Values of ε_∞ and N were calculated from the straight lines, and they are recorded in table 3.

It is clear from table 3 that both N and ε_∞ increase with increasing x and d.

4. Discussion

The above results indicated that the band gap decreases with increasing the content of thallium, which can be attributed to the creation of localized states in the band gap [23, 24]. This can be confirmed in the present work since E_e increases with increasing Tl ratio. Moreover, increasing

the value of B with increasing Tl ratio in the compositions is associated with an increase of the extent of band-tailing, and therefore the optical gap decreases. It is suggested that this arises from electron transitions between localized states where the density of the localized states is exponentially dependent on energy [25].

Regarding the effect of thickness on the optical band gap, it is found that thicker films are accompanied with larger optical gaps. This can be explained as the insufficient number of atoms deposited on the amorphous film resulting in the existence of unsaturated bonds, which are responsible for the formation of some defects in the film, which in turn, produce localized states in the band gap. So, thicker films are characterized by a homogeneous network, which minimizes the number of defects and the localized states, thereby increasing the optical gap.

Concerning the variation of the refractive index with composition and thickness, it can be shown that n increases with increasing Tl ratio, which can be attributed to the compactness of the material and/or the material aggregation.

5. Conclusion

It is concluded that increasing the thallium content x is accompanied with decreasing band gaps E_g and increasing with the extend of the band tailing A; therefore, the optical gap decreases, whereas A decreases with increasing the thickness d of the sample. The refractive index n increases with increasing the Tl ratio and decreases with increasing thickness.

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