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Optical properties of evaporated $Ge_{20}Se_{80-x}Tl_x$ thin films

M. M. ABD EL-RAHEEM, M. M. WAKKAD, N. M. MEGAHED, A. M. AHMED, E. K. SHOKR
Department of Physics, Faculty of Science, Sohag, Egypt
M. DONGOL
Department of Physics, Faculty of Science, Kena, Egypt

Chalcogenide glasses with composition $Ge_{20}Se_{80-x}Tl_x$ (x= 10, 15, 20, 25, 35%) have been prepared by the usual melt-quenching technique. Thin films of the mentioned compositions have been prepared by the electron beam evaporation. In addition, another set taken from the composition of X=30 at% with different thicknesses (d= 14.7, 30.0, 56.5, 70.0, 101.0, 180.0 nm) have been taken into consideration. The X-ray diffraction (XRD) analysis revealed the amorphous nature of the prepared films. It was found that, in contrast to the optical gap (E_{op}), both the extent of the band tailing (B), and the band gap (E_e) increase with increasing thallium content. In other side, E_{op} showed thickness independency. The refractive index (n) showed obvious dependence on both composition and thickness also on the energy of the incident radiation.

1. Introduction

Because of their promising technological properties (switching, memory and image storage, chalcogenide glasses have been investigated intensively [1, 2]. Impurities have been found to affect strongly both their electrical and optical properties [3–5]. Kolomiets [6] and Borissova [7] studied the influence of small quantities of Ga, In, Ag, Cu and Pb on the electrical properties. It has been observed [8–10] that the influence of impurities in chalcogenide glasses is less pronounced than in crystalline materials. Various Optical properties of chalcogenide glasses have been reported [23–25]. The optical properties of amorphous semiconductors are known to be sensitive to the preparation conditions [26, 27]. However, it has been proved that chalcogenide glasses are promising as solar cell materials due to the advantage of easy film formation inherent to the glasses. On the other hand, a lot of work has been done on bulk and thin film glassy germanium chalcogenides regarding the electrical and optical properties [11–13], and also on alloys of different compositions of selenium and tellurium regarding the amorphous–crystalline transition [14–17], structure [18–22], etc.

This work is a trial to ascertain the effect of composition and thickness on the optical properties of thin films of compositions based on the system $Ge_{20}Se_{80-x}Tl_x$ ($10 \leqslant x \leqslant 35\%$).

2. Experimental technique

To prepare different compositions of the system $Ge_{20}Se_{80-x}Tl_x$, the appropriate portions of Ge, Se and Tl with purity grade 99.999% were charged together into a clean quartz ampoule (8 mm diameter). The charged ampoule was evacuated to $\sim 1.333 \times 10^{-3}$ Pa and then sealed. Alloying was performed at 850 °C for 30 h. During alloying, the ampoule was shaken rigorously several times to ensure thorough mixing of the constituents, and then good homogeneity of the produced alloy. Quenching was performed quickly in ice-cold water.

Thin films of a prepared composition were deposited at room temperature by electron beam evaporation at a pressure of 1.333×10^{-3} Pa using Edward's high vacuum coating unit model E306A. The rate of deposition was 1–2 nm s^{-1}. Ultrasonically cleaned Corning glass was used as substrate. The film thickness (14.7–180 nm) was controlled by means of an Edward's high vacuum film thickness monitor (FTMS).

The microstructure analysis was carried out using X-ray diffractometer type Philips model PW1710. The X-ray diffractograms shown in Fig. 1 proved that the structure of all the used films of the composition $Ge_{20}Se_{80-x}Tl_x$ is mainly amorphous.

Both the absorbance (A) and transmittance (T) of the film were measured by means of a Cecil CE599 double beam automatic scanning spectrophotometer combined with CE836 program controller as shown in Figs 2 and 3, respectively.

3. Results

In many amorphous semiconductors, the absorption coefficients $\alpha(\omega)$ of the optical absorption near the band edge show an exponential dependence on

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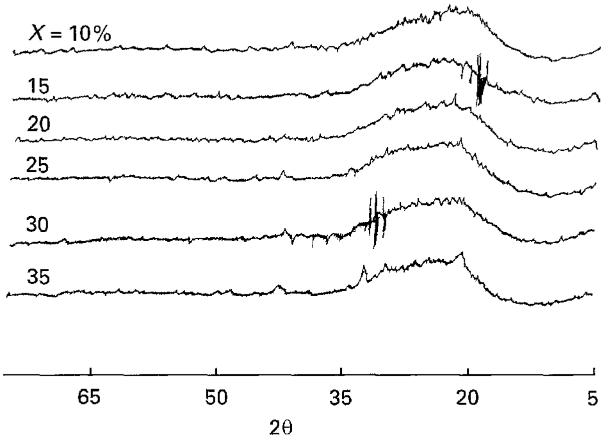

Figure 1 X-ray diffractograms of $Ge_{20}Se_{80-x}Tl_x$ films ($x = 10, 15, 20, 25, 30$ and 35%).

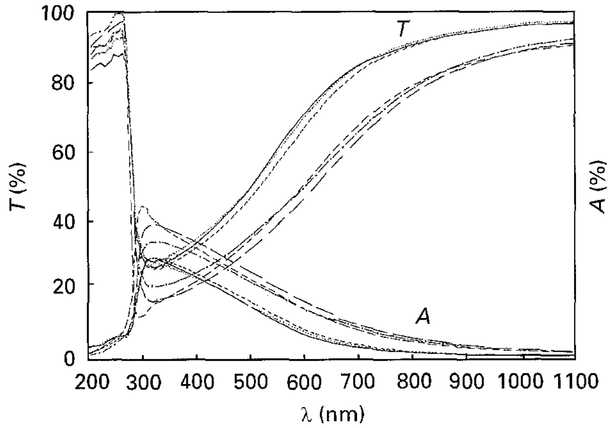

Figure 2 Spectral dependence of both absorbance and transmittance for $Ge_{20}Se_{80-x}Tl_x$ films ($x = 10, 15, 20, 25, 30$ and 35%). — S_1; ··· S_2; --- S_3; -- S_4; -- S_5; -·- S_6.

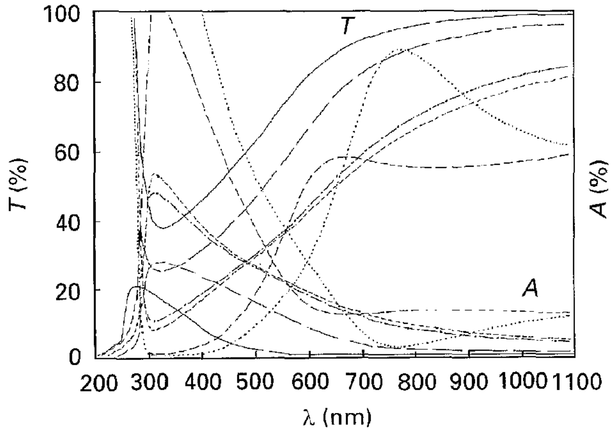

Figure 3 Spectral dependence of both absorbance and transmittance for $Ge_{20}Se_{80-x}Tl_x$ films ($d = 14.7$ (—), 30.0 (···), 56.5 (--), 70.0 (---), 101.0 (-·-) and 180.0 (——) nm).

photon energy ($\hbar\omega$) and obey Urbach's empirical formula [28]

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/E_e) \qquad (1)$$

where α_0 is a constant and E_e is the width of the band tails of the localized states in the band gap.

The optical gap E_{op} can be determined using the following relation [29, 30]

$$\alpha\hbar\omega = B(\hbar\omega - E_{op})^r \qquad (2)$$

where B is a constant and r is a number characterizing the transition process.

Fig. 2 shows the spectral variation of absorbance, A and transmittance, T with λ for equithickness films ($d = 35.0$ nm) of the different compositions of $Ge_{20}Se_{80-x}Tl_x$ ($x = 10, 15, 20, 25, 30$ and 35%). The spectral variations of A and T with λ for the composition $Ge_{20}Se_{60}Tl_{20}$ for different thicknesses $d = 14.7$, 30.0, 56.5, 70.0, 101.0 and 180.0 nm are shown in Fig. 3.

Using the value of $r = 3/2$, the plots of $(\alpha\hbar\omega)^{2/3}$ versus $\hbar\omega$ for different x and d in the range of energies from (2.64 eV) to (3.65 eV) found to be straight lines as shown in Figs 4 and 5, respectively. The optical gap E_{op} was then calculated. Figs 6 and 7 show the $\ln\alpha$ versus $\hbar\omega$ relations for different compositions and thicknesses in the range of energies from 1.8–2.2 eV. These relations were found to be straight lines from which E_e are calculated. The dependence of both E_{op} and E_e on composition x and thickness d can be studied using Table I.

From Table I it is clear that in contrast to the width of the band tails, the optical gap width decreases with increase of the ratio of thallium and decrease of selenium starting from $x = 25\%$ and $d = 30.0$ nm. Meanwhile, values of E_e increase with increasing x starting from $x = 15\%$. On other hand, E_{op} decreases with increasing the thickness of the film up to $d = 30.0$ nm, and then increases with further increase of d up to 101.0 nm, and then decreases again. Besides, values of E_e increases with increasing d up to $d = 70.0$ nm, and then decreases with further increase of the film thickness.

Table II reveals also that values of B increase with increasing x from $x = 15$–25% and then decrease with further increase of x. Besides, values of B decrease with increasing d, except for $d = 101.0$ and 180.0 nm. Furthermore, values of B linked to increasing x are smaller than those linked to increasing d by one order of magnitude. To study the optical dielectric constant, the transmittance T of a perfectly smooth film deposited on a perfectly smooth substrate is determined by the relation

$$\begin{aligned} T &= (1-R)^2\exp(-A) \\ &= (1-R)^2\exp(-\alpha d) \qquad (3) \end{aligned}$$

where R is the reflectance.

Accordingly [33], the optical dielectric constant (ε') and the square of the wavelength (λ^2) are correlated together through the following equation [33]

$$\begin{aligned} \varepsilon' &= n^2 = [(1+R^{1/2})/(1-R^{1/2})] \\ &= \varepsilon'_\infty - (e^2_\infty/\pi C^2)(N/M^*)\lambda^2 \qquad (4) \end{aligned}$$

where ε'_∞ is the infinitely high frequency dielectric constant, e is the electronic charge, N/m^* is the ratio of the concentration to the effective mass, n is the refractive index and C is the velocity of light. Values of ε'_∞ and N/m^* are calculated from the straight lines

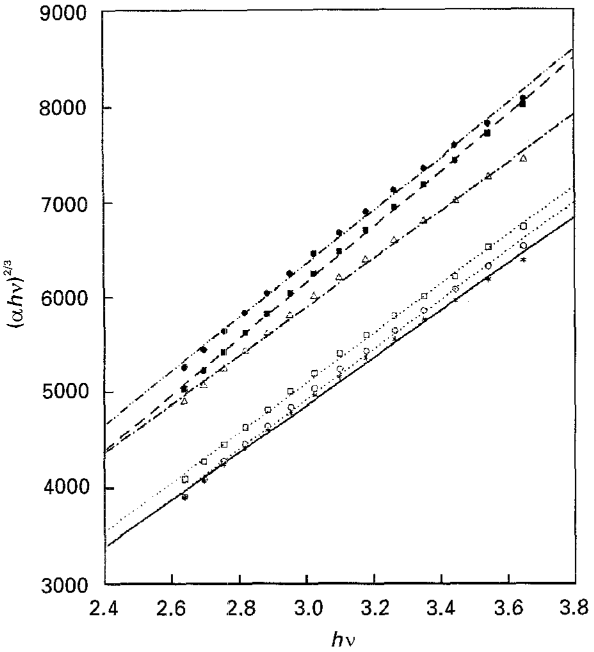

Figure 4 αħν versus ħν relations for different compositions having the same thickness. x = (○) 10, (*) 15, (□) 20, (■) 25, (●) 30 and (△) 35%.

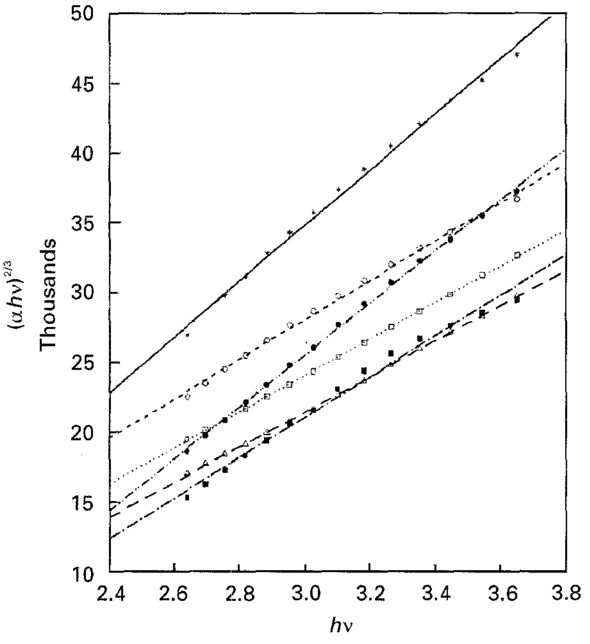

Figure 5 αħν versus ħν relations for different thicknesses of the same composition. d = (*) 14.7, (○) 30.0, (□) 56.5, (△) 70.0, (●) 101.0 and (■) 180.0 nm.

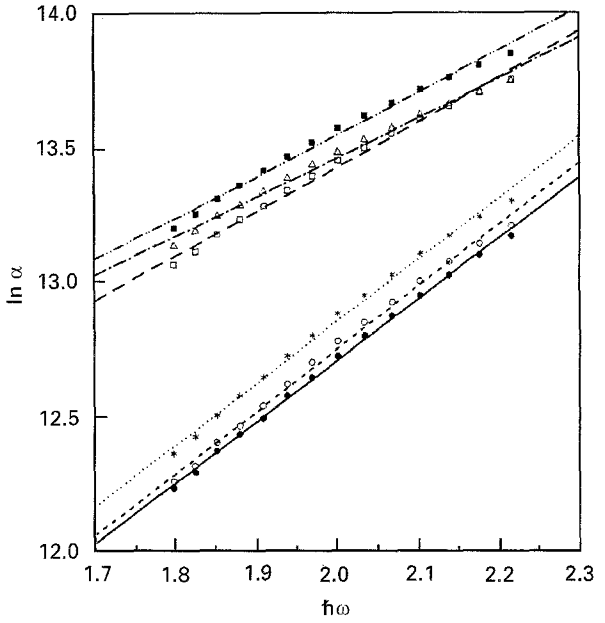

Figure 6 Ln α–ħω relations for different compositions. x = (●) 10, (○) 15, (*) 20, (□) 25, (■) 30 and (△) 35%.

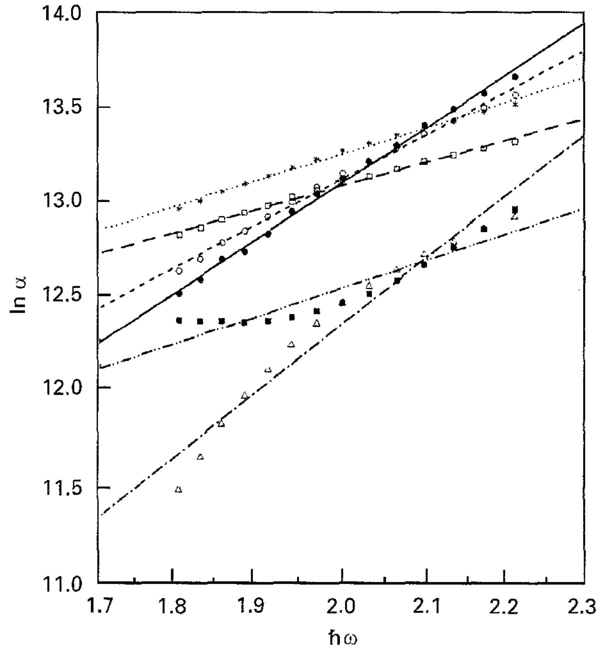

Figure 7 Ln α–ħω relations for different thicknesses. d = (●) 14.7, (□) 30.0, (*) 56.5, (□) 70.0, (■) 101.0 and (△) 180.0 nm.

representing the ε′ versus λ^2 relations recorded in Table II. It is clear from the Table II that ε_∞ and N/m^* increase with increasing x and d.

Variation of the refractive index n with λ for different x and d are shown in Figs 8 and 9, which show that n has a peak shifted toward prolongating λ, with increase in the ratio of thallium, except for $x = 35$. Also, for different thicknesses, the peak shifted towards elongating λ with increasing d, except for $d = 101.0$ and 180.0 nm.

The variation of n with both x and d at certain wavelengths as λ = 30.0, 40.0, 50.0, 60.0 and 70.0 nm, corresponding to the photon energies 4.136, 3.102, 2.482, 2.068 and 1.772 eV are taken into consideration as recorded in Table III.

It is obvious from Table III that, the refractive index decreases with increasing the energies of the incident photons with respect to composition except for x = 10, 15 and 20% where n increases with $h\nu$ starting from ħω = 2.068 eV up. Meanwhile, for d = 56.5, 70.0, 101.0 and 180.0 nm, n decreases with increasing ħω, but for d = 14.7 and 30.0 nm, n decreases with increasing ħω starting from ħω = 2.482 and 2.068 eV respectively. On other hand, Table II shows that n increases with increasing x from x = 15 to 30% for the considered energies, except for ħω = 1.772 eV where n increases with x from x = 10 to 25 and then

TABLE I Variations of E_{op} (eV) and E_e (eV) for $Ge_{20}Se_{80-x}Tl_x$ films with composition and thickness

	x(%)						d(nm)					
	10	15	20	25	30	35	14.7	30.0	56.5	70.0	101.0	180.0
E_{op}	1.115	1.040	1.044	0.909	0.742	0.688	1.263	1.010	1.149	1.301	1.626	1.549
B	1.336	1.237	1.331	1.597	1.492	1.287	2.842	1.676	1.487	1.424	1.541	1.757
E_e	0.435	1.427	0.431	0.595	0.637	0.675	0.352	0.436	0.724	0.816	0.698	0.297

TABLE II Variation of ε'_∞ and N/m^* for $Ge_{20}Se_{80-x}Tl_x$ films with composition and thickness

	x(%)				d(nm)			
	10	20	25	30	14.7	30.0	101.0	180.0
ε_∞	47.72	67.07	1646.84	8580.82	12.57	83.64	206.54	1139.41
N/m^*	8.16	12.24	351.60	1828.00	1.83	15.47	28.13	253.10

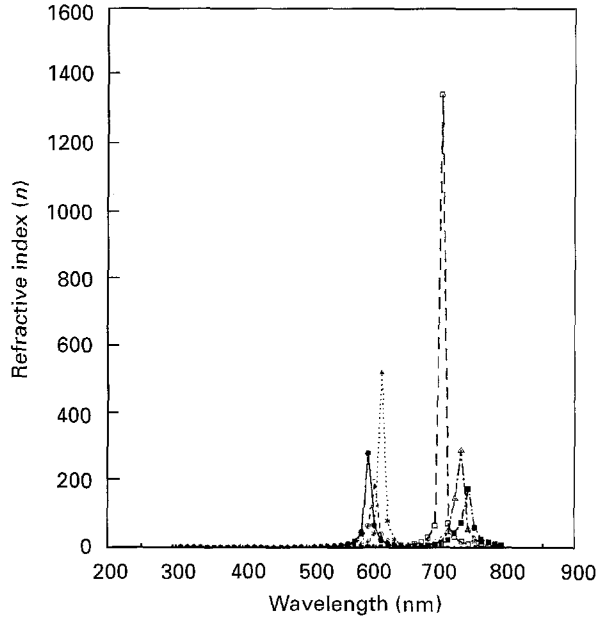

Figure 8 Relations between the refractive index (*n*) and the wavelength (nm) for different compositions having the same thickness. *x* = (●) 10, (○) 15, (*) 20, (□) 25, (■) 30 and (△) 35%.

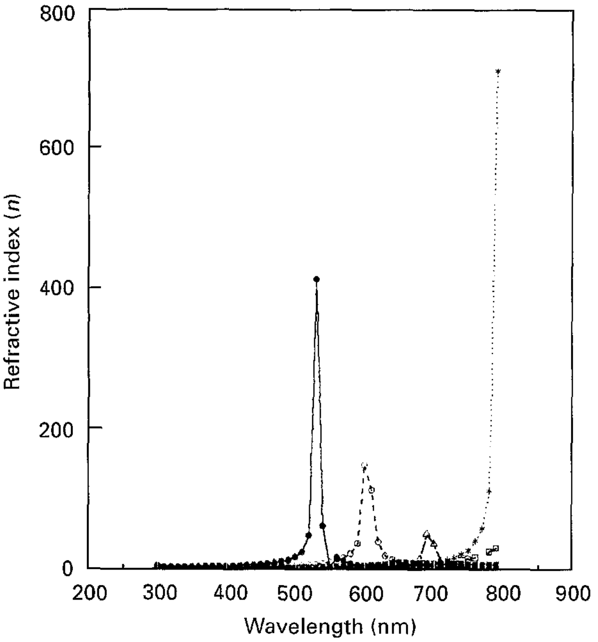

Figure 9 Relations between the refractive index and the wavelength for different thicknesses of the same composition. *d* = (●) 14.7, (○) 30.0, (*) 56.5, (□) 70.0, (■) 101.0 and (△) 180.0 nm.

fluctuates. Whereas *n* decreases with increasing *d* for the considered energies from $\hbar\omega = 2.068$ to 4.136 eV except for $\hbar\omega = 2.068$ eV at $d = 101.0$ nm. Furthermore, at $\hbar\omega = 1.772$ eV, *n* increases with increasing *d* from 14.7 to 56.5 nm and then fluctuates. Moreover, the peak values of *n* for $x = 10, 15, 20, 25, 30$ and 35% takes place at $\hbar\omega = 2.103, 2.07, 2.034, 1.745, 1.677$ and at 1.7 eV, respectively, as shown in Fig. 8. The dependence of the energies at which the peaks take place on *x* seems to have more or less the same behaviour of dependence of E_{op} and E_e on *x*. Also, for $d = 14.7, 30.0, 56.5$ and 180.0 nm, peak values of *n* found to be at $\hbar\omega = 2.341, 2.03, 1.57$ and 1.772 eV, respectively, as shown in Fig. 9.

TABLE III Variation of *n* with *x* and *d* at certain photon energies

ħω(eV)	x(%)/n						d(nm)/n					
	10	15	20	25	30	35	14.7	30.0	56.5	70.0	101.0	180.0
4.136	3.813	4.016	3.862	2.775	3.170	3.445	5.632	3.847	2.738	2.633	2.193	2.152
3.102	4.197	4.289	4.037	3.347	3.237	3.485	5.859	3.995	3.098	3.018	2.341	2.168
2.482	6.847	6.768	6.087	4.203	3.953	4.329	18.728	5.946	3.837	3.795	3.019	2.610
2.068	70.842	198.076	47.221	7.037	5.984	6.768	6.978	38.806	5.471	5.266	7.094	3.655
1.772	5.409	5.596	6.219	71.631	21.094	29.976	2.875	6.562	12.173	9.816	10.665	38.817

4. Discussion

The obtained results indicated that the band gap decreases with increasing the percentage of Tl. However, several possible reasons which explain the decrease in band gaps have been postulated [34, 35]. Therefore, the observed decrease in band gaps with increasing Tl content in compositions might be attributed to the creation of localized states in the band gaps. 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. Zanini and Tauc [36] have suggested that it arises from electron transitions between localized states where the density of the localized states is exponentially dependent on energy. But Davis and Mott [30] reported that this explanation is not valid for all disordered materials, because the slope of the observed exponential behaviour remains unchanged for many crystalline and noncrystalline materials.

In conclusion, as the thallium content increases in the glass structure, deeper band tails extended in the gap and led to an increase in the value of E_{e} and decrease in the value of E_{op}. The energy gap increases linearly with increasing the Tl content.

Regarding the effect of thickness on the optical band gap it can be concluded that in general, the optical band gap is independent of film thickness. However, in the range $d = 30.0$ to $70.0\,\mathrm{nm}$, E_{op} increases while values of B decrease. The insufficient number of atoms deposited on the amorphous film results 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. Thicker films are characterized by homogeneous network, which minimizes the number of defects and the localized states, thereby increasing the optical gap. On other hand, the exponential dependence of $\alpha(\omega)$ on $\hbar\omega$ for the films indicated that they obey Urbach's equation. Also, as the values of E_{e} are very much larger than 0.05 eV and vary with composition, Tauc's model based on electronic transitions between localized states in the band edge tails may well be valid in our materials.

Concerning the variation of the refractive index with composition and thickness, it can be concluded that n increases with increasing the content of Tl from 15 to 30%. On the other hand, n decreases with increasing the thickness. Furthermore, the peak values of n shifted toward the longer wavelength with increasing both the content of thallium except for $x = 35\%$ and thickness. Meanwhile, values of the energies where the peaks take place are more or less twice the values of E_{op} belonging to different compositions and thicknesses except for $d = 56.5$ and $180.0\,\mathrm{nm}$, where $E_{\mathrm{op}} = 1.149$ and $1.549\,\mathrm{eV}$ corresponding peaks at energies locations at 1.57 and 1.772 eV. Also, one can interpret the increase in n with increasing the content of thallium as due to the compactness of the material and/or the material aggregation.

5. Conclusion

1. The optical band gap decreases with increasing the thallium content where as it in general independent on the thickness of the film.
2. Increase of thallium content is accompanied with increase of the extend of band tailing (B) and therefore the optical gap decreases, whereas B decreases with increasing the thickness of the composition.
3. The refractive index n increases with increasing the content of Tl and decreases with increasing the thickness.
4. Peak values of the refractive index found to be located at energies having a value twice of the optical gap belonging to different compositions and thicknesses, and somewhat equals the value of E_{op} at certain thickness.

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