Effect of Ag Content on the Optical Properties of a- Ge_{15} Se_{85-x} Ag_x Alloys

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Optical reflection and transmission spectra, at normal incidence, of amorphous Ge_{15} Se_{85-x} Ag_x (x = 0, 10, 20) chalcogenide glass thin films, have been obtained in the range 400-2400 nm. Investigated films have been deposited by thermal evaporation. The optical constants of the films were determined using the method proposed by Swanepoel. The method allows determination of both the real (n) and imaginary (k) parts of the complex refractive index, and the film thickness (d). The optical energy gap has been estimated from the absorption coefficient values using Tauc's procedure. It is found that, the films exhibit indirect gap, which decreases with increasing Ag content. The dispersion of (n) is discussed in terms of the single–oscillator Wemple- DiDomenico model.

1. Introduction:

The study of chalcogenide glasses has increased in last decades because of their application in the fields of fiber optics, xerography and novel memory devices [1]. The interest in the optical properties of amorphous semiconductors and glasses has been stimulated also by their possible applications as switching elements and optical transmission media, as well as by their use as passivating materials for integrated circuits [5]. It is known that large number of metallic Ag particles are segregated on the surface of Ag–rich Ag–As (Ge)–S glasses after optical illumination [2,3]. The phenomenon, is known as photoinduced surface deposition (PSD) effect, It is a photoreaction opposite to the photodoping of Ag metal into chalcogenide glasses with respect to the movement of Ag atoms [2]. The (PSD) phenomenon has been studied with a view to application in direct positive patterning with high contrast [4].

In the present work, the results of measurements of the optical properties of Ge_{15} Se $_{85-x}$ Ag_x amorphous thin films with x = 0, 10 and 20 are reported. The measurements give information regarding the band gap (E_g), refractive index (n), absorption index (k) and absorption coefficient (α),to determine the reliability of the materials for some specific applications. An attempt has been made to highlight the optical features of the alloys in thin film form . The dispersion energy, E_d, the energy of the effective dispersion oscillator, E_0, and the static refractive index n (0). Also, the correlation between the glass-forming ability (K_g) and the number of lone-pair electrons, (L) was investigated.

2. Experimental Details:

The preparation of $Ge_{15}Se_{85-x}Ag_x$ with x = 0, 10 and 20 was previously discussed [6,7] .The proper ingots were confirmed to be completely amorphous using X-ray diffraction and differential thermal analysis given in Ref. [6,7]. For each composition, a thin film of (300 ± 2nm) thickness was evaporated onto well–cleaned quartz substrates using an (E 306 A Edwards) vacuum system. A vacuum of the order of 10^{-5} Torr was maintained during evaporation and the substrates were fixed on a rotating holder in order to obtain homogeneous films. The film thickness was controlled using a thickness monitor (Edwards FTM4) and checked by applying Tolansky's method [8] using multiple – beam Fizeau fringes. The transmittance (T) and the reflectance (R) at normal incidence for Ge_{15} Se_{85-x} Ag_x (with x = 0, 10 and 20) films were measured using a double beam spectrophotometer (Type JASCO Corp., Model V- 570).

3. Results and discussion:

3.1. Optical properties

Optical transmission (T) and reflection (R) spectra of the Ge_{15} Se_{85-x} Ag_x thin films with x =0,10 and 20, were recorded at room temperature in the spectral range 400 – 2400 nm. The later covers the fundamental optical absorption edge and the interband transition regions of the semiconductors. The obtained spectra are shown in Fig.1. Swanepoel's formula was used [9] to estimate the optical constants.
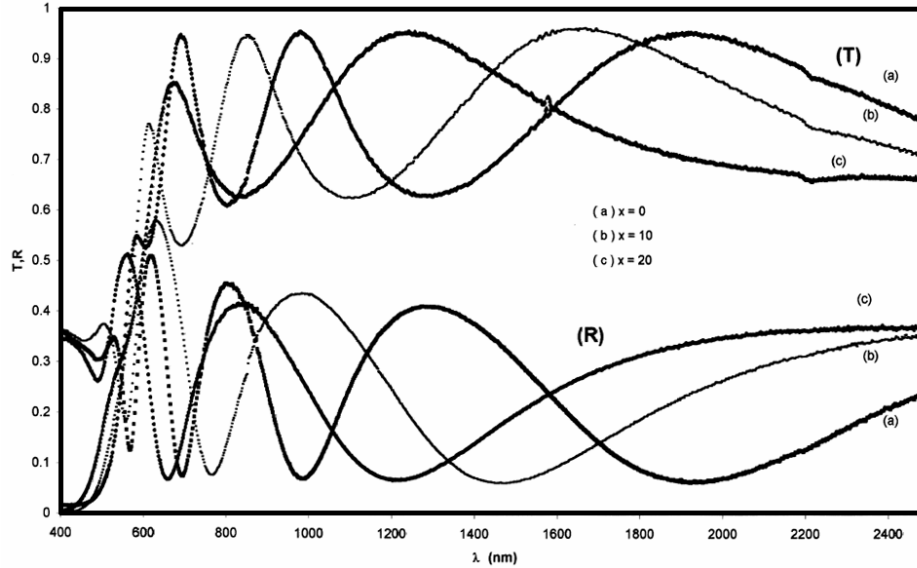
Fig.(1): The spectral distribution of T (λ) and R (λ) for $Ge_{15}Se_{85-x}Ag_x$ films (a) x = 0, (b) x = 10 and (c) x = 20.

3.1.1. Refractive index (n)

(i) In the transparent region, where the absorption coefficient, $\alpha \approx 0$, the refractive index, n, of the thin films is given by, [9]

$$n = [M + (M^2 - S^2)^{\frac{1}{2}}]^{\frac{1}{2}} \qquad (1)$$

where, M is given by,

$$M = \frac{2S}{T_m} - \frac{S^2 + 1}{2} \qquad (2)$$

and S, is the refractive index of the quartz substrate and T_m is the minima in the transmission spectra.

(ii) In the weak and medium absorption regions, where $\alpha \neq 0$, the refractive index, n, is given by, [9]

$$n = [N + (N^2 - S^2)^{\frac{1}{2}}]^{\frac{1}{2}} \tag{3}$$

where

$$N = 2S \frac{T_M - T_m}{T_M T_m} + \frac{S^2 + 1}{2} \tag{4}$$

T_M represent the maxima in the transmission spectra.

(iii) In the region of the strong absorption, values of n, can be estimated by extrapolating the values calculated from the other parts of the spectra.

3.1.2. Absorption coefficient and absorption index

For the strong absorption region, the absorption coefficient, α, is given by [9, 10].

$$\alpha = \frac{1}{d} \ln[\frac{16n^2 S}{(n+1)^3(n+S^2)T_0}], \tag{5}$$

Where d, is the film thickness, n, and S, are the refractive indices of the film and substrate, respectively, and T_0 is the measured transmittance at the covered λ range.

In the spectral region of medium absorption where interference fringes appear distinctly in the transmission spectra, α, is given by,

$$\alpha = \frac{1}{d} \ln[\frac{(n-1)^3(n-s^2)}{F - [F^2 - (n^2-1)^3(n^2-s^4)]^{\frac{1}{2}}}] \tag{6}$$

where $\quad F = \dfrac{8n^2 S}{T_i}$

and $\quad T_i = 2 \dfrac{T_M T_m}{T_M + T_m}$

Figure. 2 shows the effect of the Ag content on the calculated refractive index, n, .The obtained results reveal that n exihibits a strong dependence on Ag content. It is also observed that, the refractive index of the investigated films shows anomalous behavior at λ <1000 nm. It is clear that the observed wavelength at which the anomalous behavior appears depends on the film

composition. It is more or less, increases by increasing the value of x. The value of n, for x = o at (λ = 400 nm) is in a good agreement with Ref. [11].
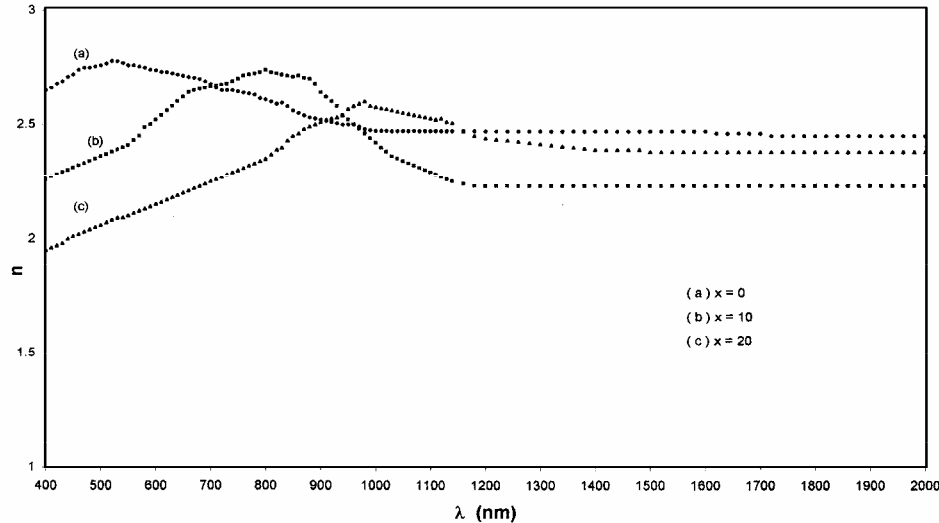
Fig.(2): The spectral distribution n (λ) for $Ge_{15}Se_{85-x}Ag_x$ films (a) x = 0, (b) x = 10 and (c) x = 20.

It was found that the absorption coefficient, α , for investigated films can be described by the relation [12,13].

$$(\alpha h \nu) = A (h \nu - E)^p \tag{7}$$

where A, is a constant and P is a number which characterizes the transition process.

Figure. 3. (a) shows the variation of $(\alpha h \nu)^{\frac{1}{2}}$ with the photon energy, $h \nu$, for the $Ge_{15} Se_{85-x}Ag_x$ films. The intercepts of the extrapolation to zero absorption with the photon energy axis are taken as the values of the indirect energy gaps. The observed results is expected, since in the absence of translation symmetry the wave vector k, is not good quantum number and hence the indirect transition is the expected one. This means that the minimum of the conduction band is not at the same k, value of the valence band.

The values of E_g^{opt} are tabulated in Table. 1. It is observed that E_g^{opt} values show tendency to decrease with increasing the Ag content . The present data are in a good agreement with Takeshi Kawaguchi, et al. [14], who reported that the optical band gap for $(Ge_{0.3} Se_{0.7})_{100-y} Ag_y$ decreases with increasing Ag content. Since the optical absorption depends on short range order in the amorphous state and defects associated with it, the decrease in optical band gap

may be explained on the basis of the "density of states" model in amorphous solids proposed by Mott and Davies Ref [12]. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous structure.
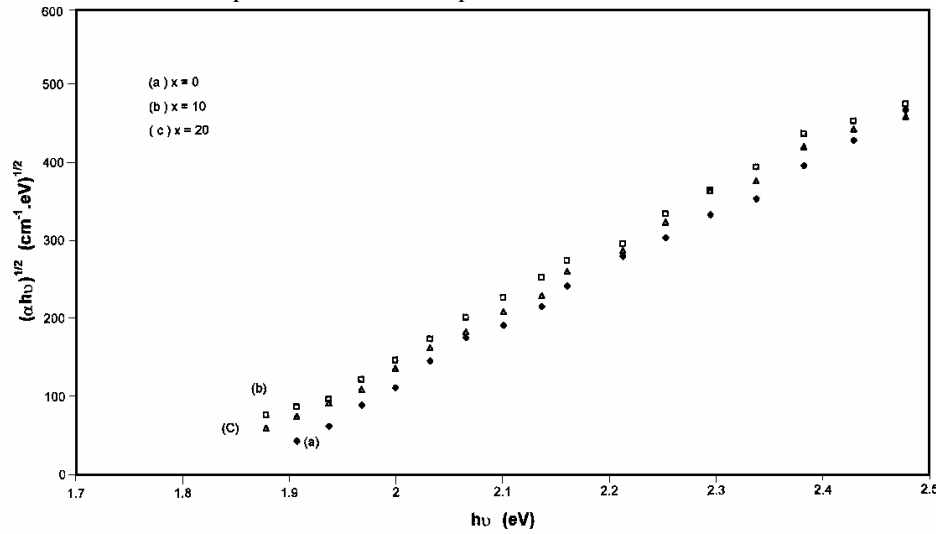
Fig.(3a): $(\alpha h\upsilon)^{1/2}$ vs. $h\upsilon$ for $Ge_{15}Se_{85-x}Ag_x$ films (a) x = 0, (b) x = 10 (c) x = 20.

Table (1): The energy gaps, single oscillator parameters, number of unshared lone-pair electrons, glass-forming ability and coordination number.

Composition	E_{g1}^{opt} (eV) According to $\alpha^{1/2}$	E_g^{opt} (eV) According to $(\alpha-\alpha_0)^{1/2}$	E_{g2}(eV)	E_d (eV)	E_0(eV)	n(0)	L	K_g	N_{co}
$Ge_{15}Se_{85}$	1.85	1.87	1.932	18.820	3.864	2.423	3.4	2.195	2.3
$Ge_{15}Se_{75}Ag_{10}$	1.82	1.83	1.351	12.023	2.702	2.332	3.2	1.474	2.4
$Ge_{15}Se_{65}Ag_{20}$	1.80	1.82	0.9115	4.640	1.823	1.884	3.0	1.140	2.5

For more accurate calculations, in order to determine the direct or indirect optical gap, the absorption data were corrected according to the background absorption, α_0, observed at lower photon energies and replotted in the form, $[(\alpha - \alpha_0) h v]^{\frac{1}{p}}$ versus $h v$, for all the samples [15]. Typical plots of $[(\alpha-_0) hv]^{\frac{1}{2}}$ against $h v$ for the $Ge_{15} Se_{85-x}Ag_x$ films with x = 0, 10 and 20 are shown in Fig. 3-(b), (α_0 = 1416.32, 966.63 and 4538.42 cm^{-1}, respectively). By extrapolating the linear portions of the plots to $[(\alpha- \alpha_0) hv]^{\frac{1}{2}} = 0$, the energy gap values were obtained and listed also in Table.1.
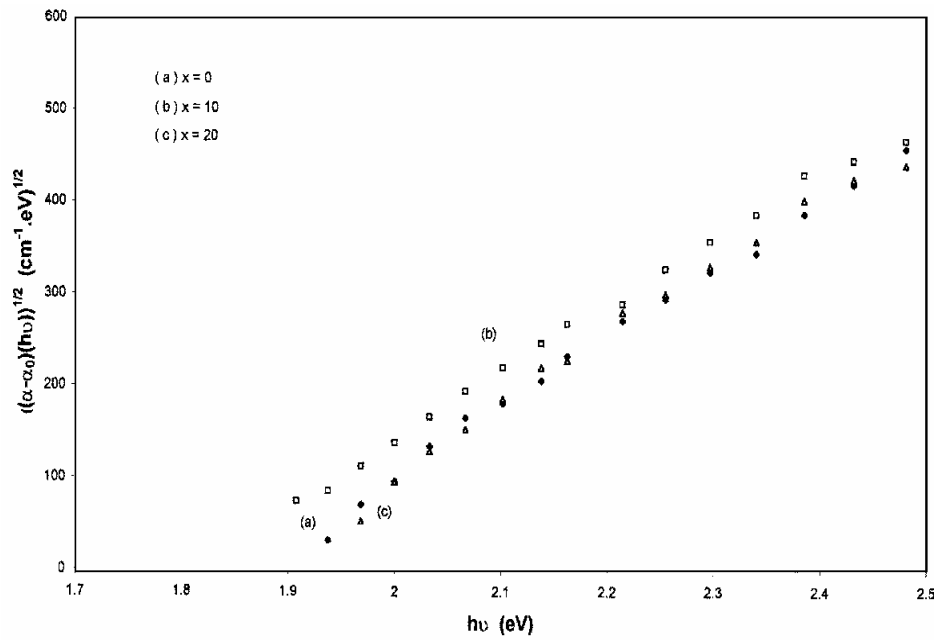
Fig.(3b): $((\alpha-\alpha_0)(h\upsilon))^{1/2}$ vs. hυ for $Ge_{15}Se_{85-x}Ag_x$ films (a) x = 0, (b) x = 10 and x = 20.

The data on the spectral dependence of the refractive index were evaluated according to the single – effective oscillator model proposed by Wemple and DiDomenico [16] and Wemple [5]. The authors considered dispersion data for more than 100 different materials, (both covalent and ionic, and both crystalline and amorphous). They found that the optical data could be described to a very good approximation, by the following formula,

$$n^2-1 = \frac{E_d E_0}{E_0^2 - E^2} \qquad (9)$$

where n, is the refractive index, E_0 is the energy of the effective dispersion oscillator, E, is the photon energy and E_d, is the so – called dispersion energy. The latter quantity measures the average strength of interband optical transitions. Plotting $(n^2-1)^{-1}$ against $(h\nu)^2$ allow us to determine the oscillator parameters by fitting a straight line to the points, see Fig.4(a,b,c). The values of E_0 and E_d can be determined directly from the slope $(E_0 E_d)^{-1}$ and the intercept on the vertical axis, (E_0 / E_d). The values obtained for the dispersion parameters, E_0, E_d and the static refractive index n(0) are tabulated in Table 1, for x = 0, 10 and 20, respectively. The values agree well with the calculated ones of $Ge_{17}Se_{83}$ [17], which were estimated from the single- oscillator model. (See Table 1).
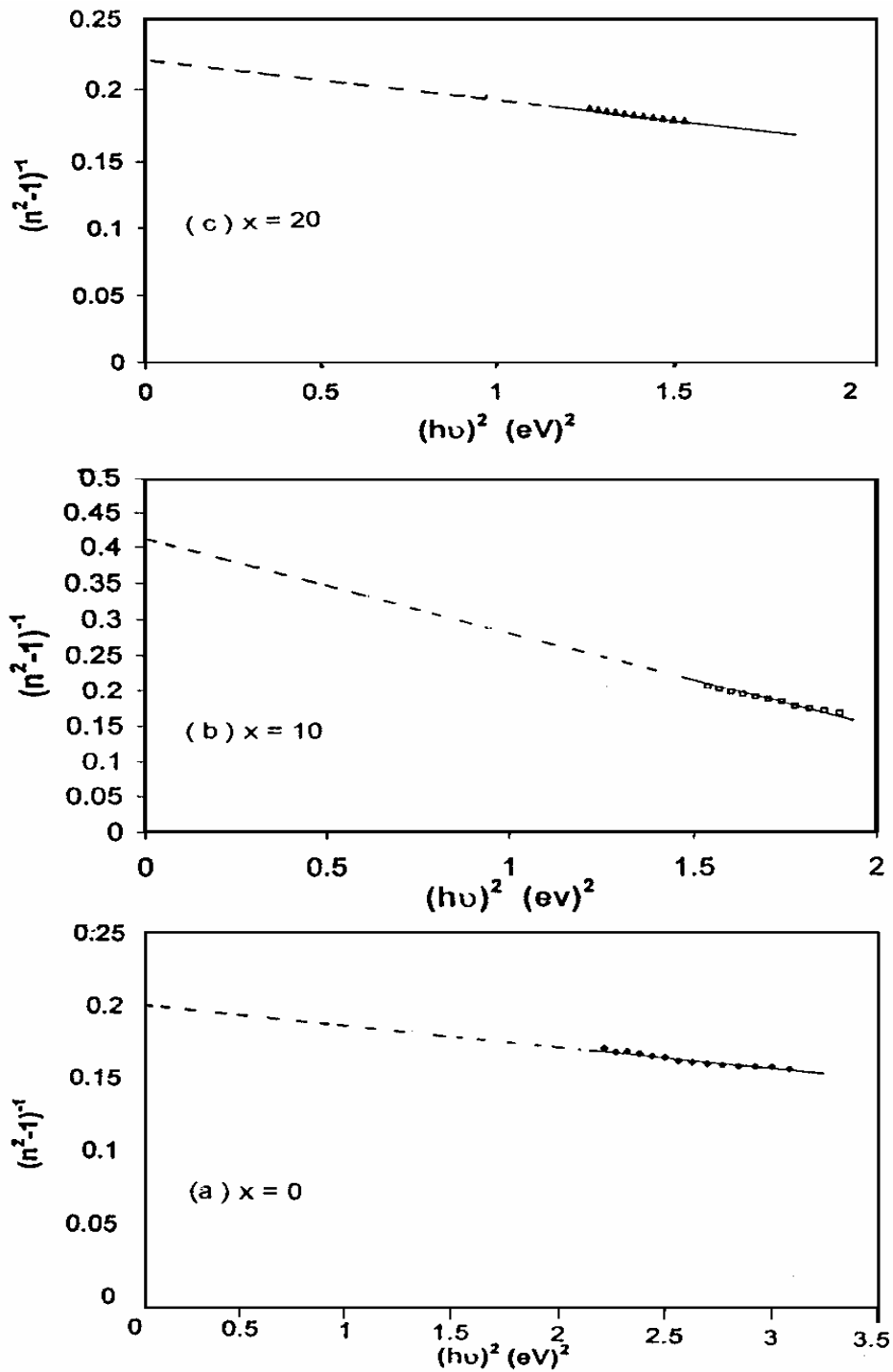
Fig.(4): $(n^2-1)^{-1}$ vs. $(h\upsilon)^2$ for $Ge_{15}Se_{85-x}Ag_x$ films (a) x = 0 , (b) x = 10 and (c) x = 20.

As was found by Tanaka [18], the first approximate value of the optical band gap, E_g^{opt} ,is also derived from the Wemple – DiDominico dispersion relationship, according to the expression $E_g^{opt} \approx E_0/2$, and we found that $E_g^{opt} \approx 1.932$eV, 1.351eV and 0.9115 eV for $x = 0$, 10 and 20, respectively. These values are almost in agreement with the values obtained from the Tauc's extrapolation using the value of the absorption coefficient calculated from the transmission and reflection measurements, (see Table.1).

3.1.4. Correlation between E_d, L and K_g

According to Ref. [19] the maximum Ag content of 30 at. % could be introduced into a Se-rich sample with the composition $GeSe_3$ while still retaining the vitreous character. This was confirmed throughout the results of the present study for L (number of unshared lone-pair electrons) and K_g (glass-forming ability) given in table 1. The decrease of E_g by Ag addition was accounted for by supposing that Ag atoms incorporated in the Se- based films break up the Ge-Se network structure through the formation of Ag-Se ionic bonds [14]. This along with supports the present data. In this respect estimated values of N_{co} (coordination number) in (Table 1) agree with those obtained in Ref. [7]. It is observed that the variation in the transition strength, E_d, results primarily from changes in the average nearest – neighbor coordination number. It is proposed that the layer-layer and chain-chain bonding, increase the effective coordination number. The primary optical effect is a reduction in the oscillator strength of the lone–pair to conduction–band transitions causing a corresponding decrease in E_d. It is observed here that increasing the Ag content increases the coordination number (N_{co}) and decreases the energy gap (E_g).

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