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Optical Properties of Non-uniform Thickness Thin Films of the Glass-Alloy System Cu–As–Se

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Abstract

The optical constants and average thickness of metal-chalcogenide glass films of chemical composition $Cu_xAs_{50}Se_{50-x}$, with x = 5, 10 and 15 at.%, are accurately determined by a novel interferometric method, based on the optical transmission spectra at normal incidence, measured over the 300 to 2000 nm spectral region. This very useful optical method takes into account the non-uniform thickness of the layers. The dispersion of the refractive index is discussed in terms of the Wemple–DiDomenico relationship corresponding to the single-oscillator model. The optical absorption edges are described using the "non-direct transition" model proposed by Tauc, and the optical energy gaps are calculated by Tauc's extrapolation. It has been found that the value of the refractive index increases clearly with copper content whereas, on the contrary, the optical band gap decreases from 1.80 to 1.64 eV.

1. Introduction

Among the reasons which explain the growing interest, during the past 20 years, in the study of chalcogenide glass thin films, worth mentioning are their excellent transmittance in the infrared spectral range [1, 2], the wide range of photo-induced phenomena which take place when they are exposed to band-gap light [3], and the continuous change in their optical constants when their chemical composition changes [4]. In order to understand the above-mentioned light-induced phenomena, and to exploit the very interesting technological possibilities they offer, an accurate knowledge is needed of the optical constants and the relative changes they undergo.

The aim of this work is to determine the change undergone by the refractive index, the absorption coefficient and the optical band gap with copper content, in the specific case of wedge-shaped $Cu_xAs_{50}Se_{50-x}$ (x = 5, 10 and 15 at.%) glass films prepared by vacuum thermal evaporation, using a novel, very accurate data-processing method, based only on their optical transmission spectra at normal incidence. The optical methods based only on transmission spectra at normal incidence are, generally, relatively simple, besides being non-destructive and not requiring any previous knowledge of the thickness of the films under study; they are also fairly accurate, as the thickness and the refractive index can be determined with an accuracy of about 2% [5, 6]. They do, however, assume a thin film with uniform thickness which, when absent (as in the present case), produces a clear shrinking in the optical transmission spectrum (i.e., the transmission maxima decrease and the transmission minima increase), leading to less accurate final results and even serious errors. In the present work, a method for non-uniform films [7] is applied and, besides calculating a parameter indicating the degree of uniformity of the film thickness, the determination of the optical constants of the thin films is carried out with excellent accuracy, despite the aforementioned, strong deformations in the transmission spectrum.

2. Materials preparation and characterization and transmission measurements

Thin-film samples were prepared by vacuum evaporation of powdered melt-quenched glassy material [8, 9] onto room-temperature glass substrates (glass microscope slides). The thermal evaporation process was carried out in a conventional coating system (Edwards, model E306A) at a pressure of $\approx 5 \times 10^{-7}$ Torr from a suitable cylindrical quartz crucible. Inside the vacuum chamber was installed a thermocouple for controling the temperature of the glass melt, and a rotary workholder with the glass substrates on which the metal-chalcogenide glass films were deposited (the substrates rotated during the deposition process at a speed of ≈45 r.p.m.). The thickness of the films was measured by a quartz-crystal monitor (Edwards, model FTM-5) and also by means of an optical method based on the interference of a reflected laser beam. The depositon rate was ≈ 5–10 Å s^{-1}; this low deposition rate results in a film composition which is very close to that of the starting bulk material. The ensuing chemical composition of the metal-chalcogenide glass films was very carefully determined by atomic absorption spectroscopy (Perkin-Elmer 3100 AA spectrometer) and EDAX-measurements (Jeol JSM-820 scanning electron microscope): the differences between the atomic percentages of each individual component of the starting bulk materials, and the associated numerical values corresponding to the glassy films under study, are clearly less than 5% of the nominal values. Additionally, in order to derive the optical constants accurately, it is necessary to know whether there is any variation in composition with depth through the metal-chalcogenide layer. Secondary ion mass spectroscopy (a CAMECA ims-4f instrument was used for these measurements) showed that the film composition is essentially uniform. The As signal falls off gradually by ≈8%, and this could be due to beam instability, because about the same extent of variation was also obtained for an

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Al test film. It should be pointed out that the optical transmittance is considerably influenced by thin-film inhomogeneity in the direction normal to the film surface [7]. The lack of crystallinity in the films was verified by X-ray diffraction analysis.

In this work, a surface-profiling stylus (Sloan, model Dektak 3030) was used to determine the film thicknesses for the sake of comparison with the results derived from the optical transmission spectra at normal incidence. These spectra were obtained over the 300 to 2000 nm spectral region by a double-beam, ratio-recording UV/VIS/NIR computer-controlled spectrophotometer (Perkin-Elmer, model Lambda-19). The spectrophotometer was set with a slit width of 2 nm. It was therefore unnecessary to make slit width corrections, since this value of the slit width was much smaller than the different linewidths. The area of illumination over which a single transmission spectrum was obtained is about 1 mm × 10 mm. It should be emphasized that the transmission spectra show that the glass films have non-uniform thickness. All the optical constants measurements reported in this paper were made at room-temperature.

3. Theoretical considerations

3.1. *Determining the refractive index and average film thickness*

The optical transmission $T_{\Delta d}$ in the transparent region at a specific wavelength λ, for the case of non-uniform thickness, can be obtained by [10]

$$T_{\Delta d} = \frac{1}{\phi_2 - \phi_1} \int_{\phi_1}^{\phi_2} \frac{A}{B - C\cos\phi + D}\,\mathrm{d}\phi, \tag{1}$$

where $A = 16n^2 s$, $B = (n+1)^3(n+s^2)$, $C = 2(n^2-1)(n^2-s^2)$, $D = (n-1)^3(n-s^2)$, $\phi = 4\pi n d/\lambda$, with $\phi_1 = 4\pi n(\bar{d} - \Delta d)/\lambda$ and $\phi_2 = 4\pi n(\bar{d} + \Delta d)/\lambda$. It is assumed that the film thickness varies linearly over the illuminated area so that the thickness is given by $d = \bar{d} \pm \eta\Delta d$, with $-1 \leqslant \eta \leqslant 1$. Δd refers to the actual variation in film thickness from the average thickness $\bar{d}$ and s is the refractive index of the substrate. The integral in eq. (1) yields

$$T_{\Delta d} = \frac{\lambda}{4\pi n\Delta d}\,\frac{a}{(1-b^2)^{1/2}} \times \left[\tan^{-1}\left(\frac{1+b}{(1-b^2)^{1/2}}\tan\frac{\phi_2}{2}\right) - \tan^{-1}\left(\frac{1+b}{(1-b^2)^{1/2}}\tan\frac{\phi_1}{2}\right)\right], \tag{2}$$

where $a = A/(B+D)$ and $b = C/(B+D)$. The expression for the envelope around the interference maxima is the following [10]

$$T_{Md} = \frac{\lambda}{2\pi n\Delta d}\,\frac{a}{(1-b^2)^{1/2}}\tan^{-1}\left(\frac{1+b}{(1-b^2)^{1/2}}\tan\frac{2\pi n\Delta d}{2}\right). \tag{3}$$

Furthermore, the expression for the envelope around the interference minima can be obtained by changing the sign of C in eq. (1). Thus, the expression for the envelope around the interference minima is

$$T_{md} = \frac{\lambda}{2\pi n\Delta d}\,\frac{a}{(1-b^2)^{1/2}} \times \tan^{-1}\left(\frac{1-b}{(1-b^2)^{1/2}}\tan\frac{2\pi n\Delta d}{2}\right). \tag{4}$$

The range of validity of eqs (3) and (4) is $0 < \Delta d < \lambda/4n$; within this range, the system has only one solution [11]. In addition, eqs (3) and (4) are two independent transcendental equations with only two unknown parameters, n and Δd. They can be solved for the experimental values using a standard computer method (Newton–Raphson iteration).

Continuing with the theoretical considerations, in the region of weak and medium absorption ($\alpha > 0$), the integration (1) should be done over both the film thickness variation Δd and absorbance x_a [with $x_a = \exp(-\alpha\bar{d})$]. This is prohibitively difficult analytically and an approximation would be to consider x_a to have an average value over the range of integration with respect to Δd. This is an excellent approximation provided $\Delta d \ll \bar{d}$. The constants a and b are now redefined as follows, $a_x = Ax_a/(B + Dx_a^2)$ and $b_x = Cx_a/(B + Dx_a^2)$. The equations for the two envelopes now become

$$T_{Mx} = \frac{\lambda}{2\pi n\Delta d}\,\frac{a_x}{(1-b_x^2)^{1/2}} \times \tan^{-1}\left(\frac{1+b_x}{(1-b_x^2)^{1/2}}\tan\frac{2\pi n\Delta d}{2}\right), \tag{5}$$

$$T_{mx} = \frac{\lambda}{2\pi n\Delta d}\,\frac{a_x}{(1-b_x^2)^{1/2}} \times \tan^{-1}\left(\frac{1-b_x}{(1-b_x^2)^{1/2}}\tan\frac{2\pi n\Delta d}{2}\right). \tag{6}$$

These expressions are again two independent transcendental equations with two unknown parameters, n and x_a, since Δd is known from solving eqs (3) and (4) in the transparent region. Equations (5) and (6) have again only one solution for n and x_a in the range $0 < x_a \leqslant 1$. The procedure to be used to calculate the absorption coefficient α will be shown later. Once the system that results from each interference extreme is solved, the corresponding refractive index is obtained. From these, one can determine the average thickness $\bar{d}$, and also apply a procedure, similar to the one for uniform films [12–14] to increase the accuracy remarkably, using the basic interference equation

$$2n\bar{d} = m\lambda \tag{7}$$

where m is the interference order, integer or half-integer, for the maxima and the minima, respectively. Applying eq. (7) to each pair of consecutive maxima and minima, the interference orders m_0 are determined, which, once rounded off to the nearest corresponding integer or half-integer, yield the refractive index and final average thickness values with an accuracy better than 3%. The subsequent fitting of these refractive index values to a specific dispersion model, described below, permits the extrapolation of the refractive index towards the spectral range with no interference effects.

3.2. *Determining the absorption coefficient and optical band gap*

In the case of a film with uniform thickness, the absorbance x_a can be obtained from the envelope around the maxima [12] by

$$x_a = \frac{E_M - [E_M^2 - (n^2-1)^3(n^2-s^4)]^{1/2}}{(n-1)^3(n-s^2)} \tag{8}$$

where

$$E_M = \frac{8n^2 s}{T_M} + (n^2-1)(n^2-s^2).$$

These formulae are also valid for non-uniform films in the spectral region where there are no interference fringes, and therefore the envelopes converge to a single curve, $T_M = T_m$. However, once the transmission is affected by the inter-

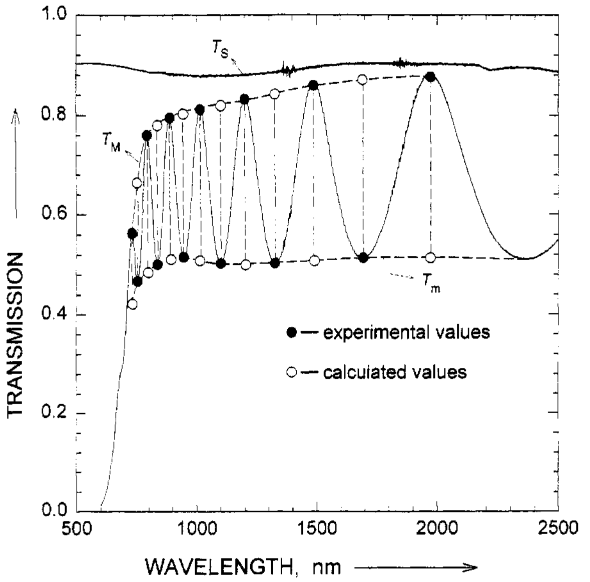

Fig. 1. Shrunk transmission spectrum of the $Cu_{10}As_{50}Se_{40}$ thin film. Curves T_M and T_m are the maximum and minimum envelopes. T_s is the transmission spectrum of the substrate alone.

ferences, i.e., when $T_M \neq T_m$, the shrinking of the spectrum influences the values of T_M and hence the absorbance calculated by eq. (8). Below we will explain how the values calculated by eq. (8) are affected by the shrinking of the transmission spectrum. Since the absorbance and the average thickness $\bar{d}$ are known, the relation $x_a = \exp(-\alpha\bar{d})$ can be solved for α, thus yielding the absorption coefficient. Moreover, from the relationship $k = \alpha\lambda/4\pi$, the extinction coefficient is obtained.

Table I. *Values of* λ, T_M *and* T_m *corresponding to the optical transmission spectrum of Fig. 1*

λ (nm)	s	T_M	T_m	n_1	Δd (nm)	n_2	ix_a
1976	1.566	0.895	*0.534*	2.840	26.7	2.843	1.000
1699	1.566	*0.888*	0.535	2.850	29.3	2.844	0.998
1490	1.591	0.881	*0.535*	2.869	26.5	2.877	1.000
1330	1.623	*0.873*	0.535	2.891	23.6	2.920	1.000
1206	1.653	0.847	*0.535*	2.945	29.9	2.927	0.995
1104	1.648	*0.828*	0.525	3.018	32.5	2.958	0.984
1021	1.650	0.823	*0.518*	3.059	30.5	3.017	0.989
950	1.644	*0.819*	0.512	3.088	28.8	3.071	0.995
889	1.641	0.817	*0.508*	3.112	27.2	3.132	1.000
837	1.633	*0.809*	0.504	3.140	26.8	3.177	1.000
793	1.616	0.803	*0.502*	3.154	26.8	3.199	1.000
754	1.597	*0.796*	0.501	3.167	26.8	3.221	1.000

Italicized transmittance values are those calculated by suitable parabolic interpolation (see Fig. 1). It is worth noting that at the smallest wavelengths, in some cases, it is very difficult to find appropriate initial solutions for eqs (5) and (6).

Table II. *Accuracy improvement procedure for the refractive index* n_2 *and determination of the average film thickness from eq. (7)*

λ (nm)	n_2	d_1 (nm)	m_0	m	d_2 (nm)	n_3
1976	2.843	—	2.78	3.0	1043	2.917
1699	2.844	—	3.23	3.5	1045	2.926
1490	2.877	1016	3.73	4.0	1036	2.933
1330	2.920	959	4.24	4.5	1025	2.945
1206	2.927	1008	4.69	5.0	1030	2.967
1104	2.958	1034	5.18	5.5	1027	2.988
1021	3.017	947	5.71	6.0	1015	3.014
950	3.071	903	6.25	6.5	1005	3.039
889	3.132	880	6.81	7.0	994	3.062
837	3.177	888	7.33	7.5	988	3.089
793	3.199	979	7.79	8.0	992	3.122
754	3.221	1049	8.25	8.5	995	3.154

$\bar{d}_1 = 966\,\text{nm}$, $\sigma_1 = 61\,\text{nm}$ (6.3%); $\bar{d}_2 = 1016\,\text{nm}$, $\sigma_2 = 21\,\text{nm}$ (2.1%).

Finally, the optical energy gap is determined from the calculated values of α. The absorption coefficient of amorphous semiconductors in the high-absorption spectral region ($\alpha \gtrsim 10^4\,\text{cm}^{-1}$) is given, according to the "non-direct transition" model proposed by Tauc [15], by the relationship:

$$\alpha(\omega) = \frac{B(\hbar\omega - E_g^{\text{opt}})^2}{\hbar\omega} \tag{9}$$

where E_g^{opt} is the Tauc bandgap and B is an energy-independent constant. Such spectral dependence of α can be attributed to interband electronic transitions since it can be written

$$\alpha(\omega) \sim \frac{M}{\hbar\omega}\int_0^{\hbar\omega} g_v(-E)\,g_c(\hbar\omega - E)\,\mathrm{d}E \tag{10}$$

where M is the transition matrix element, and g_v and g_c are the densities of states in the valence and conduction bands of the amorphous semiconductor. Assuming that these densities of states are parabolic functions, i.e., $g_v(-E) \sim E^{1/2}$ and $g_c(E) \sim (E - E_g^{\text{opt}})^{1/2}$, and that M is constant in the energy range under consideration, eq. (10) takes on the form expressed by eq. (9). Furthermore, the value of E_g^{opt} can be obtained by extrapolating $(\alpha\hbar\omega)^{1/2}$ towards zero.

4. Results and discussion

The above procedures were systematically applied to several $Cu_xAs_{50}Se_{50-x}$ metal-chalcogenide glass films of thicknesses around 1 µm, with x = 5, 10 and 15 at.%. Figure 1 shows a typical shrunk optical transmission spectrum for a non-uniform film of the representative chemical composition $Cu_{10}As_{50}Se_{40}$, together with the transmission spectrum of the substrate alone. In Table I, s represents the refractive index of the substrate, independently obtained from the transmission spectrum of the substrate alone for each wavelength through the expression [12]

$$s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1\right)^{1/2}. \tag{11}$$

Still in Table I, T_M and T_m represent the maxima and minima of the transmission spectrum, whereas T_M^* and T_m^* are the transmittance values associated, respectively, to each experimental minimum and maximum value, according to the corresponding envelopes (see Fig. 1). The latter values are calculated through parabolic interpolation among every three consecutive maxima or minima. Next, the values $[\lambda_i, T_M(\lambda_i), T_m^*(\lambda_i)]$ and $[\lambda_j, T_M^*(\lambda_j), T_m(\lambda_j)]$ are used in eqs (3) and (4) to derive the values of the refractive index and thickness variation, shown as n_1 and Δd in Table I. Of the latter values, it seems reasonable to assign a value of $\Delta d \approx 28$ nm. It should be pointed out that the low dispersion in the values obtained for Δd, shows the very good accuracy of the present optical method. The values $[\lambda_i, T_M(\lambda_i), T_m^*(\lambda_i)]$ and $[\lambda_j, T_M^*(\lambda_j), T_m(\lambda_j)]$ are again used in eqs (5) and (6) to calculate the refractive index and absorbance for each interference extreme, making use of the value $\Delta d \approx 28$ nm determined previously. These values are listed as n_2 and x_a

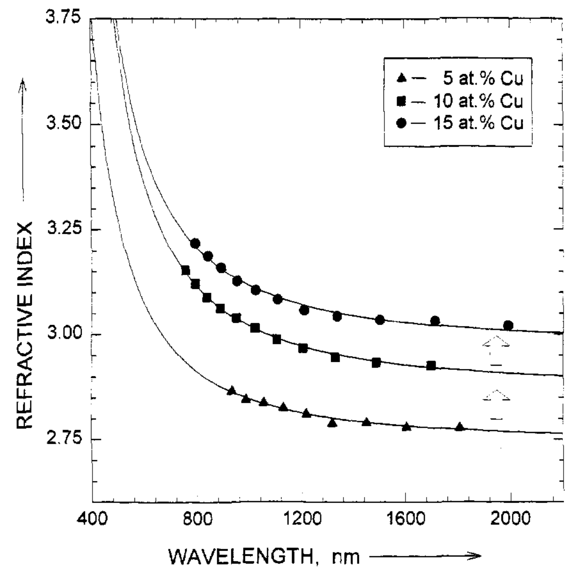

Fig. 2. Refractive index as a function of wavelength. Curves are determined according to the single-oscillator analysis.

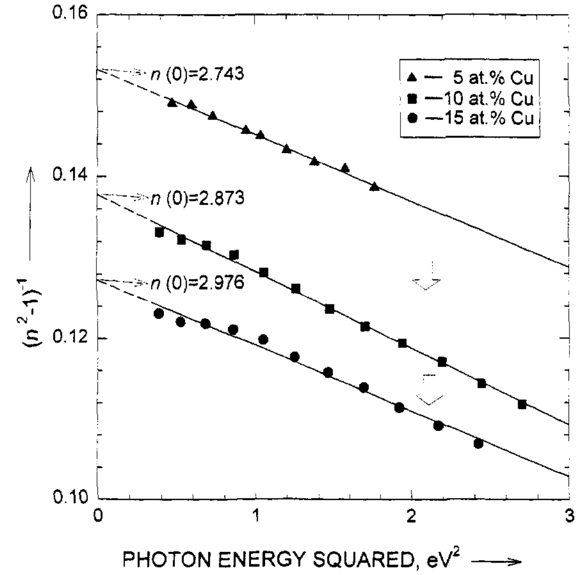

Fig. 3. Plot of refractive-index factor $(n^2-1)^{-1}$ *vs.* E^2 for the three Cu-As-Se glassy compositions studied. $n(0)$-values are the refractive indices extrapolated to $E = 0$.

Table III. *Dispersion parameters (single-oscillator analysis), the value of refractive index extrapolated to $E = 0$, the optical band gap (Tauc's extrapolation) of the three films representing the compositions under study, together with the results corresponding to the glass composition $As_{50}Se_{50}$*

Composition $Cu_xAs_{50}Se_{50-x}$	E_0 (eV)	E_d (eV)	$n(0)$	E_g^{opt} (eV)	E_0/E_g^{opt}
x = 0	3.98	22.44	2.577	1.85	2.15
x = 5	4.33	28.27	2.743	1.80	2.41
x = 10	3.81	27.62	2.873	1.70	2.24
x = 15	3.95	31.02	2.976	1.64	2.41

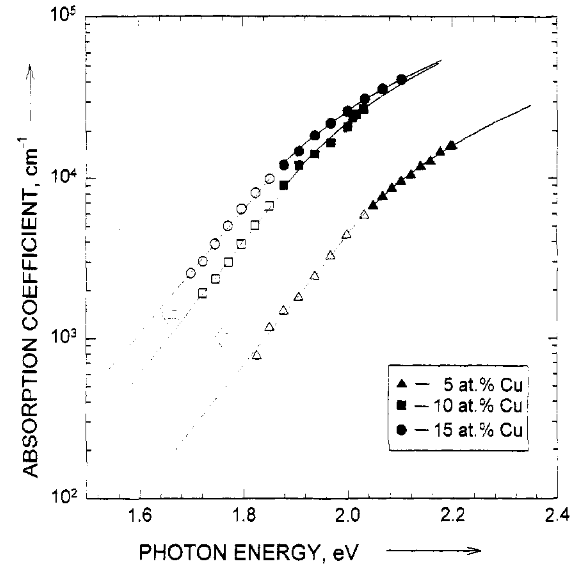

Fig. 4. Optical absorption coefficient as a function of photon energy. Dashed lines correspond to the Urbach region. Solid lines indicate the spectral dependence of α in the high-absorption region.

in Table I. Furthermore, the values of n_2 can be used to determine the average film thickness $\bar{d}$ and also new improved values for the refractive index, from the already mentioned basic equation for the interference fringes, $2n\bar{d} = m\lambda$, as described in the previous section. These improved refractive indices are shown in Table II as n_3. Finally, the value determined for $\bar{d}$ is 1083 ± 22 nm. The film thickness determined by mechanical measurements on the same film area was 1096 ± 22 nm. These mechanical measurements show an excellent agreement with that determined by the optical procedure – the difference is less than 2%. Figure 2 shows the final values of the refractive index, for three representative copper-chalcogenide glass films of each composition under study, and it can be observed that the values of the refractive index increase notably with increasing copper content.

Next, the spectral dependence of n can be fitted to the Wemple–DiDomenico dispersion relation [16]

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - E^2} \tag{12}$$

where E_0 is the energy of the effective dispersion oscillator [typically near the main peak of the $\varepsilon_2(E)$-spectrum], which is identified with the mean transition energy from the valence band of the lone-pair state to the conduction-band state (in chalcogenide materials, the valence s-states lie far below the top of the valence band and the band edge involves transitions between lone-pair p-states and antibonding conduction-band states [16]), and E_d is the dispersion energy. This latter, very important quantity obeys the empirical relationship

$$E_d = \beta N_c Z_a N_e \tag{13}$$

where $\beta = 0.37 \pm 0.04$ eV for covalent crystalline and amorphous materials, N_c is the number of the nearest-neighbour cations to the anion, Z_a is the formal chemical valence of the anion, and N_e is the effective number of valence electrons per anion. By plotting $(n^2-1)^{-1}$ against E^2 and fitting a straight line as shown in Fig. 3, the dispersion parameters E_0 and E_d can be determined directly from the slope $(E_0 E_d)^{-1}$ and the intercept (E_0/E_d). The values obtained for these dispersion parameters are listed in Table III, where the values corresponding to the chalcogenide glassy composition $As_{50}Se_{50}$ are also shown [14]. The differences in E_d values clearly suggest a different bonding structure of the amorphous network depending on the copper content. It is also noteworthy that the results

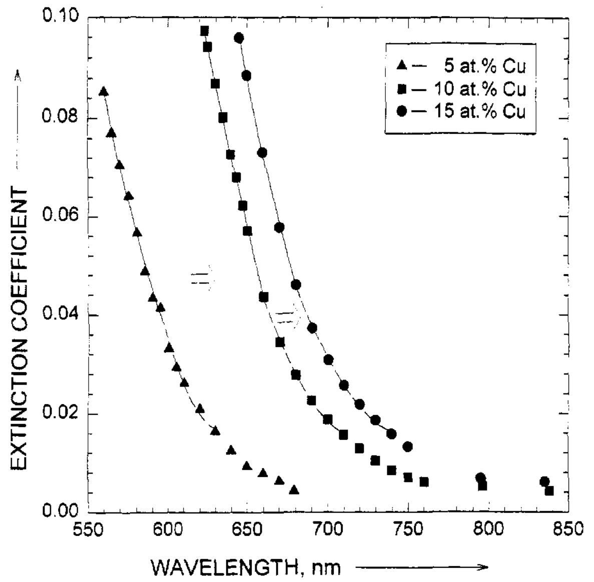

Fig. 5. Extinction coefficient against wavelength for the three films representing the Cu-As-Se alloys under study. The solid curves are obtained using the Tauc law.

obtained for E_0 and E_g^{opt}, for each composition studied, establish the following relationship $E_0 \approx 2.3E_g^{opt}$ (Tanaka obtained the relationship between these parameters, $E_0 \approx 2E_g^{opt}$, for well-annealed As_xS_{100-x} glass films [17]).

On the other hand, the values of the absorption coefficient obtained by

$$\alpha = -\frac{\ln(x_a)}{\bar{d}} \tag{14}$$

are displayed in Fig. 4. This figure clearly shows the red-shift in the optical absorption edge with increasing copper content. It should be mentioned that in order to account for the influence of the shrinking of the transmission spectrum in the interference region on the values of α, we take the realistic absolute change of $T_M \pm 0.01$. Once $\alpha(\lambda)$ is known, $k(\lambda)$ is determined from the expression $k = \alpha\lambda/4\pi$, which completes the derivation of the optical constants. Figure 5 shows the extinction coefficient against wavelength for the three films representing the compositions under study.

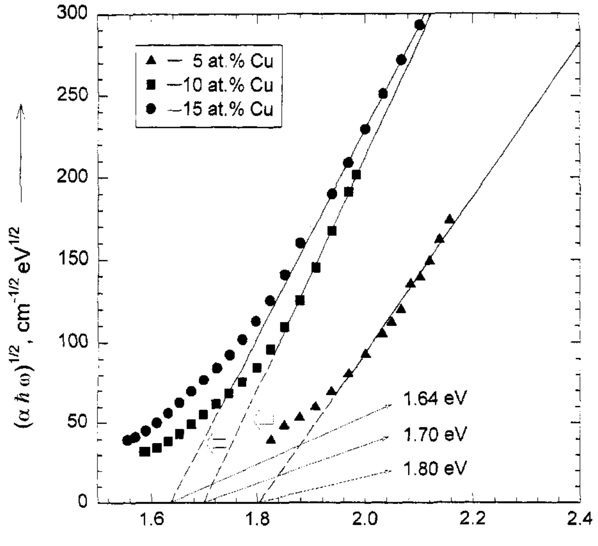

Fig. 6. Determination of the optical band gap in terms of the Tauc law for the three Cu-As-Se glassy alloys studied.

Using eq. (9), the values of the optical band gap have been calculated, and a decrease of E_g^{opt} with increasing copper content has been found (see Fig. 6). The results show that the chalcogenide amorphous semiconductors alloyed with copper change in a remarkable fashion their optical properties: the refractive index and the absorption coefficient increase significantly. It is also worth mentioning that it was previously found [18] that the electrical conductivity increases remarkably with increasing copper content in the case of Cu-As-Se bulk samples. As to the decrease of the optical band gap, Kitao *et al.* [19] consider, in the particular case of amorphous As_2Se_3 : Cu, that it is caused by an alloying effect, i.e., a compositional change in the host material itself. This effect is due to the change in bond angles and/or bond lengths. Furthermore, it is believed that in the present region of copper content the Fermi level shifts downwards, and that acceptor-like states are produced (i.e., the creation of impurity levels).

5. Conclusions

The very useful procedures reported in detail in this paper for calculating the optical constants and average thickness of thermally-evaporated $Cu_xAs_{50}Se_{50-x}$ ($x = 5$, 10 and 15 at.%) thin films take into account the lack of uniformity of the film thickness, found under the present preparation conditions. This fact gives rise to a clear shrinking of the interference fringes of the optical transmission spectrum at normal incidence that yields inaccuracies and even serious errors if n, d and α are calculated from such a transmission spectrum, assuming the film to be uniform. The optical method applied here makes it possible to determine the refractive index and average film thickness with an accuracy better than 3%. The subsequent fitting of the refractive index to the Wemple-DiDomenico relationship results in the dispersion parameters E_0 and E_d, directly related to the structure of the material under study.

Furthermore, as a result of the addition of copper to the chalcogenide glass, the refractive index and absorption coefficient increase and, hence, the optical gap decreases. These results strongly support the idea that the metallic atoms behave efficiently as modifiers of the band structure in a covalent amorphous semiconductor such as the $As_{50}Se_{50}$ glass films. In conclusion, by the addition of copper, a substantial degree of control can be exercised over all the optical properties of the chalcogenide glass.

Finally, the electrical characterization, both in d.c. and a.c. conditions, of glassy alloys from the present metal-chalcogenide system $Cu_xAs_{50}Se_{50-x}$ in thin-film form is currently underway.

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