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Derivation of the optical constants of thermally-evaporated uniform films of binary chalcogenide glasses using only their reflection spectra

J.M. González-Leal *, E. Márquez, A.M. Bernal-Oliva, J.J. Ruiz-Pérez, R. Jiménez-Garay

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real, Cádiz, Spain

Abstract

Optical reflection spectra, at normal incidence, of binary chalcogenide glass thin films of chemical compositions $As_{25}S_{75}$ and $Ge_{33}Se_{67}$, deposited by thermal evaporation, were obtained in the 400 nm to 2200 nm spectral region. The optical constants of these particular amorphous materials were accurately determined using an optical characterization method proposed by Minkov, based on the maximum and minimum envelopes of the reflection spectrum, which allows to obtain both the real and the imaginary parts of the complex refractive index, and the film thickness. The dispersion of n is discussed in terms of the single-oscillator Wemple–DiDomenico model. The optical gap has been determined from the absorption coefficient values by Tauc's procedure. © 1998 Elsevier Science S.A.

Keywords: Optical constants; Binary chalcogenic glasses; Spectra

1. Introduction

The excellent transmittance of chalcogenide amorphous semiconductors [1], reaching to the far-infrared spectral region, and the wide range of photo-induced effects that they exhibit (such as photo-crystallization, photo-polymerization, photo-decomposition, photo-vaporization, photo-dissolution of certain metals and photo-vitrification [2,3]), generally accompanied by changes in the optical constants [4,5] and, particularly shifts in the absorption edge (i.e., photo-darkening or photo-bleaching), allow their use as absorption filters and other optical elements [6]. The knowledge of the optical properties of chalcogenide semiconductors is, indeed, necessary for exploiting all their technological potential.

The refractive index, n, and extinction coefficient, k, are usually calculated by sophisticated computer iteration techniques [7–10], using both optical transmission and reflection spectra. In contrast, a relatively simple, straightforward method for determining the optical constants, using only the maximum and minimum envelopes of the reflection spectrum, has been proposed by Minkov [11] and Ruiz-Pérez et al. [12].

In this paper, Minkov's method has been used to accurately calculate the optical constants and the thickness of thermally-evaporated uniform thin films of the chemical compositions $As_{25}S_{75}$ and $Ge_{33}Se_{67}$. The optical properties of these particular materials are clearly representative of those corresponding to the whole of the binary chalcogenide glasses.

2. Experimental details

Thin-film samples were prepared by vacuum evaporation of powdered melt-quenched glassy material onto clean glass substrates (BDH microscope slides). The thermal evaporation process was performed within a coating system (Edwards, model E306A) at a pressure of about 10^{-6} Torr, using a suitable quartz crucible. During the deposition process the substrates were kept at approximately room temperature. The substrates were also rotated during the deposition process by means of a rotary workholder at a speed of ≈ 45 rpm, which makes it possible to obtain chalcogenide films of uniform thickness [13,14]. The deposition rate was ≈ 5 Å s^{-1}, and it was continuously measured by a quartz–crystal monitor (Edwards, model FTM-5). This low deposition rate results in a film composition which is very close to that of the bulk starting material (electron microprobe analysis has indicated that the film stoichiometry is correct to ±0.5 at.%).

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[*] Corresponding author. Tel.: +34-56-830966; fax: +34-56-834924; e-mail: jgonzale@galeon.uca.es.

The reflection spectra were obtained using a double-beam UV–Vis–NIR spectrophotometer with automatic computer data acquisition (Perkin-Elmer, model Lambda-19), and the wavelength range analyzed was between 400 nm and 2200 nm. The reflection measurements were carried out against an accurately calibrated front-surface aluminium mirror coated with magnesium fluoride, which was taken as a reference. Since the absolute reflectance of the calibrated mirror is known, the relative reflectance of the sample obtained by means of the spectrophotometer can be converted to absolute reflectance. A surface-profiling stylus (Sloan, model Dektak 3030) was also used to measure the film thickness which was compared with the thickness calculated from the reflection spectrum.

3. Theoretical considerations

The film is considered to be homogeneous, with a constant thickness d, and a complex refractive index $n_c = n - ik$, where the extinction coefficient k can be related to the absorption coefficient α, by the equation: $k = \alpha\lambda/4\pi$. The thickness of the substrate is several orders of magnitude larger than d and its refractive index is symbolized by s. Interference effects in the film give rise to oscillating reflectance curves similar to those in Fig. 1, which show the optical reflection spectra of two representative uniform films of the glassy compositions $As_{25}S_{75}$ (F1) and $Ge_{33}Se_{67}$ (F2) under study. These interference fringes are used to accurately calculate the optical constants and the thickness of the films.

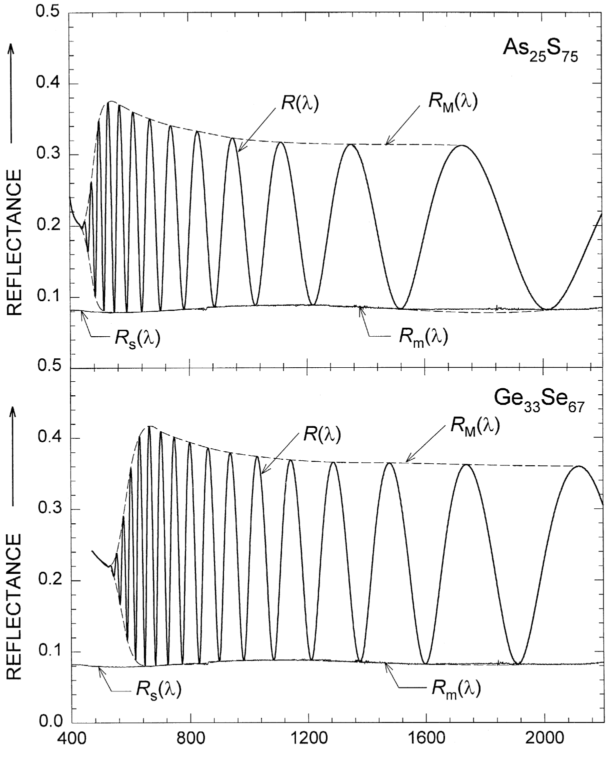

Fig. 1. Experimental optical reflection spectra corresponding to the chalcogenide glass thin films of chemical compositions $As_{25}S_{75}$ and $Ge_{33}Se_{67}$. Curves R_M and R_m are the maximum and minimum envelopes, respectively. R_s is the reflection spectrum of the bare substrate.

The envelopes of the interference maxima and minima of the reflection spectrum, R_M and R_m, are derived from the reflectance $R(\lambda, s, n, d, k)$ of the present optical system [11], for $k = 0$ and dielectric films with $n > s \gg k$, when $\varphi = 4\pi\ nd/\lambda = \pi$ and 0, respectively, are substituted. The equations for these envelopes then have the following expressions:

$$R_M, R_m = \frac{(ad \pm bcx)^2}{(bd \pm acx)^2} + \frac{gx^2}{(bd \pm acx)^2(b^3 f \pm 2abcdx + a^3ex^2)} \qquad (1)$$

where $a = n - 1$, $b = n + 1$, $c = n - s$, $d = n + s$, $e = n - s^2$, $f = n + s^2$, and $g = 64s(s-1)^2 n^4$.

The refractive index of the substrate is calculated from the reflection spectrum of the substrate alone, R_S, with the relation:

$$R_S = \frac{(s-1)^2}{s^2+1} \qquad (2)$$

from which is derived:

$$s = \frac{1 + \sqrt{R_S(2 - R_S)}}{1 - R_S} \qquad (3)$$

4. Results and discussion

4.1. Calculation of the refractive index and the film thickness

Following Minkov's method, the envelopes around the maxima and minima of the reflection spectrum are considered to be continuous functions of λ, and thus of $n(\lambda)$. First, it is necessary to draw the envelopes R_M and R_m of the interference maxima and minima of the reflection spectrum, as shown in Fig. 1; they have been obtained using two different computer programs [15,16], and both leading to similar results. Once the tangent points between the envelopes and the reflection spectrum are known, and the refractive index of the substrate is calculated from the reflection spectrum of the substrate alone, the system of transcendental equations corresponding to Eq. (1) is solved numerically by using the Newton–Raphson method. n and x are determined as solutions of the system:

$$R_M(\lambda_{extr}) - R_M(n,x) = 0$$
$$R_m(\lambda_{extr}) - R_m(n,x) = 0 \qquad (4)$$

At every interference extreme, the solution of this system provides an initial approximation for the refractive index and absorbance of the thin film studied.

Next, the values of the refractive index can be employed to determine the film thickness and also new improved values for the refractive index from the basic equation for the interference fringes, $2nd = m\lambda$ (where, in this case, the order number m is an integer for the minima and half-integer for the maxima), as described in detail in our previous work [12]. If this is carried out the values of the thickness for F1 and F2 are 1650 ± 19 nm and 1975 ± 10 nm, respectively. The accuracy of the final value of the thickness is 1.2% for F1 and 0.5% for F2. In addition, the thicknesses determined by mechanical measurements, using the surface-profiling stylus, are 1621 ± 28 nm and 1947 ± 37 nm, respectively, and are, indeed, in excellent agreement with the ones calculated by the present optical procedure—the difference for both films being less than 2%.

On the other hand, the final values of the refractive index can be fitted to an appropriate function such as the Wemple–DiDomenico dispersion relationship [17], i.e., to the single-oscillator model:

$$\varepsilon_1(\omega) = n^2(\omega) = 1 + \frac{E_0 E_d}{E_0^2 - (\hbar\omega)^2} \qquad (5)$$

where E_0 is the energy of the effective dispersion oscillator (typically near the main peak of the ε_2-spectrum), which is identified by the mean transition energy from the valence band of the lone-pair state to the conduction-band state (in these amorphous materials, the valence s-states lie far below the top of the valence band, and the valence-band edge involves transitions between lone-pair p-states and anti-bonding conduction-band states [17]), and E_d is the dispersion energy. The oscillator energy, E_0, is an 'average' energy gap, and in close approximation, it scales with the Tauc gap, E_g^{opt}, $E_0 \approx 2E_g^{opt}$, as was found by Tanaka [18]. The dispersion energy or oscillator strength, E_d, also follows a simple empirical relationship: $E_d = \beta N_c Z_a N_e$, where β is a constant, and according to Wemple [17], for covalent crystalline and amorphous materials has a value of 0.37 ± 0.04 eV. N_c is the coordination number of the cation nearest neighbour to the anion, Z_a is the formal chemical valency of the anion, and N_e is the total number of valence electrons (cores excluded) per anion.

By plotting $(n^2-1)^{-1}$ against E^2 and fitting a straight line, E_0 and E_d can be determined directly from the slope, $(E_0E_d)^{-1}$, and the intercept on the vertical axis, E_0/E_d (see Fig. 2). The straight line equations corresponding to the least-squares fit, are $(n^2-1)^{-1} = 0.245 - 0.0100\ E^2$, with a correlation coefficient, r, of 0.9996, and $(n^2-1)^{-1} = 0.211 - 0.0109\ E^2$, with a value of r of 0.9997, respectively, for F1 and F2. The values obtained for the dispersion parameters E_0 and E_d, derived from the above-mentioned equations, are 4.90 eV and 20.01 eV, respectively, for F1, and 4.38 eV and 20.78 eV, respectively, for F2. Furthermore, the Wemple–DiDomenico optical dispersion curve for both glass films are also shown in Fig. 2, along with the calculated final values for the refractive index.

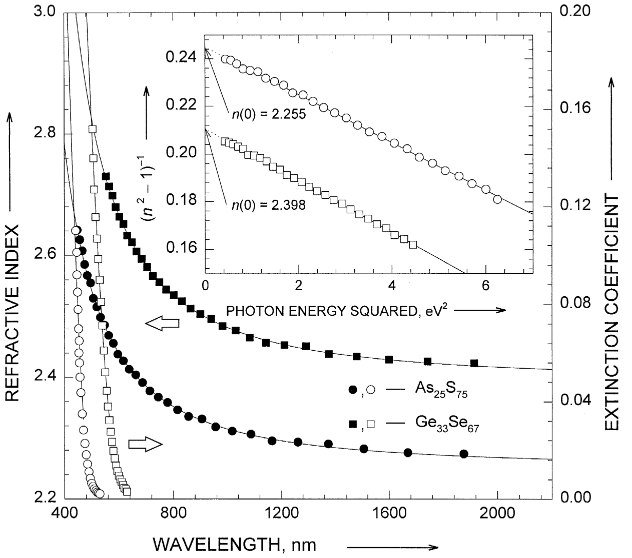

Fig. 2. Refractive index and extinction coefficient as a function of wavelength for the $As_{25}S_{75}$ and $Ge_{33}Se_{67}$ glass films; in the inset, a plot of the refractive-index factor $(n^2-1)^{-1}$ versus the photon energy squared.

Returning to the already mentioned empirical expression for the dispersion energy, E_d, found by Wemple, and using the values derived for the chalcogenide compositions studied, the value of the cation coordination number, N_c, is estimated using the relationship: $N_c = E_d/\beta Z_a N_e$, where $Z_a = 2$ and $N_e = (5\times 25 + 6\times 75)/75 = 7\ 2/3$ for F1, and $Z_a = 2$ and $N_e = (4\times 33 + 6\times 67)/67 = 8$ for F2. Thus, surprisingly, N_c is 3.5 in both cases. It is proposed for the As chalcogenide film, F1, that the layer–layer bonding increase the effective cation coordination number above the nearest-neighbour value [17–19], whereas in the case of the Ge chalcogenide film, F2, it should be pointed out that a 'shadowing' effect of the material on the substrate for incoming evaporant atoms incident at an oblique angle leads to the formation of a columnar-growth morphology [20], and consequently, the mass density and the corresponding dispersion energy decrease substantially [17,19] (curiously, this effect seems to be much less pronounced for the case of the As chalcogenides).

On the other hand, a first, approximate value of the optical band gap is also derived from the Wemple–DiDomenico dispersion relationship, according to the expression $E_g^{opt} \approx E_0/2$, obtaining the values for E_g^{opt} of ≈ 2.45 eV and ≈ 2.19 eV, respectively, for F1 and F2. These values, and particularly the one corresponding to F1, show a good agreement with the value obtained from the Tauc's extrapolation [6], using the values of the absorption coefficient calculated from reflection measurements only, as will be seen later.

4.2. Determination of the optical absorption edge and the Tauc gap

The absorbance, $x = \exp(-\alpha d)$, is derived by numerically solving either of the two expressions for the envelopes corresponding to Eq. (1); it is possible to independently solve both equations for x, thereby obtaining two different values. In addition, since x and d are already known, the absorption and extinction coefficients can be determined. The results obtained from the envelope R_M are found to be clearly superior and this can be attributed to the fact that R_m is almost independent of n and k in the region of weak absorption, where $x \approx 1$. Moreover, in the region of transparency, where $x = 1$, $R_m = R_s$, and it is seen from Eq. (2) that R_m is absolutely independent of n and k. Fig. 3 shows the results obtained for α (and in Fig. 2 those corresponding to k) using the upper envelope of the reflection spectrum.

It should be pointed out that the absorption coefficient of amorphous semiconductors, in the high-absorption region ($\alpha > \approx 10^4$ cm^{-1}), is given according to Tauc by the following equation:

$$\alpha(\hbar\omega) = B\frac{\left(\hbar\omega - E_g^{\mathrm{opt}}\right)^2}{\hbar\omega} \qquad (6)$$

where $\hbar\omega$, E_g^{opt} and B are the photon energy, optical gap and a constant, respectively. The Tauc gap is formally defined as the intercept of the plot $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$. Fig. 3 shows these plots for the two chalcogenide films studied, and also the optical gap derived for each film, 2.46 eV for F1 and 2.01 eV for F2. These values of the Tauc gap are in excellent agreement with the values given by Hajto [21], 2.41 eV, for the glassy composition $As_{25}S_{75}$ (prepared by the spin-coating technique) and by Kandil [22], 1.99 eV, for the stoichiometric glassy composition $Ge_{33}Se_{67}$ (in both cases a difference lower than 2% was found).

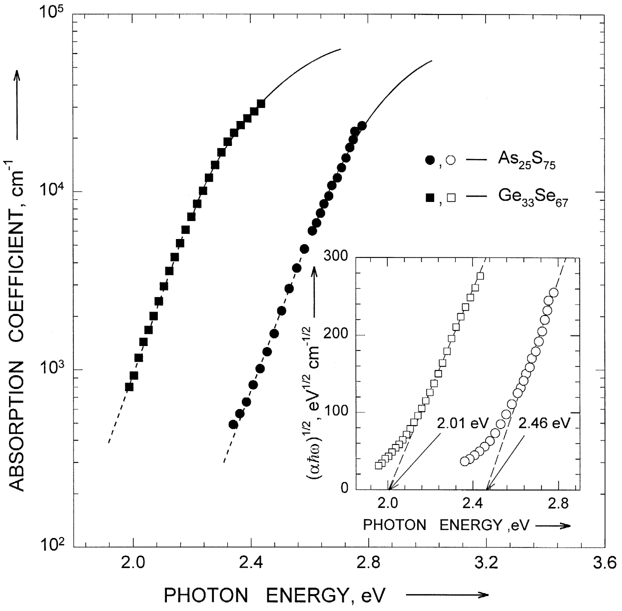

Fig. 3. Absorption coefficient as a function of the photon energy for the $As_{25}S_{75}$ and $Ge_{33}Se_{67}$ glass films. Solid curves are obtained using the Tauc law; dashed lines correspond to the Urbach region. The inset shows the determination of the optical gap.

Continuing with the analysis of the optical absorption edge, at lower values of the absorption coefficient (1 cm^{-1} $< \approx \alpha < \approx 10^4$ cm^{-1}), the absorption depends exponentially on photon energy (the so-called Urbach relation) [20]

$$\alpha(\hbar\omega) = \alpha_0 \exp\left(\frac{\hbar\omega}{E_e}\right) \qquad (7)$$

where E_e is a slope parameter (see Fig. 3); the value of E_e found for F1 and F2 is ≈ 100 meV.

5. Concluding remarks

The method devised by Minkov for calculating the film thickness and the optical constants using only the reflection spectrum, has been successfully applied to the thermally-evaporated $As_{25}S_{75}$ and $Ge_{33}Se_{67}$ chalcogenide glass films, with thicknesses ranging between around 1500 nm and 2500 nm. The almost complete agreement between the values of the reflectance corresponding to the lower envelope, and the values of the reflectance of the bare substrate (obviously, in the transparent region), is a clear consequence of the remarkably uniform thickness of the films, attained by using the very efficient rotary workholder (the variation in thickness over the area of illumination, measured by the mechanical stylus, was found to be lower than ≈ 10 nm).

Finally, the values obtained for the refractive index extrapolating the Wemple–DiDomenico dispersion equation towards the infrared spectral region, $n(0) = 2.255$ for the composition $As_{25}S_{75}$ and $n(0) = 2.398$ for the composition $Ge_{33}Se_{67}$, show a fairly good agreement with the value 2.164 given by Ramírez-Malo et al. [23] for the composition $As_{22}S_{78}$, and with the value 2.450 given by Kandil [22] for the composition $Ge_{33}Se_{67}$ (a difference lower than 5% was found in both cases).

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