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Refractive-index dispersion and optical-absorption edge of physically vapor-deposited films of the $As_{35}S_{65}$ chalcogenide glass

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The optical transmission spectra of amorphous As–S films of composition $As_{35}S_{65}$ prepared by thermal evaporation are measured over the 300 to 2000 nm spectral region. A straightforward method suggested by Swanepoel is successfully applied for determining the layer thickness, refractive index and absorption coefficient; this last value is derived according to four different formulae. Moreover, thickness measurements made by a surface-profiling stylus are also carried out to cross-check the obtained results from the optical transmission spectrum. The optical band gap E_g^{opt} has been determined from the absorption coefficient values by Tauc's procedure, i.e. from the relationship $\alpha(E) = K_2(E-E_g^{opt})^2/E$, where K_2 is a constant. Finally, the typical measured transmission spectrum has been compared to a simulated one.

1. Introduction

Chalcogenide glasses are well-known IR-transmitting materials [1] and exhibit a wide range of photoinduced effects that enable them to be used as optical recording of imaging media [2]. The knowledge of their optical constants is necessary not only for understanding the basic mechanism of these effects, but also for exploiting their technological potentials.

The refractive index and absorption coefficient are usually calculated by very elaborate computer iteration techniques [3,4], using both optical transmission and reflection spectra. In contrast, a simple straightforward method for determining the optical constants, using only the transmission spectrum has been devised by Swanepoel [5] to calculate the film thickness, refractive index and absorption coefficient of amorphous silicon films, attaining 1% accuracy. This optical method has also been applied to some chalcogenide glass films prepared by thermal evaporation, and has again proved to be easy and accurate [6,7]. In the present work, this novel method will be applied for the optical characterization of physically vapor-deposited thin films of the glass composition $As_{35}S_{65}$.

2. Experimental procedure

The vacuum evaporation process was carried out in a conventional coating unit (Edwards, model E306A) at a pressure $<10^{-6}$ Torr, from a quartz crucible. The evaporation sources used for the preparation of the a-$As_{35}S_{65}$ thin films were fragments of the melt-quenched glass. The substrates (glass microscope slides) rotated during the deposition process by means of a rotary workholder at a speed of approximately 45 rpm, which makes it possible to obtain deposited films of remarkably uniform thickness [8]. The process was carried out at room temperature. The properties of amorphous As–S films are known to be affected by the deposition rate [9], which in the present work was ≈ 0.5 nm/s and was continuously measured using the quartz crystal microbalance technique (Edwards, model FTM-5). An electron microprobe analysis of the as-deposited $As_{35}S_{65}$ films indicated that the stated chemical composition is correct to ±0.5 at%. The lack of crystallinity in the films was verified by X-ray diffraction analysis. On the other hand, the optical transmission spectra at normal incidence were obtained by a double-beam, ratio-recording UV/VIS/NIR computer-controlled spectrophotometer (Perkin-Elmer, model

Lambda-19). The wavelength range studied was from 300 up to 2000 nm. All the optical measurements reported in this paper were made at room temperature. Finally, a surface-profiling stylus (Sloan Dektak IIA) was used to determine the thickness of the films for the sake of comparison with the results derived from the optical transmission spectra.

3. Theoretical considerations

The optical system under consideration is a homogeneous film with thickness d and complex refractive index $n_c = n - ik$, where n is the refractive index and k the extinction coefficient, which can be expressed in terms of 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 s. If the film thickness d is constant, interference effects give rise to an oscillating curve such as the one in fig. 1, which shows a typical transmission spectrum of a $As_{35}S_{65}$ glass film. Such interference fringes will be used to determine the optical constants of the film, as described below.

The expression for the optical transmission at normal incidence [10] for the abovementioned optical system can be simplified significantly by neglecting the extinction coefficient of the film, an approximation that is certainly valid over most of the spectrum (fig. 1a shows that the a-$As_{35}S_{65}$ film is reasonably transparent over a wide range of the spectrum). So that, with $k=0$, the transmission T then becomes

$$T(\lambda, s, n, d, k) = \frac{Ax}{B - Cx\cos\varphi + Dx^2}, \qquad (1)$$

where $A = 16n^2s$, $B = (n+1)^3(n+s)^2$, $C = 2(n^2-1)(n^2-s^2)$, $D = (n-1)^3(n-s^2)$, $\varphi = 4\pi nd/\lambda$ and the absorbance, x, is given by $x = \exp(-\alpha d)$. Moreover, the values of the transmission at the extremes of the interference fringes can be obtained from eq. (1) by setting the interference conditions $\cos\varphi = 1$ and $\cos\varphi = -1$ for maxima and minima,respectively. Many of the equations that provide the basis for the present method are easily derived from these considerations [5].

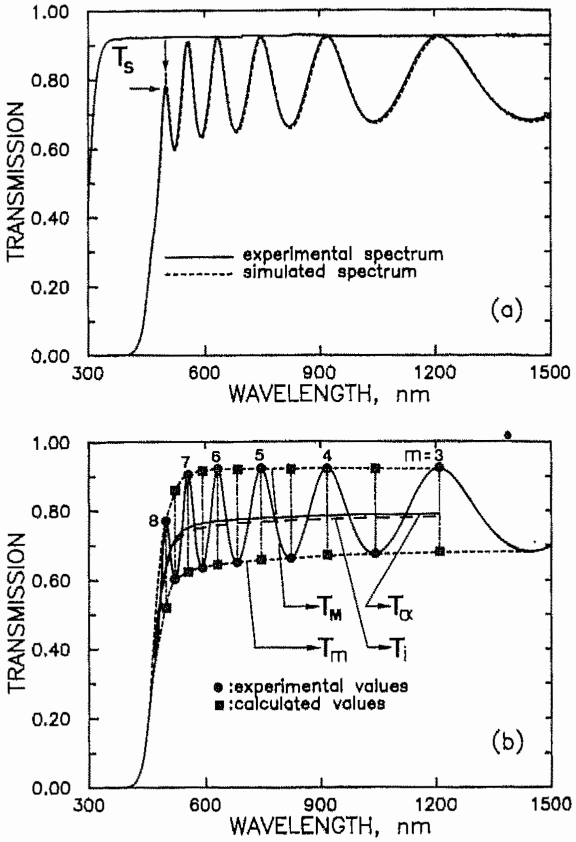

Fig. 1. (a) Experimental optical transmission spectrum corresponding to a $As_{35}S_{65}$ glass film. The simulated transmission spectrum obtained from the calculated value of the film thickness, $d = 799$ nm, and the obtained optical constants is also shown. The arrows mark the main difference between the experimental and simulated transmission spectra. Curve T_s is the transmission spectrum of the substrate alone. (b) Curves T_M and T_m are the maximum and minimum envelopes, respectively. T_i is the curve passing through the inflection points of the interference fringes and T_α is the so-called interference-free transmission curve.

4. Results and discussion

4.1. Calculation of the refractive index and film thickness

According to Swanepoel's method, which is based on the idea of Manifacier et al. [11] of creating the envelopes of interference maxima and minima (fig. 1b), a first, approximate value of the refractive index of the film n_1 in the spectral region of medium and weak absorption, can be calculated by the expression

$$n_1 = [N_1 + (N_1^2 - s^2)^{1/2}]^{1/2}, \qquad (2)$$

where

$$N_1 = 2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2+1}{2}.$$

Here T_M and T_m are the transmission maximum and the corresponding minimum at a certain wavelength λ. Alternatively, one of these values is an experimental interference extreme and the other one is derived from the corresponding envelope; both envelopes were computer-generated using a specific program devised by McClain et al. [12].

On the other hand, the necessary values of the refractive index of the substrate are obtained from the transmission spectrum of the substrate, T_s, using the well-known equation

$$s = \frac{1}{T_s} + \left(\frac{1}{T_s} - 1\right)^{1/2}. \qquad (3)$$

The values of the refractive index n_1 as calculated from eq. (2) are shown in table 1. The accuracy of this initial estimation of the refractive index is improved after calculating d, as will be explained below. Now, it is necessary to take into account the basic equation for interference fringes

$$2nd = m\lambda, \qquad (4)$$

where the order number m is integer for maxima and half integer for minima. Moreover, if n_{e1} and n_{e2} are the refractive indices at two adjacent maxima (or minima) at λ_1 and λ_2, it follows that the film thickness is given by the expression

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_{e2} - \lambda_2 n_{e1})}. \qquad (5)$$

The values of d determined by this equation are listed as d_1 in table 1. The last values usually deviate considerably from the other values and must consequently be rejected. The average value of d_1 (ignoring the last two values), $\bar{d}_1$, is 822 nm.This value can now be used, along with n_1, to calculate the "order number" m_0 for the different extremes using eq. (4). The accuracy of d can now be significantly increased by taking the corresponding exact integer or half integer values of m associated to each extreme (see also fig. 1b) and deriving a new thickness, d_2, from eq. (4), again using the values of n_1. The values of d found in this way have a smaller dispersion ($\sigma_1 > \sigma_2$) and the average value of d_2, $\bar{d}_2$, is 799 nm. It should be emphasized that the accuracy of the final thickness is better than 1%. In addition, the film thickness determined by mechanical measurements of the same film area was ≈785 nm. With the exact value of m and the very accurate value of d, eq. (4) can then be solved for n at each λ and, thus, the final values of the refractive index n_2 are obtained (see table 1).

Table 1
Values of s, λ, T_M and T_m for the typical transmission spectrum of fig. 1. Calculation of n and d

s	λ	T_M	T_m	n_1	d_1 (nm)	m_0	m	d_2 (nm)	n_2
1.517	1209	0.922	0.679	2.284	–	3.11	3.0	794	2.270
1.521	1042	0.923	0.675	2.302	–	3.63	3.5	792	2.282
1.509	917	0.923	0.669	2.309	795	4.14	4.0	794	2.295
1.500	823	0.923	0.663	2.320	821	4.63	4.5	798	2.317
1.504	745	0.922	0.657	2.342	800	5.17	5.0	795	2.331
1.499	684	0.922	0.651	2.355	801	5.66	5.5	799	2.354
1.497	633	0.921	0.645	2.373	826	6.11	6.0	800	2.377
1.499	591	0.917	0.636	2.396	818	6.66	6.5	802	2.404
1.497	555	0.907	0.624	2.421	815	7.17	7.0	802	2.431
1.498	524	0.859	0.602	2.416	898	7.58	7.5	813	2.459
1.501	498	0.770	0.520	–	–	–	–	–	–
1.501	468	0.435	0.336	–	–	–	–	–	–

$\bar{d}_1 = 822$ nm; $\sigma_1 = 33$ nm (4.0%); $\bar{d}_2 = 799$ nm; $\sigma_2 = 6$ nm (0.8%)

Furthermore, a simple complementary graphical method for deriving the values of m and d, based on eq. (4), was also used. This expression can be rewritten for that purpose as

$$l/2 = 2dn/\lambda - m_1 \,, \tag{6}$$

where $l=0, 1, 2, \ldots$, and m_1 is the first extreme. Therefore, plotting $l/2$ against n/λ yields a straight line with slope $2d$ and cut-off on the vertical axis of $-m_1$. Fig. 2 displays this plot, in which the values obtained for d and m_1 are 794 nm and 2.99 respectively.

Now, the values of n_2 are fitted by the Wemple–DiDomenico dispersion relationship [13]

$$n^2(E) = 1 + \frac{E_0 E_d}{E_0^2 - E^2} \,, \tag{7}$$

where E_0 is the single-oscillator energy and E_d the dispersion energy. By plotting $(n^2-1)^{-1}$ against E^2 and fitting a straight line as shown in fig. 3, E_0 and E_d can be determined directly from the slope, $(E_0 E_d)^{-1}$, and the intercept, E_0/E_d, on the vertical axis. Thus, $(n^2-1)^{-1} \approx 0.251 - 0.009\ E^2$, the correlation coefficient associated to the least-squares fit being 0.997. The corresponding values of E_0 and E_d, and the dispersion curve derived from the last expression, are shown in fig. 3.

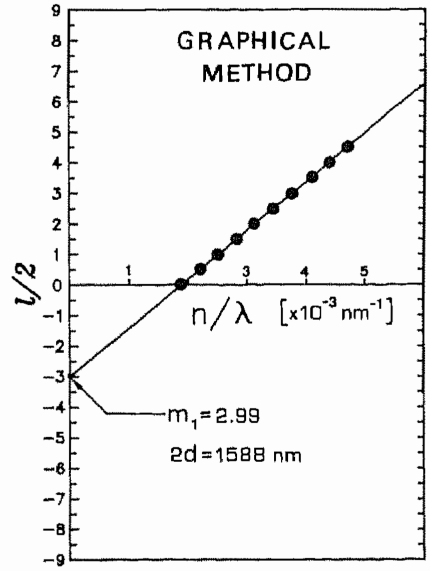

Fig. 2. Plot of $l/2$ versus n/λ to determine the order number and film thickness.

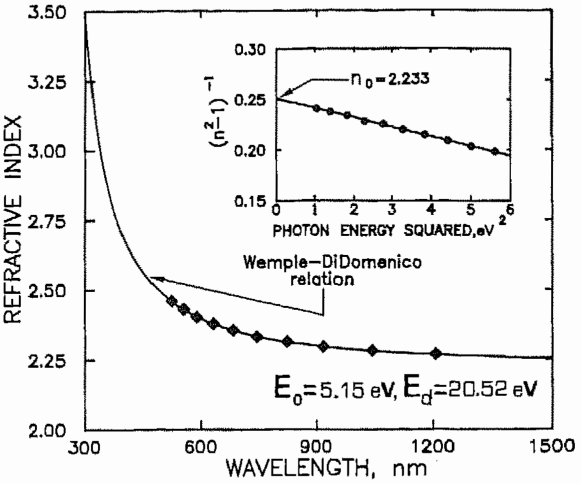

Fig. 3. Refractive index versus wavelength and, in the inset, a plot of the factor $(n^2-1)^{-1}$ versus E^2 (n_0 value is the refractive index extrapolated at $E=0$).

4.2. Determination of the absorption coefficient and optical band gap

Once the values of the refractive index are already known over the whole spectral region from the optical dispersion equation, the absorbance x is calculated in four different ways, which are respectively based on the maximum envelope T_M, on the minimum envelope T_m, on the curve T_i and finally, on the curve T_α. The curves T_i and T_α are displayed in fig. 1b. T_i represents a curve passing through the inflection points of the interference fringes and is obtained from $T_i = T_M T_m/(T_M + T_m)$, whereas T_α is the interference-free transmission and is calculated by $T_\alpha = (T_M T_m)^{1/2}$. For very large values of α, the four curves, T_M, T_m, T_i and T_α, converge to a single curve, such as is seen in fig. 1b. The formulae used in each case are described in the appendix. Once the absorbance x is known, the relation $x = \exp(-\alpha d)$ can be solved for α, $\alpha = -(1/d) \ln x$, and thus, the values of the absorption coefficient are derived. The values of α calculated following all the abovementioned procedures are shown in fig. 4. In the Urbach region ($1\ \mathrm{cm}^{-1} < \approx \alpha < \approx 10^4\ \mathrm{cm}^{-1}$), it can be seen that the α values are smoothly connected, except those which

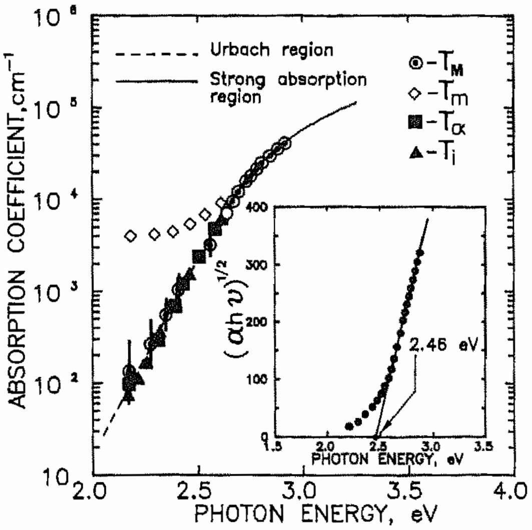

Fig. 4. Optical-absorption edge for the glass composition $As_{35}S_{65}$ and, in the inset, the associated Tauc plot.

have been calculated from T_m; from these results it is deduced that the formulae corresponding to T_m are more sensitive to inaccuracies in the parameters n, s, T_M and T_m, so they must be rejected. Moreover, error bars associated to realistic absolute changes of $T_M \pm 0.01$ and $T_m \pm 0.01$ are also displayed. From fig. 4, it is evident that α can be calculated very accurately from $\approx 10^3$ cm^{-1}, but for α smaller than this value, the accuracy decreases sharply. Additionally, in this spectral region, the absorption coefficient depends exponentially on photon energy according to the Urbach rule [14]

$$\alpha(E) = \alpha_0 \exp(E/K_1) , \tag{8}$$

where K_1 is a slope parameter. If the values of α are fitted to this relation, it is obtained that $K_1 = 0.09 \pm 0.01$.

On the other hand, continuing with the analysis of the optical-absorption edge, in the strong absorption region ($\alpha > \approx 10^4$ cm^{-1}), the results obtained from the four formulae are in excellent agreement. In this region, it should be pointed out that the absorption coefficient of amorphous semiconductors, assuming parabolic band edges and energy-independent matrix elements for interband transitions, is given according to Tauc [15] by the following equation

$$\alpha(E) = K_2 \frac{(E - E_g^{\mathrm{opt}})^2}{E} , \tag{9}$$

where E, E_g^{opt} and K_2 are the photon energy, optical gap and a constant, respectively. This constant K_2 is almost independent of the chemical compositions of the chalcogenide semiconductor films and the average value has been found to be $\approx 5.8 \times 10^5$ eV^{-1} cm^{-1}; most of the K_2 values being within a range of ±10% of this mean value [16,17]. Moreover, the optical gap E_g^{opt} is formally defined as the intercept of the plot of $(\alpha E)^{1/2}$ versus E. In this way, as shown in fig. 4, the values $K_2 = 5.92 \times 10^5$ eV^{-1} cm^{-1} and $E_g^{\mathrm{opt}} = 2.46$ eV are obtained. The value of K_2 is in excellent agreement with the above considerations, whereas the obtained value of the optical band gap agrees with the trend of E_g^{opt} to increase as the sulphur content increases, observed in the As–S glass system (for the glass compositions $As_{40}S_{60}$ and $As_{20}S_{80}$, E_g^{opt} is found to be 2.39 and 2.58 eV respectively [18]). According to Yamaguchi's approach [17], by adding S to the stoichiometric compound $As_{40}S_{60}$, the S–S chemical bonds increase, and as the bond strength of these S–S bonds is higher than those of the As–S and As–As bonds, then the average bond strength of the compound increases and so, the band gap increases also.

5. Concluding remarks

The procedures reported in this paper for calculating the thickness and optical constants of thermally evaporated a-$As_{35}S_{65}$ films have been successfully applied to layers with thicknesses ranging between around 500 and 1500 nm. The accuracy of the obtained results is also proved by comparing the experimental transmission spectrum shown in fig. 1a to the simulated transmission spectrum obtained by substituting the calculated thickness and optical constants in the exact expression for the optical transmission at normal incidence [10] (see fig. 1a). The excellent agreement between both spectra is obviously worth noting, and is a consequence of the remarkably uniform thickness of the film, 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, it should be pointed out that a lack of homogeneity in the composition or of uniformity in the thickness of the films have a large influence on the optical transmission spectrum. If either of these drawbacks is present, the method described loses accuracy and can even lead to serious errors, and therefore cannot be applied. A method which would be adequate in such a case [19] has been applied, by the authors of this work, to the study of Ag-photodoped amorphous As–S films [20], and also to other chalcogenide glass systems [21].

Appendix

Determination of the absorbance x from T_M, T_m, T_i and T_α.

(a):

$$x=\frac{E_M-[E_M^2-(n^2-1)^3(n^2-s^4)]^{1/2}}{(n-1)^3(n-s^2)}, \qquad (A.1)$$

where

$$E_M=8n^2s/T_M+(n^2-1)(n^2-s^2)\,.$$

(b):

$$x=\frac{E_m-[E_m^2-(n^2-1)^3(n^2-s^4)]^{1/2}}{(n-1)^3(n-s^2)}, \qquad (A.2)$$

where

$$E_m=8n^2s/T_m-(n^2-1)(n^2-s^2)\,.$$

(c):

$$x=\frac{F-[F^2-(n^2-1)^3(n^2-s^4)]^{1/2}}{(n-1)^3(n-s^2)}, \qquad (A.3)$$

where

$$F=8n^2s/T_i\,.$$

(d):

$$x=\frac{\{G-[G^2-(n^2-1)^6(n^2-s^4)^2]^{1/2}\}^{1/2}}{(n-1)^3(n-s^2)}, \qquad (A.4)$$

where

$$G=128n^4s^2/T_\alpha^2+n^2(n^2-1)^2(s^2-1)^2 +(n^2-1)^2(n^2-s^2)^2\,.$$

References

[1] J.A. Savage, Infrared optical materials and their antireflection coatings (Hilger, London, 1985).
[2] A.E. Owen, A.P. Firth and P.J.S. Ewen, Phil. Mag. B 52 (1985) 347.
[3] J. Szczyrbowski and A. Czapla, Thin Solid Films 46 (1977) 127.
[4] L. Vriens and W. Rippens, Appl. Opt. 22 (1983) 4105.
[5] R. Swanepoel, J. Phys. E 16 (1983) 1214.
[6] E. Márquez, J. Ramírez-Malo, P. Villares, R. Jiménez-Garay, P.J.S. Ewen and A.E. Owen, J. Phys. D 25 (1992) 535.
[7] M. Hamman, M.A. Harith and W.H. Osman, Solid State Commun. 59 (1986) 271.
[8] K.H. Behrndt, Physics of thin films, eds. G. Hass and R.E. Thun (Academic Press, New York, 1964) p. 46.
[9] K. White, B. Kumar and A.K. Rai, Thin Solid Films 161 (1988) 139.
[10] A. Mini, Thesis, L'Université Scientifique et Médicale de Grenoble, France (1982).
[11] J.C. Manifacier, J. Gasiot and J.P. Fillard, J. Phys. E 9 (1976) 1002.
[12] M. McClain, A. Feldman, D. Kahamer and X. Ying, Computer Phys. 5 (1990) 45.
[13] S.H. Wemple and W. DiDomenico, Phys. Rev. B 3 (1971) 1338.
[14] S.R. Elliott, Physics of amporphous materials (Longman Scientific and Technical, Essex, 1984).
[15] J. Tauc, Amorphous and liquid semiconductors (Plenum Press, New York, 1974).
[16] N.F. Mott and E.A. Davis, Electronic processes in non-crystalline materials (Clarendon Press, Oxford, 1979).
[17] M. Yamaguchi, Phil. Mag. B 51 (1985) 651.
[18] J.B. Ramírez-Malo, E. Márquez, P. Villares and R. Jiménez-Garay, Phys. Stat. Sol. 133a (1982) 499.
[19] R. Swanepoel, J. Phys. E 17 (1984) 896.
[20] E. Márquez, J.B. Ramírez-Malo, J. Fernandez-Peña, R. Jiménez-Garay, P.J.S. Ewen and A.E. Owen, Opt. Mater. 2 (1993) 143.
[21] J.B. Ramírez-Malo, E. Márquez, C. Corrales, P. Villares and R. Jiménez-Garay, to be published.