

Calculation of the thickness and optical constants of amorphous arsenic sulphide films from their transmission spectra

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Abstract. The interference modulated transmission spectra $T(\lambda)$ at normal incidence for amorphous arsenic sulphide semiconducting films deposited by thermal evaporation were obtained in the spectral region from 300 nm up to 2000 nm. The straightforward analysis proposed by Swanepoel, which is based on the use of the extremes of the interference fringes, has been applied in order to derive the real and imaginary parts of the complex index of refraction, and also the film thickness. Thickness measurements made by a surface profiling stylus have also been carried out to cross check the results obtained by the method employing only $T(\lambda)$. In addition, the optical band gap E_g^{opt} has been determined from the absorption coefficient values using Tauc's procedure, i.e. from the relationship $\alpha(h\nu) = K(h\nu - E_g^{opt})^2/h\nu$, where K is a constant. Finally, it is emphasised that accurate results were achieved not only with the above mentioned glass composition As_2S_3 , but also in the case of the non-stoichiometric composition $As_{30}S_{70}$.

1. Introduction

The excellent transmittance of chalcogenide amorphous semiconductors, reaching up to the far-infrared spectral region, and the possibility of a continuous shift of the optical absorption edge, allows their use as absorption filters and other optical elements (Tauc 1974). Because of the high value of the index of refraction of many crystalline materials employed in IR optics, it is necessary to coat their surface suitably with a thin film in order to reduce the corresponding reflectance (Cox *et al* 1961, Cimprl and Kosek 1987). Since by varying the chemical composition, the refractive index of chalcogenide glass systems can be continuously changed from a value of about 2.0 up to 3.5 (Rodney *et al* 1958, Hilton *et al* 1966, Young 1971, Cimprl and Kosek 1986, Minkov *et al* 1987), films of these materials can efficiently be used as anti-reflection coatings.

The refractive index and absorption coefficient are usually calculated by very elaborate computer iteration techniques (e.g. Lyashenko and Miloslavskii 1964,

Wales *et al* 1967, Szczyrbowski and Czapla 1977, Vriens and Rippens 1983), using both optical transmission and reflection spectra. In contrast, a simple straightforward process for determining the optical constants, using only the transmission spectrum, has also been devised (Swanepoel 1983). Using this method, this author calculated the thickness, refractive index and absorption coefficient of amorphous silicon films, attaining 1% accuracy, which is even better than the accuracy achieved by the elaborate iteration procedures. The method using the values of the transmittance alone has also been applied to amorphous arsenic selenide films prepared by thermal evaporation, and this technique has again proved to be easy and accurate (Hamman *et al* 1986).

This paper will check in detail the validity of using the above mentioned simple procedure in determining the optical constants of thermally evaporated thin films of another of the most important chalcogenide amorphous semiconductors, namely arsenic sulphide ($a\text{-As}_2\text{S}_3$), which is commercially available (produced by Servo Corporation of America, under the name Servofrax) and has applications in holography and inte-

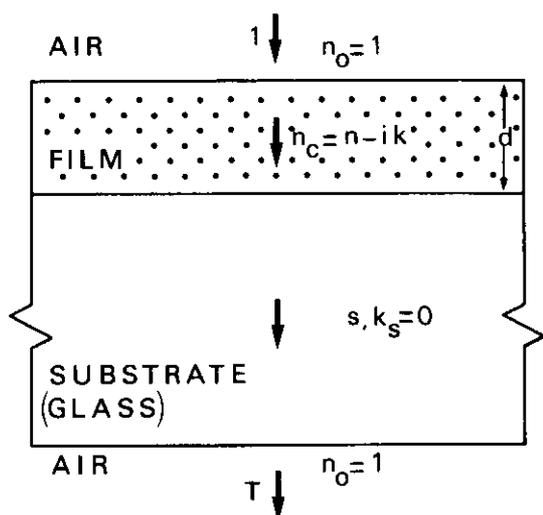


Figure 1. Diagram showing the transmission of light incident *normal* to the surface of a thin homogeneous layer of thickness d , refractive index n and extinction coefficient k upon a transparent substrate (glass microscope slide) of refractive index s .

grated optics (Andriesh *et al* 1986) as well as in the areas referred to above.

2. Experimental details

Thin film samples were prepared by vacuum evaporation of powdered melt-quenched glassy material onto a clean glass substrate. The thermal evaporation process was carried out in a coating system (Edwards, model E306A) at a pressure of $\approx 5 \times 10^{-7}$ Torr from a suitable quartz crucible. During the deposition process, the substrate was kept at approximately room temperature. The evaporation rate was $\approx 5 \text{ \AA s}^{-1}$, and this quantity was continuously measured by a quartz crystal monitor (Edwards, model FTM-5). Such a low deposition rate produces 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. % (Ewen *et al* 1988)). The thickness of the as-deposited a-As₂S₃ films studied ranged mostly between around $0.4 \mu\text{m}$ and $1.2 \mu\text{m}$, although some thicker films were also prepared.

In this work, a surface profiling stylus (Sloan Dektak IIA) was used to determine the thickness of the films for the sake of comparison with the results deduced from the transmission spectra. These spectra were obtained using a double-beam UV-VIS-NIR spectrophotometer with automatic data acquisition by computer (Perkin-Elmer, model Lambda-19), and the wavelength range analysed was from 300 nm up to 2000 nm. The transmission measurements were carried out in various parts of the film, scanning the entire sample, and a good reproducibility of the respective transmission spectra was generally achieved. The spectrophotometer was set with a slit width of 2 nm. It was therefore unnecessary to make slit width correc-

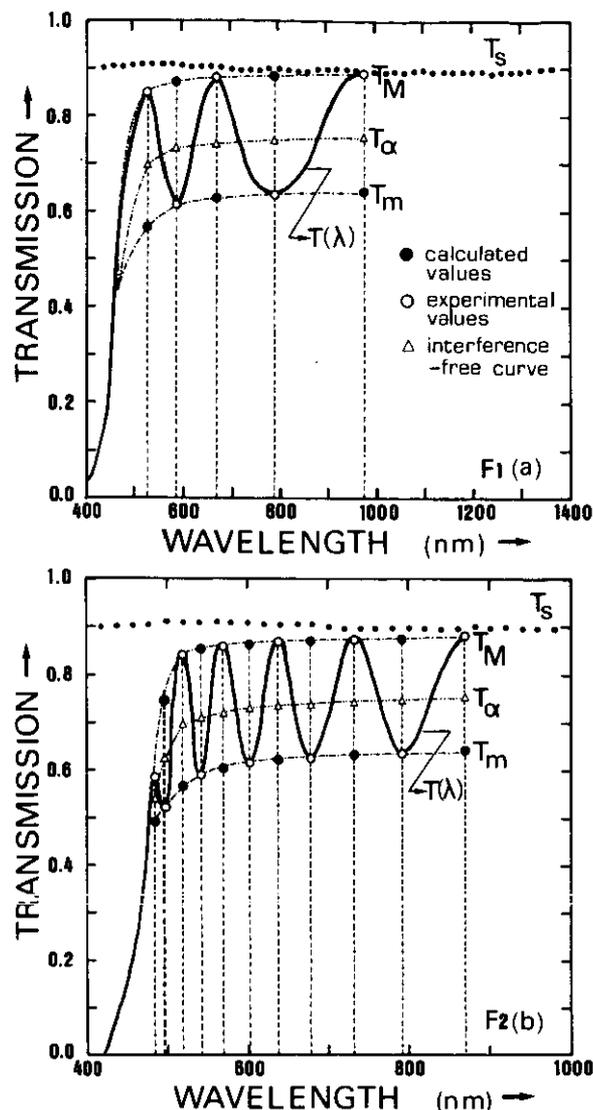


Figure 2. Two typical transmission spectra (full curve) for: (a) 410 nm thick film of a-As₂S₃ on a glass substrate [F1] and (b) 915 nm thick film with the same chemical composition and substrate [F2]. Curves T_M , T_α and T_m according to the text.

tions, since this value of the slit width was much smaller than the different linewidths (Swanepoel 1983). All measurements reported here were performed at room temperature.

3. Preliminary theoretical considerations

The optical system depicted in figure 1 corresponds to the case under consideration, namely a-As₂S₃ thin films evaporated onto thick, finite, transparent substrates. The homogeneous film has 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 index of refraction is s . If the thickness d is constant, interference effects give rise to oscillating curves like those in figure 2, which shows two typical transmission

spectra of two a-As₂S₃ films with different thicknesses. Such interference fringes will be used to determine the optical constants of the films, as described below.

The transmission $T(\lambda, s, n, d, k)$ for the case of the optical system shown in figure 1 is a very complex function (see, for example, Heavens (1955) and Mini (1982)). However, this expression can be simplified significantly by neglecting the extinction coefficient of the film, an approximation that is certainly valid over most of the spectrum (figure 2 shows that the a-As₂S₃ films are reasonably transparent over a wide range of the spectrum). The expression for T then becomes

$$T(\lambda, s, n, d, k)|_{k=0} = \frac{Ax_a}{B - Cx_a \cos \varphi + Dx_a^2} \quad (1)$$

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 $x_a(\lambda)$, the absorbance, is given by the formula $x_a = \exp(-\alpha d)$. Moreover, the values of the transmission at the extremes of the interference fringes can be obtained from equation (1) by setting the interference condition $\cos \varphi_c = +1$ for maxima and $\cos \varphi_c = -1$ for minima. From these two new formulae, many of the equations that provide the basis of the method in use are easily derived (Swanepoel 1983).

4. Results and discussion

4.1. Calculation of the index of refraction and film thickness

According to Swanepoel's method, which is based on the idea of Manificier *et al* (1976) of creating the envelopes of interference maxima and minima (figure 2), 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

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

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 , one being measured and the other calculated. The intermediate values have been derived by a suitable computer program (all the necessary computations in the present study will be carried out through this comprehensive computer program), with parabolic interpolation between the three nearest experimentally determined points, since linear interpolation is clearly not accurate enough. For performing such interpolation, either the mathematical function $y_v(x) = c_1x^2 + c_2x + c_3$ (describing a parabola with vertical symmetry axis) or $y_h(x) = c_1 + (c_2 + c_3x)^{1/2}$ (representing a branch of a parabola of horizontal axis) were used, depending on the extreme positions, in order to be able to construct two smooth envelopes. Further-

more, the refractive index of the substrate at each λ was derived by independently measuring the transmittance of the substrate alone, T_s , and using the well known equation (Jenkins and White 1957)

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

The values of the refractive index n_1 as calculated from equation (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

$$2nd = m\lambda \quad (4)$$

where the order number m is an integer for maxima and half integer for minima. Equation (4) is obviously equivalent to the conditions for deriving the extremes of the transmission curve indicated in section 3. 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

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

The values of d determined by this equation are listed as d_1 in table 1. The last value usually deviates considerably from the other values and must consequently be rejected. The average value of d_1 (ignoring the last value), \bar{d}_1 , corresponding to the two films F1 and F2, is 443 nm for F1 and 953 nm for F2. The value of \bar{d}_1 can now be used, along with n_1 , to calculate the 'order number' m_0 for the different extremes using equation (4). The accuracy of d can now be significantly increased by taking the corresponding exact integer or half integer values of m associated with each extreme point and deriving a new thickness, d_2 from equation (4), again using the values of n_1 . The values of d found in this way have a smaller dispersion and the average value of d_2 , \bar{d}_2 , corresponding to F1 is 410 nm, and for F2 is 915 nm. The accuracy of these two final values of the film thickness is better than 2% for both samples.

With the accurate values of m and d , expression (4) can then be solved for n at each λ and, thus, the final values of the index of refraction n_2 are obtained (these values are listed in table 1). Now, the values of n_2 can be fitted to a reasonable function such as the two-term Cauchy dispersion relationship, $n(\lambda) = a + b/\lambda^2$, which can be used for extrapolation to shorter wavelengths (Moss 1959). The least squares fit of the two sets of values of n_2 listed in table 1, yields $n = 2.303 + 6.909 \times 10^4/\lambda^2$ for F1 and $n = 2.255 + 8.005 \times 10^4/\lambda^2$ for F2, the values of the correlation coefficient r being 0.997 and 0.992, respectively. Continuing with the analysis, in the transparent region of the spectrum, n can be calculated exclusively from T_m (in this spectral

Table 1. Values of λ , T_M and T_m for the two a-As₂S₃ transmission spectra of figure 2; the underlined values of transmittance are the values calculated by suitable parabolic interpolation. The calculated values of refractive index and film thickness are based on the envelope method.

Sample	λ (nm)	T_M	T_m	s	n_1	d_1 (nm)	m_0	m	d_2 (nm)	n_2
F1	975	0.884	<u>0.644</u>	1.606	2.418	—	2.03	2.0	403	2.379
	790	<u>0.882</u>	<u>0.635</u>	1.595	2.434	—	2.53	2.5	406	2.410
	670	0.880	<u>0.624</u>	1.570	2.447	427	2.99	3.0	411	2.452
	587	<u>0.870</u>	<u>0.615</u>	1.559	2.449	458	3.42	3.5	419	2.507
	530	0.850	<u>0.570</u>	—	—	—	—	—	—	—
$\bar{d}_1 = 443 \text{ nm}, \sigma_1 = 23 \text{ nm} (5.1\%); \bar{d}_2 = 410 \text{ nm}, \sigma_2 = 7 \text{ nm} (1.7\%)$										
F2	870	0.879	<u>0.642</u>	1.607	2.418	—	5.29	5.0	900	2.378
	792	<u>0.876</u>	<u>0.635</u>	1.595	2.423	—	5.83	5.5	899	2.381
	733	<u>0.873</u>	<u>0.630</u>	1.585	2.425	945	6.30	6.0	907	2.404
	679	<u>0.869</u>	<u>0.625</u>	1.575	2.428	968	6.81	6.5	909	2.413
	639	0.867	<u>0.620</u>	1.571	2.437	989	7.26	7.0	918	2.445
	603	<u>0.863</u>	<u>0.615</u>	1.563	2.439	1065	7.70	7.5	927	2.472
	570	<u>0.857</u>	<u>0.603</u>	1.554	2.466	974	8.24	8.0	924	2.493
	543	<u>0.851</u>	<u>0.590</u>	1.554	2.502	890	8.78	8.5	922	2.523
	520	<u>0.839</u>	<u>0.576</u>	1.554	2.533	919	9.28	9.0	924	2.558
	498	<u>0.745</u>	<u>0.520</u>	1.554	2.580	871	9.87	9.5	917	2.586
	487	0.585	<u>0.495</u>	—	—	—	—	—	—	—
	$\bar{d}_1 = 953 \text{ nm}, \sigma_1 = 62 \text{ nm} (6.5\%); \bar{d}_2 = 915 \text{ nm}, \sigma_2 = 10 \text{ nm} (1.1\%)$									

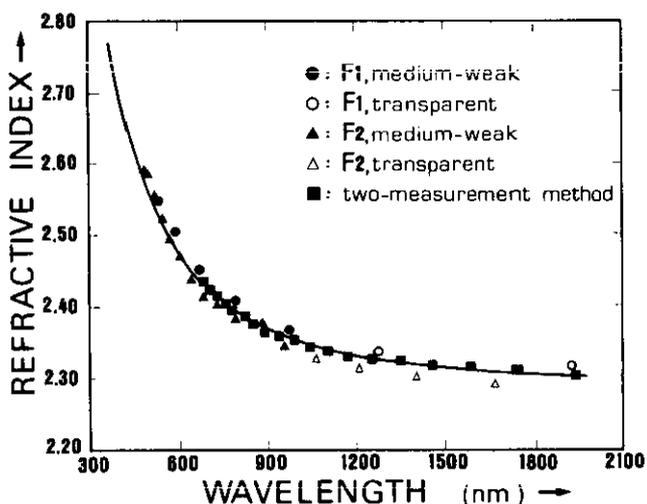


Figure 3. Refractive index of thermally evaporated vitreous As₂S₃ against wavelength at room temperature. The curve corresponding to the n values obtained by the two independent measurement method is also displayed (see text).

region $\alpha = 0$ or $x_a = 1$ and, therefore, $T_M = T_s = 2s/(s^2 + 1)$ using the following equation

$$n = [N_2 + (N_2^2 - s^2)^{1/2}]^{1/2} \tag{6}$$

where

$$N_2 = \frac{2s}{T_m} - \frac{s^2 + 1}{2}$$

The refractive index as obtained from this equation, for the samples F1 and F2, is plotted in figure 3, which also shows the preceding values of the index of refraction

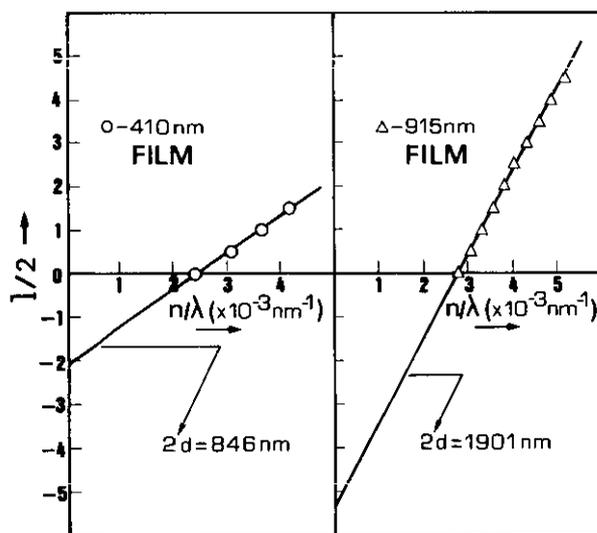


Figure 4. Plot of $l/2$ against n/λ to calculate the order number and film thickness for the samples F1 and F2.

in the spectral region of medium and weak absorption for both samples.

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

$$l/2 = 2d(n/\lambda) - m_1 \tag{7}$$

where $l = 0, 1, 2, \dots$ 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 y axis of $-m_1$. Figure 4 displays this graph for the two samples F1 and F2. From this plot the values of m_1 have been obtained,

being 2.06 for F1 and 5.28 for F2 (the values of r were 0.998 and 0.991, respectively). The values of d deduced from the two slopes are 423 nm and 950 nm, respectively, which are quite close to those corresponding to \bar{d}_2 . This graphical procedure is certainly very advantageous: in principle only the values of λ and n of two extremes are necessary to calculate the order number m and the film thickness, d .

On the other hand, an alternative conventional method for determining the refractive index of thin films (e.g. Wales *et al* 1967, Young 1971), which requires the wavelength positions of the interference maxima in the transmission spectrum and the independent measurement of the film thickness (in this work, as pointed out previously, by a surface profiling stylus), has been used in order to cross check the preceding results. The index of refraction was derived from the interference condition expressed by equation (4). The measurements were initially made on some films thin enough for the values of m to be assigned unambiguously, and these values of n were then used to obtain the appropriate m values for thicker films. The uncertainty in the value of λ at each maximum is so much smaller than the relative error in the measured thickness, which is estimated at $\pm 2\%$ by the manufacturer, that the relative error in n may be taken equal to the relative error in d , i.e. $|\delta n|/n = |\delta d|/d$. Figure 3 shows the calculated refractive index as a function of the wavelength for a film whose thickness is 3674 nm. The least squares fit of these new n values to the truncated Cauchy dispersion formula yields $a = 2.283$ and $b = 6.834 \times 10^4 \text{ nm}^2$ ($r = 0.997$). It should be emphasised that the values of n_2 in table 1, along with the data on the refractive index in the transparent region of the spectrum, are found to be in excellent agreement with those determined by the alternative cross checking procedure (it is verified that $|n_2 - n^*|/n^* \leq 1.3\%$, over the whole spectrum, where n^* represents the n value derived by the two independent measurement techniques). Alternatively, the film thicknesses measured directly by the mechanical profilometer method are usually very close to those calculated by the procedure of the envelope curves; for instance, for the samples F1 and F2 the measured values were 424 nm and 925 nm, respectively, the differences with the corresponding \bar{d}_2 values being 3.3% and 1.1%, respectively.

Interestingly, it was observed that the film of thickness $\approx 3.7 \mu\text{m}$ had a wedge-shaped profile and its interference pattern shrank considerably; nevertheless the wavelength positions of the extremes of the transmission curve remained unchanged. Also, when the procedure presented above for films of uniform thickness was used for this particular sample the values of the refractive index surprisingly decreased with decreasing λ . In the literature (Swanepoel 1984) a method has been proposed to solve this relatively common problem, based on finding the unique solution of two independent transcendental equations associated with T_M and T_m , respectively. Application of this procedure making use of the Newton-Raphson iteration

technique is currently underway. From this study, it will be possible to obtain not only the correct values of the refractive index, but also the actual variation in thickness from the average value.

4.2. Determination of the extinction coefficient and optical band gap

Since the values of the refractive index are already known from the Cauchy dispersion equation, the absorbance $x_a(\lambda)$ can be calculated from the interference-free transmission curve T_α (see figure 2), using the well known equation, often used in optical and infrared studies, proposed by Connell and Lewis (1973)

$$x_a = \{P + [P^2 + 2QT_\alpha(1 - R_2R_3)]^{1/2}\}/Q \quad (8)$$

where

$$P = (R_1 - 1)(R_2 - 1)(R_3 - 1)$$

and

$$Q = 2T_\alpha(R_1R_2 + R_1R_3 - 2R_1R_2R_3)$$

and R_1 , R_2 and R_3 , the reflectances of the air-film, film-substrate and substrate-air interfaces: $R_1 = [(1 - n)/(1 + n)]^2$, $R_2 = [(n - s)/(n + s)]^2$ and $R_3 = [(s - 1)/(s + 1)]^2$, respectively. For $\alpha \leq 10^5 \text{ cm}^{-1}$, the imaginary part of the complex index of refraction is much less than n , so that the previous expressions to calculate the reflectance are valid. In the spectral region with interference fringes, T_α is the geometric mean of T_M and T_m (Swanepoel 1983), i.e. $T_\alpha = (T_M T_m)^{1/2}$ —in the region of strong absorption the interference fringes disappear, in other words, for very large α the three curves T_M , T_α and T_m converge to a single curve. Moreover, since d is also known, the relation $x_a = \exp(-\alpha d)$ can then be solved for α , $\alpha = -(1/d) \ln x_a$, and thus, the values of the absorption coefficient are derived. The values of α at some extremes of the spectra of F1 and F2, as well as those of the interference-free strong absorption region, are shown in figure 5. The sensitivity of the formulae given for deriving α from the curve T_α to inaccuracies in the experimental parameters s , n , T_M and T_m has been examined, and from this analysis it is deduced that α is more sensitive to the errors in T_m (a realistic absolute change of T_m of ± 0.01 or 1% has been taken). Figure 5 displays the error associated with each value of α . In view of these results, it is evident that α can be calculated accurately from $\sim 10^3 \text{ cm}^{-1}$, but for α smaller than this value, the accuracy decreases sharply. Next, in order to complete the calculation of the optical constants, the extinction coefficient is estimated from the values of α and λ using the already mentioned formula $k = \alpha\lambda/4\pi$; figure 6 illustrates the dependence of k on wavelength for both films (the optical absorption edge corresponding to these two a-As₂S₃ films can clearly be seen).

Finally, the optical band gap will be found from the calculated values of α . To that end, it should be pointed out that the absorption coefficient of amorphous

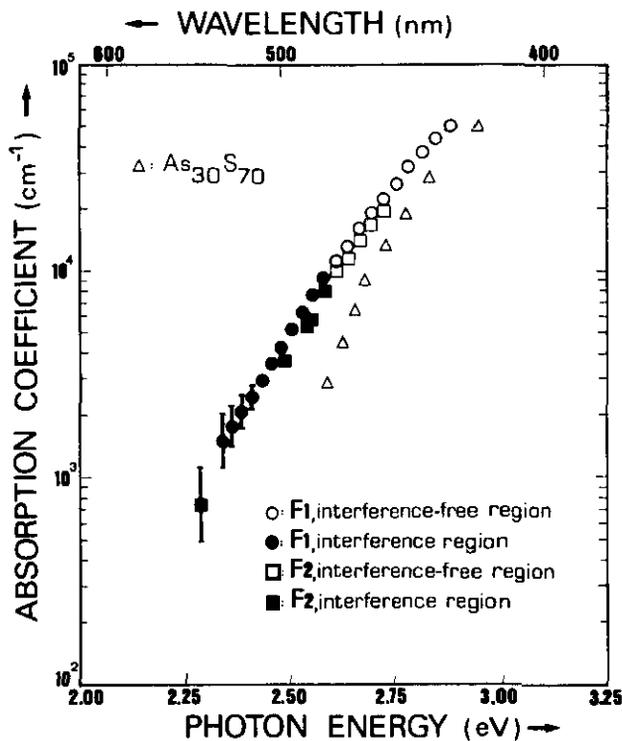


Figure 5. The optical absorption coefficients α in a-As₂S₃ thin films at room temperature as a function of photon energy $h\nu$, for both samples F1 and F2. Additionally, the average values of α for a-As₃₀S₇₀ films are displayed.

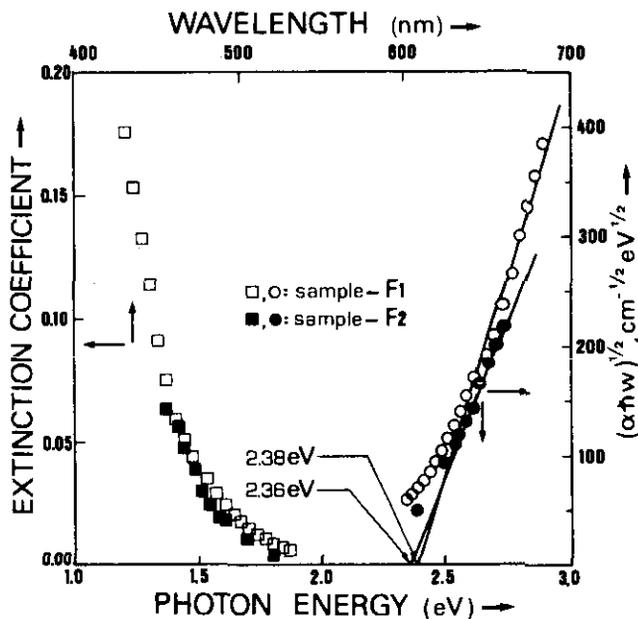


Figure 6. The extinction coefficient k against wavelength λ for the two films F1 and F2. Furthermore, the dependence of $(\alpha h\nu)^{1/2}$ on photon energy $h\nu$ in a-As₂S₃ films from which the optical band gap E_g^{opt} is estimated (Tauc's extrapolation).

transitions, is given according to Tauc (1974) by the following equation

$$\alpha(h\nu) = K(h\nu - E_g^{opt})^2/h\nu. \quad (9)$$

Here $h\nu$, E_g^{opt} and K denote the photon energy, optical gap and a constant, respectively. This constant K is almost independent of the chemical compositions of the chalcogenide semiconductor films and the average value has been found to be $\approx 5.8 \times 10^5 \text{ eV}^{-1} \text{ cm}^{-1}$, most of the K values being within a range of $\pm 10\%$ of this mean value (Mott and Davis 1979, Yamaguchi 1985). A clear result of this quasi-constancy is that, in accordance with equation (9), α decreases with increasing E_g^{opt} for each particular photon energy. On the other hand, the optical gap E_g^{opt} is formally defined as the intercept of the plot of $(\alpha h\nu)^{1/2}$ against $h\nu$. Figure 6 shows these plots for samples F1 and F2 and also the optical band gap derived for each film, 2.38 eV for F1 and 2.36 eV for F2; the values of the correlation coefficient were 0.990 and 0.98, respectively. The estimated values of E_g^{opt} of these a-As₂S₃ films are in excellent agreement with those published in the literature, around 2.36 eV (Zallen *et al* 1971, Tauc 1974, Yamaguchi 1985). In addition, the values of K for the two samples were found to be $5.44 \times 10^5 \text{ eV}^{-1} \text{ cm}^{-1}$ and $5.25 \times 10^5 \text{ eV}^{-1} \text{ cm}^{-1}$, respectively, which agree fairly well with the above mentioned value of K .

5. Concluding remarks

The procedure reported in this paper for calculating the thickness and optical constants of thermally evaporated a-As₂S₃ films has successfully been applied not only to films with $d > 0.8 \mu\text{m}$, with a reasonable number of interference fringes, but also to films with $d \sim 0.4 \mu\text{m}$, which have only a few fringes. The correctness of employing the presented method with a non-stoichiometric composition of the As-S glass system, i.e. As₃₀S₇₀, has also been checked. This last composition is of great interest as far as the metal photodissolution effect in chalcogenide glass films is concerned, because of its high silver photoreaction rate (Ewen *et al* 1988, Márquez *et al* 1991). Furthermore, regarding its optical properties, a large increase of n takes place when this glass composition is very heavily photodoped ($\Delta n > 0.5$ over a wide wavelength range for a Ag photodoping level of nearly 27 at.%). This feature, along with the high transmittance in the IR region of both undoped and photodoped films (the values of T_α being approximately 0.85 and 0.80, respectively), makes the material suitable for IR grating fabrication (Zakery *et al* 1988, Ewen *et al* 1991). It should be stressed that the results of using the envelope method with these a-As₃₀S₇₀ films showed the same accuracy as in the case of the composition As₂S₃ and, as is known (Tanaka and Ohtsuka 1979, Yamaguchi 1985), it was found that in the wavelength range studied the refractive index and absorption coefficient of the more S-rich composition are both lower. The

ous semiconductors, in the high-absorption region ($\alpha \geq 10^4 \text{ cm}^{-1}$), assuming parabolic band edges and energy-independent matrix elements for interband

average values of the Cauchy coefficients for this glass composition are $a = 2.214$ and $b = 5.776 \times 10^4 \text{ nm}^2$ and the average values of the absorption coefficient are plotted in figure 5. Moreover, the optical band gap obtained by Tauc's procedure is slightly higher, 2.49 eV, while the value of K is $5.96 \times 10^5 \text{ eV}^{-1} \text{ cm}^{-1}$, again being well inside the limits for K .

To summarize, the new appealing technique proposed by Swanepoel for using the optical transmission spectrum only to derive d , $n(\lambda)$ and $k(\lambda)$ has proved to be highly useful and accurate in the case of our amorphous As-S semiconducting thin films as long as they have uniform thickness.

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