Influence of substrate absorption on the optical and geometrical characterization of thin dielectric films

Juan-María González-Leal, Rafael Prieto-Alcón, José-Andrés Angel, Dorian A. Minkov, and Emilio Márquez

The role played by a glass substrate on the accurate determination of the optical constants and the thickness of a thin dielectric film deposited on it, when well-known envelope methods are used, is discussed. Analytical expressions for the two envelopes of the optical transmission spectra corresponding to films with both uniform and nonuniform thicknesses are derived, assuming the substrate to be a weakly absorbing layer. It is shown that accurate determination of the refractive index and the film thickness is notably improved when the absorption of the substrate is considered. The analytical expressions for the upper and lower envelopes are used to characterize optically and geometrically both uniform and nonuniform amorphous chalcogenide films. The results obtained are compared with those derived by use of expressions for the envelopes that neglect the substrate absorption. The comparison shows that overestimated refractive indexes and underestimated thicknesses are obtained when the conventional approach, in which the substrate absorption is neglected, is used. © 2002 Optical Society of America

OCIS code: 310.6860, 120.4530.

1. Introduction

Accurate determination of the optical constants of thin-film materials is a key factor in some technological applications.[1–5] Optical characterization methods based on the ideas of Manifacier *et al.*[6] of using the envelopes of the transmission spectra (or reflection spectra or both), instead of purely the spectra, have shown to be a useful, nondestructive tool for determining the optical constants and the thickness of thin dielectric films deposited onto thick glass substrates.[7–15] These methods assume that the glass substrate is transparent. However, some of the most popular commercial glass substrates used by researchers, namely, fused silica and, mainly, borosilicate microscope slides, show significant losses in the optical spectral region (see Fig. 1). It is worth mentioning that a method, based on the envelopes of the reflection spectrum, that takes into account the absorption in the substrates has already been developed for the optical characterization of thin dielectric films deposited onto Si wafers,[16] but we are not dealing with that in this paper.

The aim of the present paper is to derive analytical expressions for the transmission spectrum and its envelopes, taken at normal incidence of irradiation, for thin dielectric films with both uniform and nonuniform thicknesses, deposited onto a weakly absorbing substrate. Optical and geometrical characterization of amorphous $As_{40}S_{60}$ chalcogenide films with both uniform and nonuniform thicknesses, deposited on glass substrates, is performed, taking into account substrate absorption. The results are compared with those obtained by use of the traditional analytical expressions for the envelopes of the transmission spectrum, in which the substrate absorption is neglected.[7,8] It is shown that the accuracy in the calculation of both the refractive index and the thickness of the films is notably improved when the substrate absorption is taken into account.

2. Analysis of the Transmission and the Reflection of Substrates

Optical characterization methods based on the envelopes of the transmission or reflection spectra or both

J. M. González-Leal (jmg62@cam.ac.uk) is with the Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW, Cambridge, United Kingdom. R. Prieto-Alcón, J. A. Angel, and E. Márquez are with the Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain. D. A. Minkov is with the Fracture Research Institute, Department of Mechanical Engineering, Tohoku University, Aoba-ku, Sendai 980-8579, Japan.

Received 18 March 2002.
0003-6935/02/347300-09$15.00/0

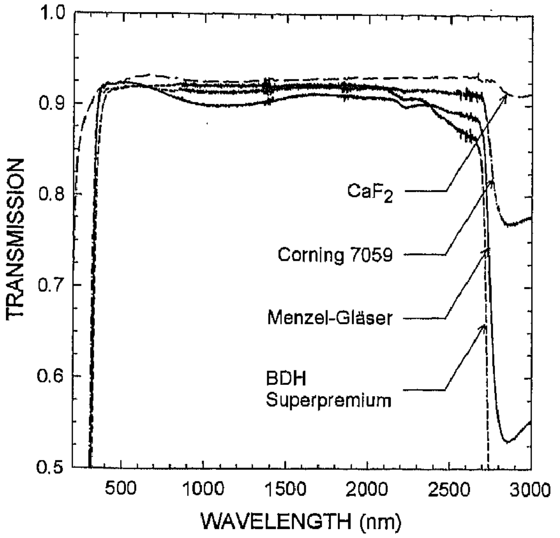

Fig. 1. Optical transmission spectra taken at normal incidence for some of the most popular borosilicate glass substrates used for thin-film optical studies. The transmission spectrum corresponding to a CaF_2 substrate is shown for comparison.

systematically assume that the refractive index of the substrate, s, is a known parameter and the extinction coefficient, k_s, equals zero.[7–15] The refractive index is usually considered to be constant (typically, 1.51) over the whole optical range, or it is independently derived from only either the transmission or the reflection spectrum of the substrate, taken at normal incidence. We will show in this paper, however, that although these approaches are useful in practice, they are certainly not accurate, or valid, for every glass substrate.

For any wavelength of the incident radiation, λ, in the spectral range from ultraviolet (UV) to near infrared (NIR), it is possible to obtain the optical constants of the substrate, s and k_s, from transmittance, T_s, and reflectance, R_s, measurements, taken at normal incidence. According to Ref. 17, when $s \gg k_s$, the transmittance T_{sm} of a substrate with perfectly flat and strictly parallel surfaces illuminated by monochromatic radiation is expressed as follows:

$$T_{sm} = \frac{(1 - R_1)^2 x_s}{1 + R_1^2 x_s^2 - 2R_1 x_s \cos(\phi)}, \qquad (1)$$

where $x_s = \exp(-\alpha_s t_s)$ is the optical absorbance, $\alpha_s = 4\pi k_s/\lambda$ is the absorption coefficient, t_s is the thickness of the substrate, $\phi = 4\pi s t_s/\lambda_m$ is the phase of the monochromatic light, λ_m is the wavelength of the monochromatic radiation, and $R_1 = |1 - s + ik_s|^2/|1 + s - ik_s|^2 = [(1 - s)^2 + k_s^2]/[(1 + s)^2 + k_s^2]$ is the Fresnel reflection factor for the air–substrate interface.

However, the spectrophotometer radiation is not perfectly monochromatic, having, instead, an energetic distribution with a spectral half-width $\Delta\lambda$ (typically, ~1 nm), around the mean wavelength λ. It can be easily verified from the above equation for the phase ϕ that the distance between two neighboring extrema (i.e., between two consecutive maxima and minima) of the transmission spectrum of the substrate is $\Delta\lambda_e = \lambda^2/(4st_s)$. Thus, for a typical substrate with thickness $t_s \sim 1$ mm, $\Delta\lambda_e < 1$ nm and $\Delta\lambda > \Delta\lambda_e$, which means that the spectrophotometer cannot resolve the interference fringes of the spectrum. This lack of interference resolution is mathematically performed as an integration of T_{sm} over ϕ, and therefore the transmittance of the substrate, measured by the spectrophotometer, is

$$T_s = \frac{1}{2\pi}\int_0^{2\pi} T_{sm} d\phi = \frac{(1 - R_1)^2 x_s}{1 - R_1^2 x_s^2}. \qquad (2)$$

Similarly, the measured reflectance of the substrate is

$$R_s = \frac{R_1[1 + (1 - 2R_1)x_s^2]}{1 - R_1^2 x_s^2}. \qquad (3)$$

The above expressions for T_s and R_s are also valid for substrates whose surfaces are not perfectly flat because surface imperfections would be introduced mathematically in the equations for T_s and R_s by additional integration of T_{sm} and R_{sm} with respect to ϕ, which gives, respectively, Eqs. (2) and (3) once again.

It is seen from Eqs. (2) and (3) that the exponential terms, x_s, dominate the attenuation of the transmission and the reflection, and, in the case of weakly absorbing substrates, it is plausible to neglect k_s with respect to s in the Fresnel reflection factor, R_1, and therefore preserve only the term x_s in Eqs. (2) and (3). It should be mentioned that, in the case of thinner glass substrates, it is possible to observe interference fringes at large wavelengths because $\Delta\lambda \sim \Delta\lambda_e$ and these fringes disappear when the wavelength decreases. This effect introduces a difficulty in the use of the averaged Eqs. (2) and (3). However, this problem can be solved by an increase in $\Delta\lambda$, so that the detector performs the averaging process over a larger spectral range, and the interference fringes disappear.

The values of the refractive index, s, and the optical absorbance, x_s, can therefore be obtained for every wavelength, λ, over the whole spectral range by solution of the following system of equations:

$$\begin{aligned} T_s(\lambda) - T_s(\lambda; s, x_s) &= 0, \\ R_s(\lambda) - R_s(\lambda; s, x_s) &= 0, \end{aligned} \qquad (4)$$

where $T_s(\lambda)$ and $R_s(\lambda)$ are measured values and $T_s(\lambda; s, x_s)$ and $R_s(\lambda; s, x_s)$ are their corresponding analytical expressions. As mentioned before, it has been traditionally assumed that the substrates are transparent, i.e., $x_s = 1$. In such a case, the refractive index of the substrate could be independently obtained from the transmission or reflection spectrum by use of, respectively, the following well-known equations:

$$T_s = \frac{2s}{1 + s^2}, \qquad (5)$$

$$R_s = \frac{(1 - s)^2}{1 + s^2}. \qquad (6)$$

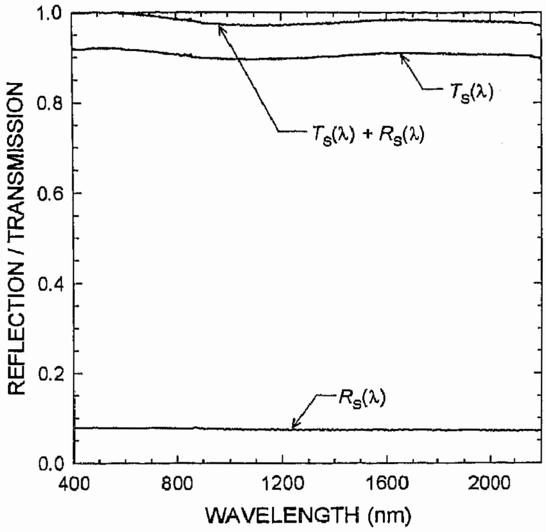

Fig. 2. Optical transmission and reflection spectra taken at normal incidence, $T_s(\lambda)$ and $R_s(\lambda)$, respectively, for a representative BDH glass substrate. The $T_s(\lambda) + R_s(\lambda)$ curve clearly shows significant losses in the spectral range of interest, i.e., $T_s(\lambda) + R_s(\lambda) < 1$.

Equations (5) and (6) suggest that the relationship, $T_s + R_s = 1$, should be verified for every wavelength. However, Fig. 2 shows that, within experimental error, this relationship is not strictly valid for every wavelength, i.e., $T_s(\lambda) + R_s(\lambda) < 1$. It is also observed that, unlike the reflectance, the transmittance is not constant over the spectral range of interest, which is due to the fact that the substrate is not completely transparent, and therefore the transmitted radiation undergoes a notable attenuation. Furthermore, it can be easily verified that different values for s are obtained from the transmission and the reflection spectra shown in Fig. 2, by use of, respectively, Eqs. (5) and (6). In particular, overestimated values of s are calculated from the transmission spectrum.

3. Assumptions and Formulation

The formulation presented in this paper is based on the following assumptions:

(i) A thin isotropic dielectric layer covers a thick, weakly absorbing substrate, and this optical system is immersed in air.

(ii) Radiation, of mean wavelength λ and spectral half-width $\Delta\lambda$, is incident normally on the sample.

(iii) Interference of internally reflected radiation occurs in the thin film [$\Delta\lambda \ll \lambda^2/(2nt)$] and is negligible in the substrate [$\Delta\lambda \gg \lambda^2/(2st_s)$], where n and t are the refractive index and the thickness of the film, respectively.

(iv) The refractive index of the film is larger than the refractive index of the substrate, i.e., $n > s$.

(v) The film and the substrate are weakly absorbing in the studied spectral region, i.e., $n^2 > s^2 \gg k^2$ and $s^2 \gg {k_s}^2$, where k is the extinction coefficient of the film.

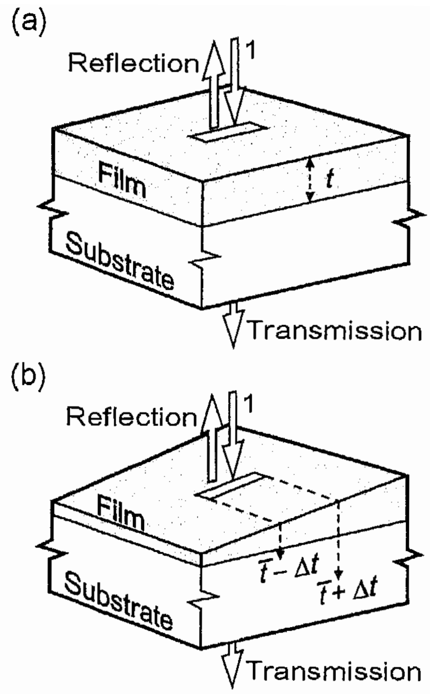

Fig. 3. Sketches of the two studied optical systems: (a) a uniform thin film with constant thickness, t, on a thick substrate and (b) a nonuniform wedge-shaped thin film that is geometrically characterized by its average thickness, $\bar{t}$, and thickness variation, Δt, over the illuminated area (white rectangle) on a thick substrate.

It has been shown[9] that, when the above assumptions are satisfied and the thickness of the dielectric film is uniform, the transmittance of such a two-layer optical system [see Fig. 3(a)] can be expressed as follows:

$$T(\lambda; n, x, t, s, x_s) = A/B, \quad (7)$$

where

$$A = (1 - R_1)(1 - R_2)(1 - R_3)xx_s,$$
$$B = 1 + R_1R_2x^2 - R_1R_3x^2{x_s}^2 - R_2R_3{x_s}^2 + 2r_1r_2(1 - R_3{x_s}^2)x \cos(\varphi),$$
$$R_1 = {r_1}^2, \quad R_2 = {r_2}^2, \quad R_3 = {r_3}^2,$$
$$r_1 = \frac{1-n}{1+n}, \quad r_2 = \frac{n-s}{n+s}, \quad r_3 = \frac{s-1}{s+1},$$
$$\alpha = 4\pi k/\lambda, \quad x = \exp(-\alpha t),$$
$$\alpha_s = 4\pi k_s/\lambda, \quad x_s = \exp(-\alpha_s t_s),$$
$$\varphi = 4\pi nt/\lambda.$$

The mathematical expressions for the upper and lower envelopes, T_+ and T_-, respectively, can be easily derived from Eq. (7) by substitution of $\cos(\varphi) = \pm 1$. Correspondingly,

$$T_\pm(\lambda; n, x, s, x_s) = A/B_\pm, \quad (8)$$

where the auxiliary variable B is rewritten as

$$B_{\pm} = 1 + R_1R_2x^2 - R_1R_3x^2x_s^2 - R_2R_3x_s^2 \pm 2r_1r_2(1 - R_3x_s^2)x.$$

A formula for the transmittance of this optical system, when the dielectric film has a nonuniform thickness, can be derived from Eq. (7). In particular, if the thickness varies linearly over the film surface, this thickness can be considered to change within the interval $[\bar{t} - \Delta t, \bar{t} + \Delta t]$ over the illuminated area, as shown in Fig. 3(b). In such a case, the film thickness is characterized by the average thickness, $\bar{t}$, and the wedging parameter, Δt. The transmission spectrum has to be measured in such a way that the same area is illuminated at all wavelengths, in which case Δt can be considered to be independent of the wavelength. It is important to note that, as stated in Ref. 8, the present formulation is also valid when some irregularities occur periodically over the illuminated area, in the form of surface roughness. Hence the analytical expression for the transmittance of the optical system under consideration is obtained by integration of Eq. (7) over t. However, this is prohibitively difficult analytically because x depends on t. An acceptable approximation is to consider x to equal its average value over the range of integration with respect to t, $[\bar{t} - \Delta t, \bar{t} + \Delta t]$. This approximation is an excellent one, provided that $\Delta t \ll \bar{t}$. The optical absorbance x is then redefined as $x = \exp(-\alpha\bar{t})$, and the integration of Eq. (7) with respect to t (or, equivalently, φ),

$$T_{\Delta t} \approx \frac{1}{\varphi_2 - \varphi_1}\int_{\varphi_1}^{\varphi_2} T\mathrm{d}\varphi, \tag{9}$$

with integration boundaries $\varphi_1 = 4\pi n\,(\bar{t} - \Delta t)/\lambda$ and $\varphi_2 = 4\pi n\,(\bar{t} + \Delta t)/\lambda$, gives the following analytical expression for the transmittance:

$$T_{\Delta}(\lambda;\, n,\, x,\, \bar{t},\, \Delta t,\, s,\, x_s) = \frac{1}{2\theta}\frac{A}{(C^2 - D^2)^{1/2}} \times \left\{\tan^{-1}\left[\frac{C + D}{(C^2 - D^2)^{1/2}}\tan\frac{\varphi_2}{2}\right] - \tan^{-1}\left[\frac{C + D}{(C^2 - D^2)^{1/2}}\tan\frac{\varphi_1}{2}\right]\right\}, \tag{10}$$

where

$$C = 1 + R_1R_2x^2 - R_1R_3x^2x_s^2 + R_1R_2R_3x_s^2,$$
$$D = -2r_1r_2(1 - R_3x_s^2)x,$$
$$\theta = 2\pi n\Delta t/\lambda.$$

Equation (10) exhibits discontinuities around the minima of the transmission spectrum that are due to the $\tan^{-1}[\ldots\tan[\ldots]]$ functions. Nevertheless, these discontinuities can be avoided to obtain the mathematical expressions of the envelopes, which are the basis of this type of characterization method. Taking into account that the tangent points $\lambda_{\tan}$ between the transmission spectrum and its two envelopes are characterized by the dependence[7,8]

$$2n\bar{t} = m\lambda_{\tan}, \tag{11}$$

where the order number m is an integer for $\lambda_{\tan}$ from the upper envelope of the transmission spectrum, $T_{\Delta+}$, and a half-integer for $\lambda_{\tan}$ from the lower envelope, $T_{\Delta-}$, the following analytical expressions for the upper and lower envelopes are obtained:

$$T_{\Delta\pm}(\lambda;\, n,\, x,\, \Delta t,\, s,\, x_s) = \frac{1}{\theta}\frac{A}{(C^2 - D^2)^{1/2}} \times \tan^{-1}\left[\frac{C \pm D}{(C^2 - D^2)^{1/2}}\tan\theta\right] \tag{12}$$

The formulas collected in Eqs. (8) and (12) are, respectively, primary sources for the optical and geometrical characterization of thin dielectric films with uniform and nonuniform thicknesses, deposited on weakly absorbing glass substrates. Both systems of equations can be expressed in the following implicit form:

$$T_+(\lambda) - T_+(\lambda;\, n,\, x) = 0,$$
$$T_-(\lambda) - T_-(\lambda;\, n,\, x) = 0 \tag{13}$$

for uniform thin films and

$$T_{\Delta+}(\lambda) - T_{\Delta+}(\lambda;\, n,\, x,\, \Delta t) = 0,$$
$$T_{\Delta-}(\lambda) - T_{\Delta-}(\lambda;\, n,\, x,\, \Delta t) = 0 \tag{14}$$

for nonuniform thin films.

The system of Eqs. (13) can be solved analytically for n and x for every wavelength λ, from the spectral region of medium absorption to transparency. Nevertheless, a better approach is to limit the set of wavelength values to those to which the optical transmission spectrum and its envelopes are tangential, $\lambda_{\tan}$. This approach allows the use of Eq. (11) to improve the accuracy of the results for the refractive index, as well as to determine the film thickness. However, the system of the two transcendental Eqs. (14) cannot be solved as expressed, and it would need, obviously, one further equation in order to be solved. Thus the present method requires that the thin dielectric film be transparent in some part of the spectral region of interest in which it is possible to consider $x = 1$ (more details will be given in Section 4). It is also important to note that, in the case of nonuniform thin dielectric films, the range of validity of the system of transcendental Eqs. (14) is $0 < \Delta t < \lambda/4n$. The reason for the upper limit in the wedging parameter is the presence of new discontinuities in the expressions for the top and bottom envelopes. Above this limit, i.e., $\Delta t \geq \lambda/4n$, both envelopes would intersect and therefore $T_{\Delta+} \leq T_{\Delta-}$.[13] Finally, it is interesting to point out that the method presented here is also valid for $n < s$. In such a case, the labels of upper and lower are switched around.

4. Optical Characterization of Thin Dielectric Films Taking into Account the Substrate Absorption

To illustrate the validity of the mathematical expressions, as well as the accuracy achieved in the determination of the optical constants and the thickness of thin dielectric films, we used the present envelope method to characterize, optically and geometrically, two thin amorphous chalcogenide real films. The first one is an amorphous $As_{40}S_{60}$ thin film deposited by thermal evaporation by use of a planetary rotary system, which makes it possible to obtain films of outstanding uniform thickness; i.e., to a good approximation, it can be assumed that the film has a constant thickness.[18,19] The second one is an amorphous thin film, with the same chemical composition, prepared by plasma-enhanced chemical vapor deposition, which is nonuniform, and its thickness varies along the surface of the film.[20] All the details about the preparation of these kinds of amorphous film by use of these deposition techniques are given in the above references. Both of these films have been deposited onto similar 1-mm-thick borosilicate glass substrates (BDH Superpremium). The transmission and reflection spectra corresponding to this kind of glass substrate are shown in Fig. 2. All the spectra shown in this paper were obtained, at normal incidence, by a double-beam UV/visible/NIR spectrophotometer (PerkinElmer, Model Lambda-19). The experimental reflection spectrum of the substrate was measured by use of two identical specular reflectance accessories; the conventional protocol for these reflectance measurements was followed. Values of the refractive index, s, and the absorbance, x_s, of the uncoated substrate, for every wavelength in the spectral range of interest, are obtained from the transmission and the reflection spectra, by solution of the system of Eqs. (4). The transmission spectra of the uniform and the nonuniform films analyzed are shown in Figs. 4(a) and 4(b), respectively, along with the transmission spectrum of the bare substrate. The shrinking in the amplitude of the interference fringes for the spectrum shown in Fig. 4(b) is a clear indication of the lack of thickness uniformity of the film.

Following the well-known steps for applying the methods based on the envelopes, the first and crucial step is the drawing of the envelopes. Different approaches, which usually involve complicated algorithms, have been suggested to do this task.[11,12,21,22] In particular, the method proposed by McClain *et al.*[21] has shown to be an accurate tool for drawing the upper and lower envelopes of an optical transmission spectrum and determining the points at the wavelengths, λ_{tan}, to which these envelopes and the spectrum are tangential. The envelope curves and the tangent points for the spectra under study are also shown in Figs. 4(a) and 4(b).

Once the tangent points are known, the systems of two equations given in Eqs. (13) and Eqs. (14) are solved to estimate initial values for the refractive index of the thin uniform film and nonuniform film,

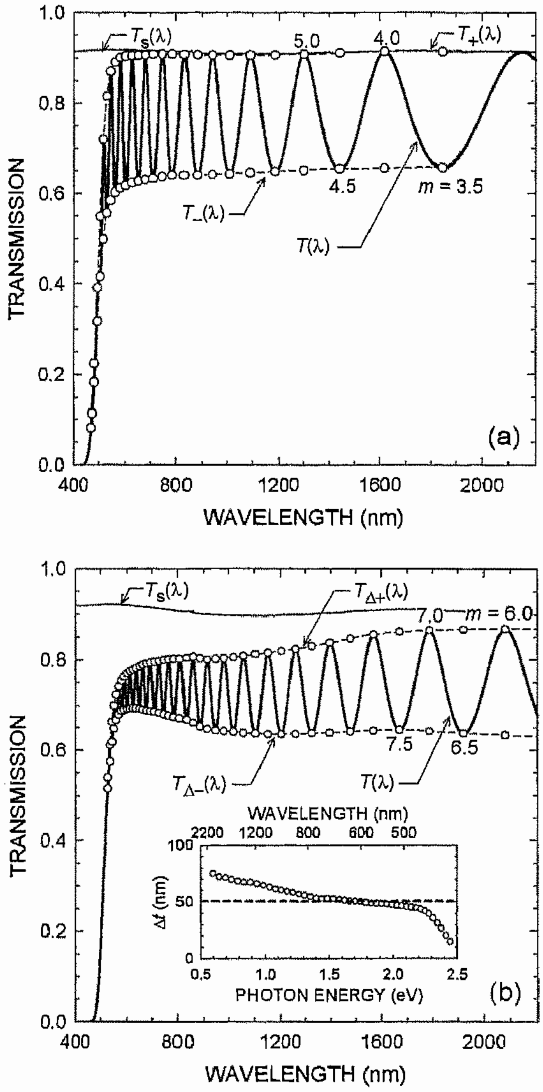

Fig. 4. (a) Experimental optical transmission spectrum, $T(\lambda)$, taken at normal incidence, corresponding to a representative thermally-evaporated amorphous $As_{40}S_{60}$ uniform film. $T_+(\lambda)$ and $T_-(\lambda)$ are, respectively, the upper and lower envelopes, and $T_s(\lambda)$ is the transmission of the uncoated substrate. The order numbers, m's, for some tangent points are marked for convenience. (b) Experimental optical transmission spectrum, $T(\lambda)$, taken at normal incidence, corresponding to a representative amorphous $As_{40}S_{60}$ nonuniform film, prepared by plasma-enhanced chemical vapor deposition. $T_{\Delta+}(\lambda)$ and $T_{\Delta-}(\lambda)$ are, respectively, the upper and lower envelopes, and $T_s(\lambda)$ is the transmission of the uncoated substrate. The order numbers, m's, for some tangent points are marked for convenience. Values for the thickness variation, Δt, derived by solution of the system of transcendental Eqs. (14), assuming $x = 1$, are plotted in the inset as a function of photon energy for the case of a quasi-constant spacing between the points. The system of Eqs. (14) is very sensitive to errors in the envelope drawing, and overestimated Δt values are usually obtained for smaller energies. The values of Δt drastically decrease for higher energies because the assumption $x = 1$ is not valid in this spectral region.

respectively. The system of Eqs. (13) can be analytically solved for n and x. The set of n's obtained from the spectrum of Fig. 4(a) is listed as n^0 in Table 1.

Table 1. Calculation of the Thickness and the Refractive Index of a Representative Uniform Film[a]

λ_{tan} (nm)	s^b	s	x_s	T_+	T_-	n^0	m	t^b (nm)	t (nm)	n^b	n
1846	**1.557**	1.492	0.9831	0.9140	0.6563	2.308	3.5	**1356**	1400	**2.344**	2.293
1618	**1.555**	1.493	0.9839	0.9140	0.6555	2.311	4.0	**1358**	1400	**2.348**	2.297
1441	**1.580**	1.496	0.9783	0.9112	0.6541	2.311	4.5	**1347**	1403	**2.353**	2.301
1301	**1.596**	1.494	0.9735	0.9083	0.6513	2.310	5.0	**1340**	1408	**2.360**	2.308
1185	**1.605**	1.500	0.9725	0.9068	0.6481	2.323	5.5	**1333**	1403	**2.365**	2.313
1091	**1.608**	1.501	0.9718	0.9061	0.6455	2.330	6.0	**1333**	1405	**2.375**	2.323
1010	**1.607**	1.503	0.9729	0.9059	0.6433	2.340	6.5	**1334**	1402	**2.382**	2.330
941	**1.602**	1.507	0.9753	0.9062	0.6413	2.353	7.0	**1338**	1400	**2.390**	2.337
882	**1.591**	1.512	0.9794	0.9069	0.6403	2.365	7.5	**1347**	1399	**2.400**	2.347
831	**1.569**	1.510	0.9844	0.9076	0.6404	2.366	8.0	**1365**	1405	**2.412**	2.359
786	**1.559**	1.509	0.9872	0.9083	0.6405	2.369	8.5	**1377**	1410	**2.424**	2.371
746	**1.550**	1.510	0.9895	0.9085	0.6376	2.381	9.0	**1383**	1410	**2.436**	2.383
711	**1.536**	1.508	0.9929	0.9076	0.6336	2.394	9.5	**1392**	1411	**2.451**	2.397
679	**1.531**	1.508	0.9940	0.9066	0.6311	2.401	10.0	**1398**	1414	**2.464**	2.410
651	**1.528**	1.508	0.9949	0.9060	0.6285	2.410	10.5	**1405**	1418	**2.480**	2.426
625	**1.519**	1.508	0.9972	0.9053	0.6241	2.425	11.0	**1410**	1417	**2.495**	2.440
602	**1.514**	1.508	0.9985	0.9038	0.6185	2.443	11.5	**1413**	1417	**2.512**	2.457
582	**1.513**	1.509	0.9990	0.9011	0.6126	2.460	12.0	**1417**	1419	**2.534**	2.478
563	**1.509**	1.510	1.0000	0.8910	0.6037	2.476	12.5	**1421**	1421	**2.554**	2.497
546	**1.507**	1.510	1.0000	0.8708	0.5858	2.509	13.0	**1416**	1414	**2.575**	2.519
531	**1.506**	1.510	1.0000	0.8153	0.5572	2.522	13.5	**1424**	1421	**2.601**	2.544
517	**1.507**	1.510	1.0000	0.7200	0.5000	2.575	14.0	**1408**	1405	**2.626**	2.568
504	**1.510**	1.509	0.9998	0.5498	0.4162	2.540	14.5	—	—	**2.652**	2.593
	$\langle t\rangle^b$ = 1378 ± 33 nm (2.39%)							$\langle t\rangle$ = 1409 ± 7 nm (0.50%)			

[a] λ_{tan}, wavelengths with tangent points; s and x_s, values of the refractive index and absorbance of the substrate at λ_{tan}, respectively; T_+ and T_-, values of the upper and lower envelopes at λ_{tan}, respectively; n^0, estimated values for the refractive index obtained by solution of the system of Eqs. (13); m, order numbers for the tangent points; t, final values for the film thickness; n, final values for the refractive index at λ_{tan}; $\langle t\rangle$, average value of the thickness (of the t's).

[b] Bold data are values for the refractive index of the uncoated substrate, s [derived from its transmission spectrum and Eq. (5)] and final values for the refractive index, n, and for the film thickness, t. These are data obtained with the traditional approach in which the substrate absorption is neglected. Note that the final average value for the average value $\langle t\rangle$ = 1409 ± 7 nm (0.50%) is $\langle t\rangle$ = 1378 ± 33 nm (2.39%).

As mentioned in Section 3, the system of transcendental Eqs. (14) can be initially solved assuming $x = 1$. This assumption is valid for the case of amorphous chalcogenide glasses, which are well known to be transparent in the IR.[23] After solving the system of Eqs. (14) for n and Δt, we can estimate a value for the wedging parameter by analyzing the set of Δt's obtained. It is important to note that, as shown in Ref. 13, this system of equations is very sensitive in the region of transparency to the presence of errors that are due to inaccuracy of the envelope drawing. However, the values of Δt drastically decrease for shorter wavelengths, owing to the fact that the assumption $x = 1$ is not valid in this spectral region. Therefore the average of the whole set of Δt's is not a good approach for determining an accurate value for this parameter, and hence it is necessary to study these values carefully. It should be noted that, in the medium absorption region, the values obtained for Δt are less sensitive to these possible errors; they are therefore more reliable. These comments are illustrated in Table 2, in which high dispersion in the values of Δt obtained is seen clearly. The dependence of the values of Δt on the wavelength (or, equivalently, on the photon energy) is shown in the inset of Fig. 4(b), and the final value Δt = 50 nm, which is suggested for this particular amorphous thin film, is marked. It is important to note that the same value was obtained when the traditional approach, in which the substrate absorption is neglected, was used. Once the value for the wedging parameter is known, the system of transcendental Eqs. (14) can be resolved with respect to n and x. The set of n's obtained from the spectrum of Fig. 4(b) is listed as n^0 in Table 2.

Following the sequence for the methodology proposed by Swanepoel,[7,8] the estimated values for n, after the systems of Eqs. (13) or (14) are solved, can be used together with Eq. (11) to derive more accurate values of the refractive index, as well as to determine the film thickness, t, or the average thickness, $\bar{t}$, depending on the film geometry. All final results for n and t ($\bar{t}$) are listed in Table 1 (Table 2), along with the average value of the t's ($\bar{t}$'s). The values for n and t ($\bar{t}$) obtained by use of the conventional expressions for the transmission envelopes,[7,8] as well as the traditional approach of determining the values of the refractive index of the bare substrate, s, from only its transmission spectrum, when the substrate absorption is neglected, are also listed in Table 1 (Table 2), for comparison. Clearly, there is an improvement in the accuracy achieved in the calculation of those optical parameters when the absorption in the glass substrate is considered. The relative error for t and,

Table 2. Calculation of the Thickness and the Refractive Index of a Representative Nonuniform Film[a]

λ (nm)	s^b	s	x_s	$T_{\Delta+}$	$T_{\Delta-}$	Δt (nm)	n^0	m	$\bar{t}^b$ (nm)	$\bar{t}$ (nm)	n^b	n
2080	**1.569**	1.487	0.9788	0.8686	0.6341	75.0	2.346	6.0	**2552**	2660	**2.449**	2.320
1922	**1.565**	1.492	0.9811	0.8672	0.6382	72.1	2.343	6.5	**2568**	2666	**2.452**	2.323
1787	**1.557**	1.489	0.9825	0.8647	0.6426	71.4	2.329	7.0	**2593**	2685	**2.455**	2.326
1670	**1.558**	1.493	0.9833	0.8610	0.6449	69.6	2.328	7.5	**2601**	2690	**2.458**	2.329
1567	**1.559**	1.492	0.9826	0.8558	0.6435	68.2	2.332	8.0	**2594**	2688	**2.460**	2.331
1477	**1.573**	1.491	0.9789	0.8472	0.6414	67.4	2.330	8.5	**2580**	2695	**2.464**	2.334
1396	**1.583**	1.493	0.9766	0.8377	0.6394	67.1	2.329	9.0	**2569**	2697	**2.465**	2.336
1325	**1.595**	1.493	0.9736	0.8299	0.6377	66.1	2.328	9.5	**2556**	2703	**2.470**	2.341
1261	**1.602**	1.496	0.9725	0.8234	0.6362	64.7	2.336	10.0	**2545**	2699	**2.474**	2.345
1203	**1.607**	1.496	0.9711	0.8188	0.6354	63.0	2.342	10.5	**2531**	2696	**2.479**	2.349
1150	**1.607**	1.498	0.9716	0.8150	0.6358	61.6	2.351	11.0	**2525**	2691	**2.482**	2.352
1103	**1.609**	1.499	0.9712	0.8114	0.6367	60.3	2.354	11.5	**2523**	2694	**2.489**	2.359
1058	**1.609**	1.501	0.9719	0.8082	0.6386	59.2	2.359	12.0	**2520**	2691	**2.491**	2.361
1018	**1.607**	1.505	0.9731	0.8056	0.6408	58.1	2.365	12.5	**2522**	2690	**2.497**	2.366
980	**1.606**	1.502	0.9728	0.8034	0.6423	56.9	2.371	13.0	**2510**	2686	**2.500**	2.369
947	**1.602**	1.508	0.9754	0.8013	0.6440	55.8	2.388	13.5	**2511**	2677	**2.509**	2.377
914	**1.599**	1.507	0.9758	0.8002	0.6474	54.8	2.392	14.0	**2504**	2675	**2.511**	2.379
885	**1.594**	1.511	0.9782	0.8031	0.6521	53.3	2.415	14.5	**2495**	2657	**2.518**	2.386
858	**1.577**	1.509	0.9822	0.8058	0.6603	52.9	2.403	15.0	**2538**	2677	**2.526**	2.393
833	**1.575**	1.510	0.9831	0.8040	0.6676	53.1	2.373	15.5	**2583**	2720	**2.534**	2.400
808	**1.564**	1.509	0.9857	0.8018	0.6706	52.7	2.378	16.0	**2594**	2718	**2.537**	2.404
786	**1.559**	1.509	0.9872	0.8013	0.6731	51.9	2.400	16.5	**2579**	2702	**2.545**	2.411
765	**1.555**	1.510	0.9881	0.8009	0.6765	51.2	2.418	17.0	**2560**	2689	**2.552**	2.418
746	**1.550**	1.510	0.9895	0.7996	0.6798	50.8	2.432	17.5	**2552**	2684	**2.562**	2.427
727	**1.544**	1.509	0.9909	0.7975	0.6831	50.5	2.445	18.0	**2531**	2660	**2.568**	2.433
709	**1.539**	1.509	0.9922	0.7955	0.6855	50.1	2.814	18.5	—	—	**2.574**	2.439
		$\langle \bar{t} \rangle^b$ = 2548 ± 32 nm (1.26%)							$\langle \bar{t} \rangle$ = 2689 ± 15 nm (0.56%)			

[a] λ_{tan}, wavelengths with tangent points; s and x_s, values of the refractive index and absorbance of the substrate at λ_{tan}, respectively; $T_{\Delta+}$ and $T_{\Delta-}$, values of the upper and lower envelopes at λ_{tan}, respectively; Δt, thickness variation; m, order numbers for the tangent points; n^0, estimated values for the refractive index obtained by solution of the system of Eqs. (14) after the determination of the thickness variation Δt; $\bar{t}$, final values for the average film thickness; n, final values for the refractive index at λ_{tan}; $\langle \bar{t} \rangle$, average value of the average film thickness (of the $\bar{t}$'s).

[b] Bold data are values for the refractive index of the uncoated substrate, s [derived from its transmission spectrum and Eq. (5)] and final values for the refractive index, n, and for the average film thickness, $\bar{t}$. These are data obtained with the traditional approach in which the substrate absorption is neglected. Note that the final average value for the average value $\langle \bar{t} \rangle$ = 2689 ± 15 nm (0.56%) is $\langle \bar{t} \rangle$ = 2459 ± 32 nm (1.26%).

consequently, for n [it is easily derivable from Eq. (11) that $|\Delta t|/t = |\Delta n|/n$], decreases from 2.39% to 0.50% for the uniform film, and therefore there is an improvement of approximately 79% in the accuracy of the calculations. Similarly, in the case of the nonuniform film, the relative error decreases from 1.26% to 0.56%, giving an improvement of approximately 56%. It is worth noting that when the values of s obtained only when the transmission spectrum of the substrate and Eq. (5) are used, i.e., when the substrate absorption is neglected, these values are larger and show a notable variation with the wavelength, compared with the values of s obtained by solution of the system of Eqs. (4). The fact that s is overestimated when the substrate absorption is neglected induces errors in the calculation of t ($\bar{t}$) and n, and underestimated t's ($\bar{t}$'s) and overestimated n's are derived in such cases. The spectral dependencies of the refractive index, $n(\lambda)$, for both studied films are shown in Figs. 5(a) and 5(b), respectively, along with the values obtained by use of the traditional approach, in which the substrate absorption is neglected, for uniform and nonuniform thin dielectric films.

Once the values of n over a particular spectral range are known, some model describing the dispersion of the refractive index, $n(\lambda)$, can be used to extrapolate the values of n toward shorter wavelengths. The model particularly used for describing the dispersion of n in this paper is based on the single-oscillator formula that was proposed by Wemple and DiDomenico,[24]

$$n^2(\hbar\omega) = 1 + \frac{E_o E_d}{E_o^{\,2} - (\hbar\omega)^2}, \tag{15}$$

where $\hbar\omega$ is the photon energy, E_o is the single-oscillator energy, and E_d is the dispersion energy. Thus, to complete the calculation of the optical constants, the extinction coefficient of the uniform and nonuniform thin dielectric films, k, is obtained in the strong absorption region by use of the extrapolated values for n, by solution of, respectively, the equations corresponding to the upper envelope in Eqs. (13)

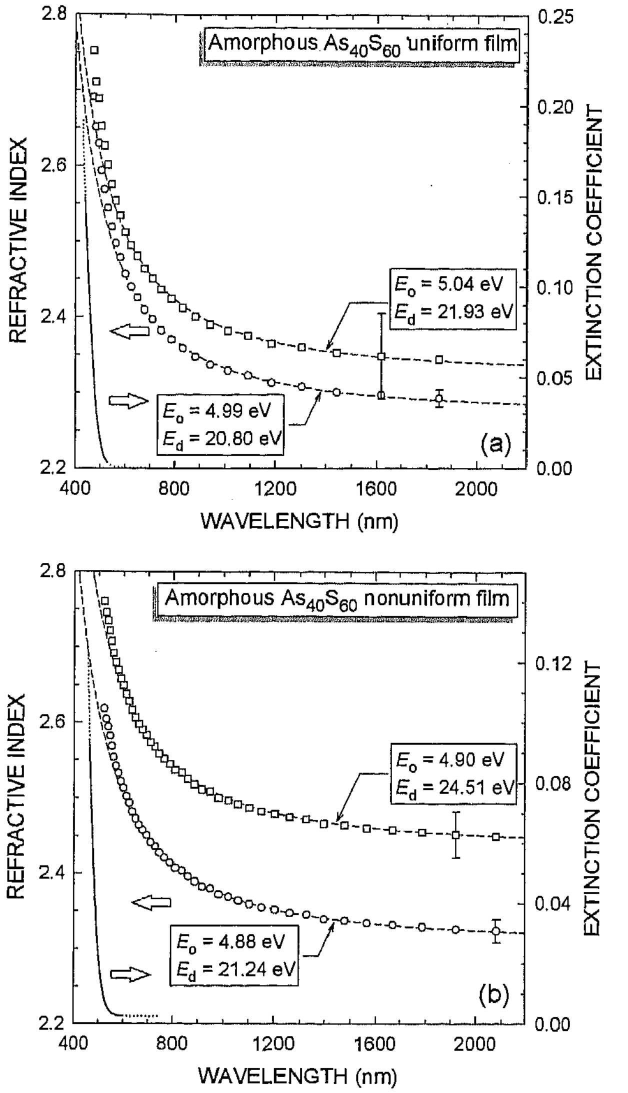

Fig. 5. Final values of n (circles) and k (solid curve) as a function of the wavelength, derived from (a) the optical transmission spectrum shown in Fig. 4(a) (uniform film) and (b) the optical transmission spectrum shown in Fig. 4(b) (nonuniform film). The values of n (squares) and k (dotted curve) obtained by use of the traditional approach are also plotted for comparison. The difference between both sets of k values is insignificant. Dashed curves have been drawn by use of the refractive-index dispersion relationship given in Eq. (15). The values of the fitting parameters E_o and E_d, are shown in the figure.

and (14) for x. It has been shown[7,13] that the upper envelope is more sensitive than the lower envelope to the absorption effects of the material. The spectral dependencies of the extinction coefficient, $k(\lambda)$, for the studied films are also shown in Figs. 5(a) and 5(b), respectively, along with the values obtained by the traditional approach for uniform and nonuniform thin dielectric films. It is seen that, for these particular thin-film systems, the values of $k(\lambda)$ obtained by use of both approaches are quite similar.

5. Concluding Remarks

Most of the commercial glass substrates used by researchers (typically, fused silica and, mainly, borosilicate microscope slides) have notable optical losses that are due to absorption or scattering or both in the optical spectral region. If this absorption is not considered in both the determination of the optical constants of the substrate and the analytical expressions for the upper and lower envelopes of the optical transmission spectrum, overestimated refractive-index values and underestimated values for the film thickness or the average film thickness, in the case of nonuniform thin dielectric films, are obtained. However, the influence of the absorption of the substrate on the calculation of the wedging parameter, Δt, characterizing the film's nonuniformity and on the calculation of the extinction coefficient, k, is insignificant. The degree of accuracy in the determination of both n and t ($\bar{t}$) is notably improved when the absorbance of the bare substrate, x_s, is considered in the expressions for the envelopes.

The authors are grateful to M. Vlcek (Department of General and Inorganic Chemistry, University of Pardubice, Czech Republic) for supplying us with the thin-film samples. The authors are also grateful to S. R. Elliott (Department of Chemistry, University of Cambridge, UK) for a critical reading of the paper. This paper has been partially supported by the European Commission (HPMF-CT-2000-01031), and the Ministerio de Ciencia y Tecnología (Spain) and Fonds Européen de Développement Regional under the project MAT2001-3333.

References

1. J. A. Savage, *Infrared Optical Materials and Their Antireflection Coatings* (Hilger, Bristol, UK, 1985).
2. H. A. Macleod, *Thin-Film Optical Filters*, 2nd ed. (Institute of Physics, Bristol, UK, 1986).
3. O. S. Heavens, *Optical Properties of Thin Solid Films* (Dover, New York, 1991).
4. K. Shwartz, *The Physics of Optical Recording* (Springer-Verlag, Berlin, 1994).
5. R. G. Hunsperger, *Integrated Optics: Theory and Technology*, 4th ed. (Springer-Verlag, Berlin, 1995).
6. J. C. Manifacier, J. Gasiot, and J. P. Fillard, "A simple method for the determination of the optical constants n, k and the thickness of a weakly absorbing thin film," J. Phys. E **9**, 1002–1004 (1976).
7. R. Swanepoel, "Determination of the thickness and optical constants of amorphous silicon," J. Phys. E. **16,** 1214–1222 (1983).
8. R. Swanepoel, "Determination of surface roughness and optical constants of inhomogeneous amorphous silicon films," J. Phys. E **17,** 896–903 (1984).
9. R. Swanepoel, "Transmission and reflection of an absorbing thin film on an absorbing substrate," S. Afr. J. Phys. **12,** 148–156 (1989).
10. D. A. Minkov, "Calculation of the optical constants of a thin layer upon a transparent substrate from the reflection spectrum," J. Phys. D **22,** 1157–1161 (1989).
11. E. Márquez, J. B. Ramírez-Malo, P. Villares, R. Jiménez-Garay, and R. Swanepoel, "Optical characterization of wedge-shaped thin films of amorphous arsenic trisulphide based only

on their shrunk transmission spectra," Thin Solid Films **254,** 83–91 (1995).
12. S. C. Chiao, B. G. Bovard, and H. A. Macleod, "Optical-constant calculation over an extended spectral region: application to titanium dioxide film," App. Opt. **34,** 7355–7360 (1995).
13. J. J. Ruiz-Pérez and E. Márquez, *Nuevos Métodos de Caracterización Óptica de Semiconductores Basados en Medidas Espectroscópicas de Reflexión* (Ministerio de Defensa, Secretaría General Técnica, Madrid, 1997), pp. 6-1.
14. V. V. Filippov, "Method of the ratio of envelopes of the reflection spectrum for measuring optical constants and thickness of thin films," Opt. Spectrosc. **88,** 581–585 (2000).
15. J. J. Ruíz-Pérez, J. M. González-Leal, D. A. Minkov, and E. Márquez, "Method for determining the optical constants of thin dielectric films with variable thickness using only their shrunk reflection spectra," J. Phys. D **34,** 1–8 (2001).
16. Rusli and G. A. J. Amaratunga, "Determination of the optical constants and thickness of thin films on slightly absorbing substrate," Appl. Opt. **34,** 7914–7924 (1995).
17. D. A. Minkov, "Flow-graph approach for optical analysis of planar structures," Appl. Opt. **33,** 7698–7703 (1994).
18. E. Márquez, J. M. González-Leal, R. Prieto-Alcón, R. Jiménez-Garay, and M. Vlcek, "On the photo- and thermally-induced darkening phenomenon in $As_{40}S_{40}Se_{20}$ amorphous chalcogenide thin films," J. Phys. D **32,** 3128–3134 (1999).
19. E. Márquez, J. M. González-Leal, R. Jiménez-Garay, and M. Vlcek, "Thermally- and photo-induced changes in the structure and optical properties of amorphous $As_{40}S_{30}Se_{30}$ films," Thin Solid Films **396,** 183–190 (2001).
20. E. Márquez, P. Nagels, J. M. González-Leal, A. M. Bernal-Oliva, E. Sleeckx, and R. Callaerts, "On the optical constants of amorphous $Ge_xSe_{(1-x)}$ thin films of non-uniform thickness prepared by plasma-enhanced chemical vapour deposition," Vacuum **52,** 55–60 (1998).
21. M. McClain, A. Feldman, D. Kahaner, and X. Ying, "An algorithm and computer program for the calculation of envelope curves," Comput. Phys. **5,** 45–48 (1991).
22. D. A. Minkov and R. Swanepoel, "Computerization of the optical characterization of a thin dielectric film," Opt. Eng. **32,** 3333–3337 (1993).
23. S. R. Elliott, "Chalcogenide glasses," in *Materials Science and Technology*, J. Zarzycki, ed. (VCH, Weinheim, 1991), Vol. 9, pp. 375–454.
24. S. H. Wemple and M. DiDomenico, "Behavior of the electronic dielectric constants in covalent and ionic materials," Phys. Rev. B **3,** 1338–1351 (1971).