

Determination of the surface roughness and refractive index of amorphous $\text{As}_{40}\text{S}_{60}$ films deposited by spin coating

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Abstract

An envelope method, based on the optical reflection spectrum taken at normal incidence, has been successfully applied to the geometrical–optical characterization of thin dielectric films having significant surface roughness. Such a method allows the determination of the average thickness and the refractive index of the films with accuracies better than 1%, as well as the average amplitude of the surface roughness with an accuracy of about 2%. Amorphous $\text{As}_{40}\text{S}_{60}$ thin films have been deposited by spin coating, onto glass substrates, from a solution of the bulk material in *n*-propylamine. Indications of the surface roughness in these films were found from total (specular plus diffuse) reflectance measurements using an integrating sphere, and also from mechanical measurements using a stylus profiler. The latter technique provided a value for the average surface roughness of 20 ± 4 nm, which is in excellent agreement with the optically determined value of 17.4 ± 0.4 nm.

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1. Introduction

Optical properties of thin dielectric films have been the subject of intense study during the last decades, and great efforts have been made to develop the mathematical formulation describing the transmittance and reflectance of different optical systems [1–9]. Thus, theoretical works dealing with films showing thickness inhomogeneities can be found in the literature [3,7,9], and the calculation algorithms suggested have been applied successfully to characterize geometrically and optically thin dielectric films showing a linear thickness variation [9–11]. Nevertheless, to the best of our knowledge, they have not been applied, as yet, to the case of films having a significant surface roughness.

Reflectometry in the spectral interval covering UV, visible and near infrared (UV/Vis/NIR) yields valuable information about non-uniformities in the thickness of films. In the present paper, we have applied an envelope method, based on specular reflection spectra, in order to obtain the refractive index, *n*, of thin dielectric films having significant surface roughnesses, deposited onto transparent substrates. The procedure has proved itself to be a useful tool to determine the average thickness, the average amplitude of the surface roughness and the refractive index of amorphous films with a chemical composition $\text{As}_{40}\text{S}_{60}$, deposited by spin coating onto glass substrates from a solution of the bulk chalcogenide in *n*-propylamine.

2. Description of the method

The interference method used for the geometrical–optical characterization of thin dielectric films having surface roughness, is mainly based on the following assumptions:

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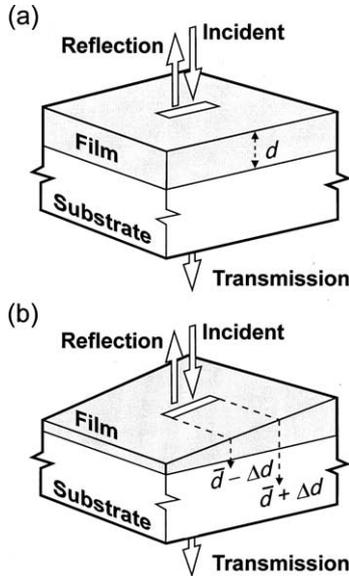


Fig. 1. Illustrations of the optical systems corresponding to (a) a uniform thickness film, and (b) a non-uniform thickness film, deposited onto a transparent substrate.

- (i) The optical system under study is composed of a thin isotropic film with refractive index, n , deposited onto a substrate with refractive index, s , whose thickness, d_s is several orders of magnitude larger than the thickness of the film, d . This two-layer optical system is surrounded by air (see Fig. 1(a)).
- (ii) The light radiation used to measure the optical reflectance of this system, with mean wavelength, λ , and spectral half-width, $\Delta\lambda$, is incident normally on the surface of the film.
- (iii) Interference phenomena stemming from the multiple reflections at the dielectric-film interfaces are resolved by the experimental measurement system ($\Delta\lambda \ll \lambda^2/(2nd)$), while those occurring at the substrate interfaces cannot be discriminated by the instrument due to the spectral distribution of the probe light ($\Delta\lambda \gg \lambda^2/(2sd_s)$).
- (iv) The refractive index of the film is larger than that of the substrate, i.e., $n > s$.
- (v) The dielectric film absorbs weakly in the considered spectral region, i.e., $n^2 > s^2 \gg k^2$, while the substrate is transparent in that particular spectral region, i.e., $k_s = 0$. The quantities k and k_s are the extinction coefficients of the film and the substrate, respectively.

If the above assumptions are all met, and the thickness of the dielectric film is uniform, the reflectance of such a two-layer system, for a wavelength λ , can be expressed as follows [7,9,12]:

$$R(\lambda; n, x, d, s) = \frac{C}{E} - \frac{2(AD + B^2)}{EF}, \quad (1)$$

where

$$A = r_2 r_3 (1 + R_1 x^2) + r_1 r_3 (1 + R_2) x \cos(\varphi),$$

$$B = r_1 r_3 (R_2 - 1) x \sin(\varphi),$$

$$C = R_1 + R_2 x^2 + R_3 x^2 + R_1 R_2 R_3 + 2r_1 r_2 (1 + R_3) x \cos(\varphi),$$

$$D = r_2 r_3 (x^2 + R_1) + r_1 r_3 (1 + R_2) x \cos(\varphi),$$

$$E = 1 + R_1 R_2 x^2 - R_1 R_3 x^2 - R_2 R_3 + 2r_1 r_2 (1 - R_3) x \cos(\varphi),$$

$$F = 1 + R_1 R_2 x^2 + 2r_1 r_2 x \cos(\varphi),$$

$$r_1 = \frac{1-n}{1+n}, \quad r_2 = \frac{n-s}{n+s}, \quad r_3 = \frac{s-1}{s+1},$$

$$R_1 = r_1^2, \quad R_2 = r_2^2, \quad R_3 = r_3^2,$$

$$\varphi = 4\pi n d / \lambda,$$

$$x = \exp(-\alpha d),$$

$$\alpha = 4\pi k / \lambda.$$

The quantities α and x are, respectively, the absorption coefficient and the optical absorbance of the dielectric film deposited onto the transparent substrate.

Let us now consider an optical system such as that displayed in Fig. 1(b). This is the case of a wedge-shaped film, characterized by an average thickness, \bar{d} , and a parameter, Δd , that measures the actual variation in thickness at the extrema of the area illuminated by the spectrophotometer. Thus, the thickness can be expressed as: $d = \bar{d} + \eta \Delta d$, with $-1 \leq \eta \leq 1$. Such a wedge-shaped profile has been chosen only for the sake of descriptive simplicity, but the formulation that will be presented below is also valid for surface-roughness profiles such as those shown in Fig. 2 [7,9]. From Eq. (1), one can obtain the optical reflectance, $R_{\Delta d}$, corresponding to the geometry mentioned above, by integration of R over the thickness, d , or equivalently over the phase φ ,

$$R_{\Delta d} \approx \frac{1}{2\Delta d} \int_{\bar{d}-\Delta d}^{\bar{d}+\Delta d} R(d) dd = \frac{1}{\varphi_2 - \varphi_1} \int_{\varphi_1}^{\varphi_2} R(\varphi) d\varphi, \quad (2)$$

with

$$\varphi_1 = \frac{4\pi n(\bar{d} - \Delta d)}{\lambda}, \quad \varphi_2 = \frac{4\pi n(\bar{d} + \Delta d)}{\lambda},$$

and by further assuming the optical absorbance, x , to be given by $\bar{x} = \exp(-\alpha \bar{d})$, which is a reasonable approximation as long as $\Delta d \ll \bar{d}$. The complete expression for $R_{\Delta d}$, which results after solving this integral, as well as a detailed explanation of the calculation procedure, can be found in our previous work [9]. As already mentioned, $R_{\Delta d}$ is also valid in the case of surface profiles such as those shown in Fig. 2. It is easy to show, on the basis of the areas below these profiles, that the total change in the phase over the measured area is the same for all the profiles shown in Fig. 1(b) and in Fig. 2(b) and (c). Similarly, it is also easy to check that the total change in the phase for the sinusoidal profile would be the same as for the others, if the amplitude were $\pi \Delta d / 4$. Hence, the

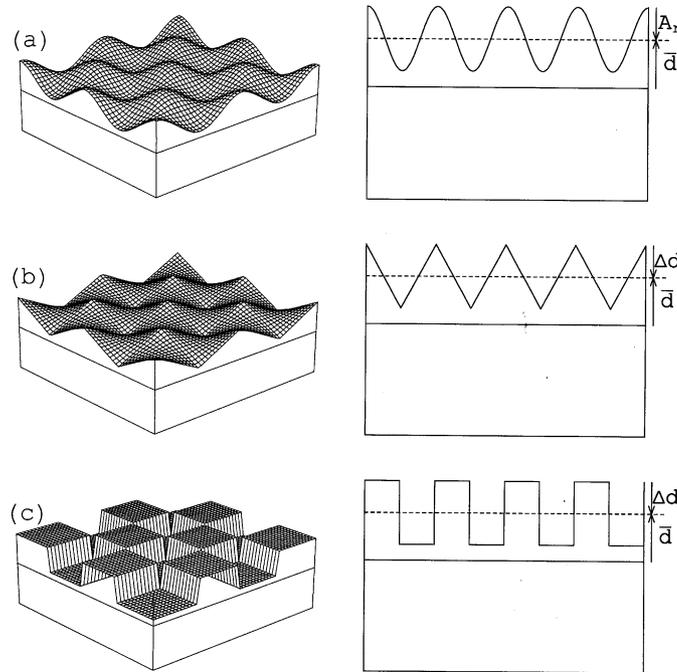


Fig. 2. Different types of surface profiles considered in the formulation presented in this paper: (a) sinusoidal; (b) triangular; (c) rectangular (step).

change of variable $A_r = \pi\Delta d/4$ must be employed in Eq. (2) when dealing with this particular profile.

Following the description of the mathematical formulation, we will only present here analytical expressions for the upper and lower envelopes, $R_{\Delta+}$ and $R_{\Delta-}$, respectively, of the reflection spectrum at normal incidence, $R_{\Delta d}$, corresponding to a non-uniform thickness film, with a surface profile such as those displayed in Figs. 1(b) and 2. Hence, the geometrical–optical characterization method is based on the following equations:

$$\begin{aligned}
 R_{\Delta\pm}(\lambda; n, x, \Delta d, s) &= 1 - \frac{1}{\theta(A - C)} \\
 &\times \left\{ \frac{64n^4s(s-1)^2x^2}{(C^2 - D^2)^{1/2}} \tan^{-1} \left[\frac{C' \mp D'}{(C^2 - D^2)^{1/2}} \tan \theta \right] \right. \\
 &\left. - \frac{(A' - B')(A' - C')}{(A^2 - D^2)^{1/2}} \tan^{-1} \left[\frac{A' \mp D'}{(A^2 - D^2)^{1/2}} \tan \theta \right] \right\}, \tag{3}
 \end{aligned}$$

where

$$\begin{aligned}
 A' &= (n+1)^2(n+s)^2 + (n-1)^2(n-s)^2x^2, \\
 B' &= (n-1)^2(n+s)^2 + (n+1)^2(n-s)^2x^2, \\
 C' &= (n+1)^3(n+s^2) + (n-1)^3(n-s^2)x^2, \\
 D' &= 2(n^2-1)(n^2-s^2)x, \\
 \theta &= 2\pi n\Delta d/\lambda.
 \end{aligned}$$

Assuming that the numerical values of the *experimental* envelopes, $R_{\Delta\pm}(\lambda)$, as well as the refractive index of the substrate, s , for each wavelength, λ , in the spectral region studied are known, one further equation would still be necessary in order to solve the two-equation system defined by the expressions in Eq. (3). Considering the dielectric film to be transparent in some part of the spectral region of interest, we can use the equation $x = 1$. Thus, the number of unknown parameters is reduced to only two, n and Δd , and the two-equation system can be expressed analytically as follows:

$$\begin{cases} R_{\Delta+}(n, \Delta d) - R_{\Delta+}(\lambda) = 0 \\ R_{\Delta-}(n, \Delta d) - R_{\Delta-}(\lambda) = 0 \end{cases} \tag{4}$$

The solution of the system of equations (4) gives both a first estimation of the refractive index of the film, n^0 , for each wavelength in the spectral range under study, and a set of values for the parameter Δd . It should be emphasized that some of the values obtained for Δd are not meaningful. In particular, at short wavelengths, for which the equation $x = 1$ is no longer valid due to the optical absorption in this spectral region, the values of Δd certainly lack physical meaning. On the other hand, in the case of long wavelengths, the system of equations (4) is very sensitive to the presence of experimental errors, and hence, the Δd values obtained in this spectral region show a very high statistical dispersion. Therefore, it is necessary to analyse carefully the values of Δd , as we will illustrate later.

Finally, the envelope method for the geometrical–optical characterization of non-uniform dielectric films,

deposited onto transparent substrates, depends eventually on the well-known equation for the occurrence of interference fringes,

$$2n_i\bar{d} = m_i\lambda_i, \quad (5)$$

to determine the average film thickness, \bar{d} , and to refine the refractive-index values, n_i , on the basis of finding out the *exact* order numbers, m_i , corresponding to the wavelengths λ_i , m_i having integer values for those points where the reflection spectrum and the lower envelope are *tangential*, and half-integer values for the tangent points with the upper envelope. From Eq. (5), it is easy to prove that the relative error in the determination of the refractive index is the same as that corresponding to the average film thickness, as illustrated by the following equation:

$$\frac{\sigma_{n-1}(\bar{d})}{\bar{d}} = \frac{\sigma_{n-1}(n)}{n}, \quad (6)$$

with σ_{n-1} being the standard deviation of these two parameters. A detailed description of this iterative procedure, based on Eq. (5), can be found in Ref. [9].

3. Experimental

Bulk chalcogenide samples were prepared by direct synthesis from high-purity elements (5N), heated together in an evacuated quartz ampoule, at a temperature of approximately 900 °C, for about 24 h. After the synthesis, the melt was air-quenched, resulting in a bulk glass of the required chemical composition, As₄₀S₆₀. Amorphous thin films of such a composition, and about 1 μm thick, were deposited by spin coating onto ~1 mm thick (three orders thicker than the chalcogenide film) weakly-absorbing glass substrates, with refractive index, s , of about 1.5, from 0.8 M solutions of the bulk material in *n*-propylamine (CH₃CH₂CH₂-NH₂). Before the deposition, the solution was filtered with a 0.5 μm filter to remove any undissolved material. The spin speed was maintained at 3000 rpm, during 20 s. The films were annealed under nitrogen, at a temperature of 90 °C, (well below the glass-transition temperature, $T_g = 180$ °C [13]), for 30 min to remove any solvent that could be present.

The amorphous nature of the samples was checked by X-ray diffraction measurements. Also, electron microprobe analysis of the samples showed the film chemical composition to be As_{35.7 ± 1.8}S_{64.3 ± 1.7}. The films were kept in complete darkness and in a dry environment, in order to avoid any risk of hydrolysis or oxidation of the surface of the films.

The specular optical reflection spectra were obtained at 6 degrees of incidence in the spectral range between 400 and 2200 nm, by a double-beam UV/Vis/NIR spectrophotometer (Perkin Elmer, model Lambda-19).

The measuring-beam spot size was set at 1 × 4 mm². The spectral bandpass, $\Delta\lambda$, was automatically set by the spectrophotometer in the NIR range, in such a fashion that the energy reaching the detector is maximised. It was checked that $\Delta\lambda$ typically varies in the range of 1 to 2.5 nm when obtaining the reflection spectra of the films under study in this spectral window ($\Delta\lambda$ being larger when increasing the wavelength). On the contrary, the spectrophotometer allows the user to set $\Delta\lambda$ at a fixed value in the UV/Vis range, which was set at 1 nm when measuring the spectra shown in this work, over this spectral range. Measurements of the total (specular plus diffuse) reflectance of the samples were taken in the same spectral range, using an integrating sphere. The surface roughness of the films was measured at two different levels of magnification by means of a stylus-based profilometer (Sloan, model Dektak 3030), and also using atomic force microscopy (AFM).

4. Results and discussion

As stated in Section 2 of the paper, the present geometrical–optical characterization method is based on a set of assumptions, which are experimentally fulfilled by the spin-coated amorphous chalcogenide/glass substrate samples under study:

- (i) The thickness of the glass substrates is three orders of magnitude larger than the thickness of the spin-coated chalcogenide films deposited onto them, and the optical system is surrounded by air.
- (ii) The spectrophotometer radiation is not perfectly monochromatic, having instead an energetic distribution with a spectral half-width $\Delta\lambda$ (typically in the range of 1 nm, for the UV/Vis spectral window, up to 2.5 nm, at NIR wavelengths), around the mean wavelength λ , over the spectral range used. Specular reflection spectra were obtained at 6 degrees of incidence. For this angle, the hypothesis of normal incidence remains valid [12].
- (iii) The *period* of the modulation of the reflection spectrum associated with the interference phenomena stemming from the multiple reflections at the substrate interfaces, $\lambda^2/(2sd_s)$, varies in the studied spectral range from 0.05 nm up to 1.6 nm, when increasing the wavelength from 400 nm up to 2200 nm. These values are smaller than the spectral half-width of the probe light beam, and the spectrophotometer cannot therefore resolve these interference fringes. That is why such a modulation is not observed in the measured reflection spectra (see Fig. 3).
- (iv) The reflection spectra of the spin-coated films under study were always above the corresponding spectrum of the substrate alone (see Fig. 3), which con-

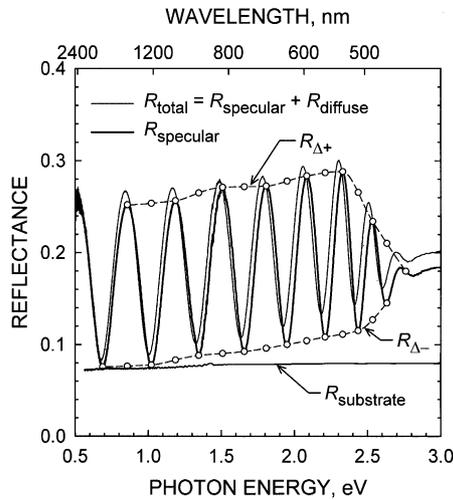


Fig. 3. Specular and total reflectance of a representative amorphous film of chemical composition $As_{40}S_{60}$, deposited by spin coating, along with the reflection spectrum of the glass substrate alone. $R_{\Delta+}$ and $R_{\Delta-}$ are, respectively, the upper and lower envelopes. The points in both envelopes at those wavelengths where these curves and the specular reflection spectrum are tangential, λ_i , have been marked (see Table 1).

firmly that the refractive index of the dielectric film is greater than that corresponding to the glass substrate.

(v) Even though the optical absorption in the substrate is weak, but significant, its effect on the reflection spectrum of the amorphous chalcogenide/glass substrate bilayer is not as notable as for the corresponding transmission spectrum, and therefore, the substrate can be considered transparent [14].

Fig. 3 shows the specular and total (specular plus diffuse) reflection spectra, for one of the films studied. The reflectance has been plotted against photon energy instead of wavelength for clarity, for in this way the interference maxima and minima are approximately equidistant from each other. The difference between the spectra shown in Fig. 3 indicates that there is a loss of energy reaching the detector when the specular reflectance is measured, due to the presence of a scattering phenomenon. Such a difference was not found between the specular and total reflection spectra of the substrate alone. It should be also mentioned that such significant differences between the specular and total reflection spectra, were never detected by us in samples prepared by other film-preparation techniques, such as thermal evaporation (TE) or plasma-enhanced chemical vapour deposition (PECVD). Microanalysis by X-ray energy dispersion (with a resolution better than 1 μm), showed that the spin-coated samples were homogeneous from the compositional point of view, so we can neglect the idea of the presence of microparticles in the films, which could produce scattering of the incident radiation. On the other hand, unlike the above-mentioned film-depo-

sition techniques, the spin-coating preparation technique employed in the present work produces a uniform distribution of the chalcogenide material over the substrate, so that a wedge-shaped profile, which is characteristic of the TE and PECVD films [10,11], should not be expected in this case. Therefore, the non-specular reflection observed should mainly be due to the presence of a certain degree of surface roughness on the films, which is a product of the deposition technique used.

In fact, mechanical measurements performed with the profilometer gave clear evidence of such surface roughness in the studied films. No noticeable surface roughness was measured on the glass substrates, as expected. Fig. 4(a) shows a representative plot corresponding to a spin-coated amorphous $As_{40}S_{60}$ film. The average film thickness, as well as the average amplitude of the surface roughness, obtained from the analysis of these measurements, are $\bar{d} = 864 \pm 13$ nm and $A_r = 20 \pm 4$ nm, respectively. On the other hand, Fig. 4(b) illustrates the surface roughness of this film at a higher level of magnification. A statistical study of this surface AFM map, extending over a film area of 1000×1000 nm², yields an average amplitude for this low-level surface roughness of 1.6 nm. It should be noted that both AFM and scanning electron microscopes were unable to discern the high-amplitude surface roughness, due to the small area covered by our apparatus (4 μm^2), in the former case, and the fact that the resolution was not high enough compared with the roughness dimensions, in the latter.

Geometrical–optical characterization of the amorphous $As_{40}S_{60}$ films prepared by spin coating was carried out from the specular-reflection spectra. The upper and lower envelopes of the spectra, $R_{\Delta+}$ and $R_{\Delta-}$, respectively, along with the corresponding tangent points between these two envelopes and the reflection spectrum, were determined using the very useful computer program ‘Envelope’ developed by McClain et al. [15], as shown in Fig. 3. Application of the optical method presented here, based on the set of equations (4), yielded an average thickness, $\bar{d} = 878 \pm 6$ nm, as well as an average amplitude of the surface roughness, $A_r = \pi \Delta d / 4 = 17.4 \pm 0.4$ nm ($A_r > \sigma_{n-1}(\bar{d}) = 6$ nm), for a representative amorphous $As_{40}S_{60}$ film whose reflection spectrum is shown in Fig. 3. These values are in excellent agreement, indeed, with those determined from the mechanical measurements. Table 1 shows the procedure for the calculation of the average thickness, \bar{d} , and the refractive index of the film, n , at those wavelengths, λ_i , for which there are tangent points between the envelopes and the reflection spectrum. The value for the average amplitude of the surface roughness of this film was determined from the graph displayed in the inset of Fig. 5. As previously pointed out, a high statistical dispersion can be observed in this plot for the values of A_r (or equivalently, for the values of Δd), which are obtained by solution of the system of equa-

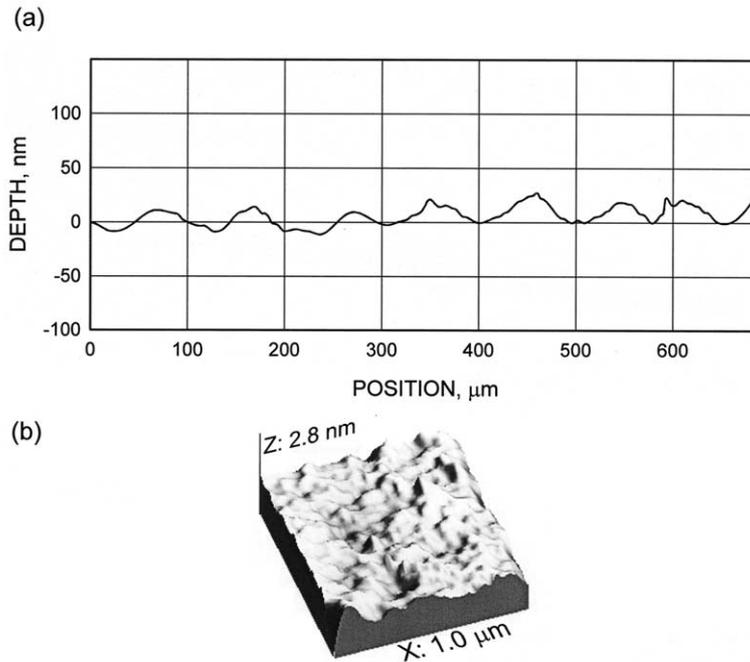


Fig. 4. Measurement of the film surface profile by use of (a) a profilometer, and (b) an AFM image, of an amorphous film of chemical composition $\text{As}_{40}\text{S}_{60}$, deposited by spin coating.

Table 1

Calculation of the average thickness, \bar{d} , and the refractive index, n , taking into account the effect of the surface roughness of the film, for a representative sample of chemical composition $\text{As}_{40}\text{S}_{60}$, deposited by spin coating, using only the specular optical reflection spectrum shown in Fig. 3

λ_i (nm)	s	$R_{\Delta+}$	$R_{\Delta-}$	n^0	n^0	m	\bar{d} (nm)	d (nm)	n	n
1449	1.504	0.2521	0.0764	2.060	2.131	2.5	879	850	2.070	2.247
1215	1.506	0.2537	0.0777	2.066	2.141	3.0	882	851	2.083	2.261
1046	1.510	0.2566	0.0832	2.085	2.231	3.5	878	820	2.092	2.271
922	1.513	0.265	0.0882	2.120	2.299	4.0	870	802	2.108	2.288
822	1.508	0.2711	0.0904	2.143	2.338	4.5	863	791	2.114	2.295
748	1.513	0.2718	0.0925	2.149	2.353	5.0	870	795	2.138	2.320
686	1.516	0.2725	0.0960	2.158	2.379	5.5	874	793	2.156	2.341
636	1.518	0.2778	0.1000	2.182	2.421	6.0	874	788	2.181	2.367
595	1.518	0.2834	0.1042	2.207	2.464	6.5	876	785	2.211	2.399
561	1.517	0.2869	0.1082	2.226	2.500	7.0	882	785	2.245	2.436
532	1.518	0.2881	0.1112	2.235	2.522	7.5	–	–	2.281	2.475
509	1.518	0.2656	0.1151	2.178	2.475	8.0	–	–	2.327	2.526
489	1.520	0.2341	0.1270	2.117	2.439	8.5	–	–	2.376	2.578
471	1.515	0.2102	0.1452	2.098	2.444	9.0	–	–	2.423	2.630

Data shown in bold are the estimated values for the refractive index, n^0 , the values eventually calculated, n , and the film thickness, d , all of them determined using Minkov's method [5], in which the surface roughness is *not* considered. Values of \bar{d} (and d , in the case of Minkov's method) associated with those wavelengths where the hypothesis of transparency ($x = 1$) is not valid, are not considered in the calculation of the final value, by averaging this set of data, and, consequently, they are not presented in the table.

tions (4) for the envelope points corresponding to long wavelengths. Moreover, at short wavelengths, an increase in the values of A_r is also observed when the transparency hypothesis, $x = 1$, is no longer valid.

On the other hand, it must be mentioned that if we assume our films to have a uniform thickness, and use the interference method proposed by Minkov [5] (based also only on the reflection spectrum), whose validity has been proved by us [16–18] on numerous occasions,

underestimated and inaccurate values are obtained for the thickness of the films. In fact, the thickness calculated in this way for the film whose reflection spectrum is shown in Fig. 3, was $d = 806 \pm 26$ nm. This leads in turn to overestimated refractive-index values. The results of the application of this envelope method for uniform-thickness films are also listed in Table 1.

The spectral dependence of the refractive index, $n(\lambda)$, for the representative $\text{As}_{40}\text{S}_{60}$ film is displayed in Fig. 5.

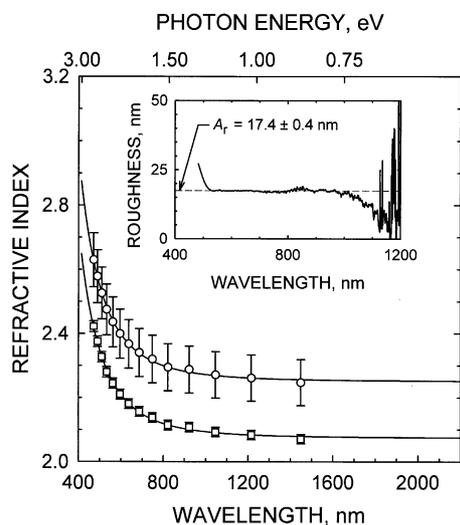


Fig. 5. Spectral dependence of the refractive index obtained from the specular reflection spectrum displayed in Fig. 3, taking into account the existence of surface roughness (square points), and ignoring this characteristic (circular points). Fits to the experimental data using the Cauchy dispersion relationship given in Eq. (7), are shown by the solid curves. The inset shows the values for the average amplitude of the surface roughness of the film, obtained at each wavelength, using the optical method outlined in this paper.

This figure also shows the n values obtained when ignoring the effect of the roughness of the surface of the film. It can be clearly seen that these n values are too large, due to errors made in the determination of the film thickness. Finally, in both cases, the n values have been fitted to the three-term Cauchy dispersion relation:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}, \quad (7)$$

where the values of the three constants obtained from the fits are, $A = 2.074$, $B = 3734 \text{ nm}^2$ and $C = 1.62 \times 10^{10} \text{ nm}^4$, and $A = 2.251$, $B = 4052 \text{ nm}^2$ and $C = 1.76 \times 10^{10} \text{ nm}^4$, respectively, for the n values calculated by the equations proposed in the present paper, and for those calculated neglecting the existence of surface roughness. The curves that best fit the data are also shown in Fig. 5.

5. Conclusions

Amorphous films of chemical composition $\text{As}_{40}\text{S}_{60}$ have been deposited by spin coating onto glass substrates, from a solution of the bulk chalcogenide material in n -propylamine. The presence of a significant surface roughness is characteristic of these samples, and this has been shown by both mechanical and total-reflectance measurements. Geometrical–optical characterization of the films has been carried out using the

specular reflection spectra, in the spectral range between 400 and 2200 nm. The average thickness and the refractive index of the films have been determined with accuracies better than 1%, and the average amplitude of the surface roughness has been obtained with an accuracy of about 2%. There is an excellent agreement between the values of the amplitude of the surface roughness measured mechanically, and those calculated from the reflection spectra, that is, between the contact and non-contact techniques. Finally, it should be emphasized that neglect of surface roughness, when using an optical method appropriate for uniform-thickness films, produced incorrect values for the thickness and the refractive index of the film, from the analysis of the optical reflection spectra.

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References

- [1] J.C. Manificier, J. Gasiot, J.P. Fillard, *J. Phys. E: Sci. Instrum.* 9 (1976) 1002.
- [2] R. Swanepoel, *J. Phys. E: Sci. Instrum.* 16 (1983) 1214.
- [3] R. Swanepoel, *J. Phys. E: Sci. Instrum.* 17 (1984) 896.
- [4] D.P. Arndt, R.M.A. Azzam, J.M. Bennett, J.P. Borgogno, C.K. Carniglia, W.E. Case, J.A. Dobrowolski, U.J. Gibson, T.T. Hart, F.C. Ho, V.A. Hodgkin, W.P. Klapp, H.A. Macleod, E. Pelletier, M.K. Purvis, D.M. Quinn, D.H. Strome, R. Swenson, P.A. Temple, T.F. Thonn, *Appl. Opt.* 23 (1984) 3571.
- [5] D.A. Minkov, *J. Phys. D: Appl. Phys.* 22 (1989) 1157.
- [6] J.M. González-Leal, E. Márquez, A.M. Bernal-Oliva, R. Jiménez-Garay, *Bol. Soc. Esp. Cerámica y Vidrio* 36 (1997) 282.
- [7] J.J. Ruiz-Pérez, E. Márquez, *Nuevos métodos de caracterización óptica de semiconductores basados en medidas espectroscópicas de reflexión*, Ministerio de Defensa, Secretaría General Técnica, Madrid, 1997.
- [8] V.V. Filippov, *Opt. Spectrosc.* 88 (2000) 581.
- [9] J.J. Ruiz-Pérez, J.M. González-Leal, D.A. Minkov, E. Márquez, *J. Phys. D: Appl. Phys.* 34 (2001) 2489.
- [10] E. Márquez, J.M. González-Leal, R. Jiménez-Garay, S.R. Lukic, D.M. Petrovic, *J. Phys. D: Appl. Phys.* 30 (1997) 690.
- [11] E. Márquez, P. Nagels, J.M. González-Leal, A.M. Bernal-Oliva, E. Smeets, R. Callaerts, *Vacuum* 52 (1999) 55.
- [12] O.S. Heavens, *Optical Properties of Thin Solid Films*, Butterworths, London, 1955.
- [13] Z.U. Borisova, *Glassy Semiconductors*, Plenum Press, New York, 1981.

- [14] J.M. González-Leal, R. Prieto-Alcón, J.A. Ángel, D.A. Minkov, E. Márquez, *Appl. Opt.* 41 (2002) 7300.
- [15] M. McClain, A. Feldman, D. Kahaner, X. Ying, *Comput. Phys.* 5 (1991) 45.
- [16] E. Márquez, J.M. González-Leal, R. Prieto-Alcón, M. Vlcek, A. Stronski, T. Wagner, D. Minkov, *Appl. Phys. A* 67 (1998) 371.
- [17] E. Márquez, J.M. González-Leal, A.M. Bernal-Oliva, R. Prieto-Alcón, P.J.S. Ewen, A.E. Owen, *Phys. Chem. Glasses* 40 (1999) 18.
- [18] E. Márquez, J.M. González-Leal, A.M. Bernal-Oliva, R. Prieto-Alcón, J.C. Navarro-Delgado, M. Vlcek, *Surf. Coat. Tech.* 122 (1999) 60.