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A new study of the refractive-index dispersion of Ag-photodoped thin films of $As_{30}S_{70}$ chalcogenide glass

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Abstract

Optical transmission spectra are very sensitive to inhomogeneities in thin films. In particular, non-uniform thicknesses produce a shrinking on the transmission spectrum at normal incidence. This deformation should be taken into consideration, because not doing so may lead to errors in the values of the refractive index and film thickness. This paper presents a novel method for enabling the transformation of the optical transmission spectrum of a thin film of wedge-shaped thickness into the spectrum of a uniform film whose thickness is equal to the average thickness of the non-uniform film. This leads subsequently to the derivation of the refractive index, the average thickness, as well as a parameter indicating the degree of film thickness uniformity. This optical procedure is applied to the case of Ag-photodoped thin films of the $As_{30}S_{70}$ chalcogenide glass. The refractive-index dispersion is discussed in terms of the single-oscillator Wemple and DiDomenico model.

Keywords: Chalcogenide glass; Ag-photodoped films; Wedge-shaped thin films; Non-uniform thickness; Envelopes of optical transmission spectra

1. Introduction

The effect of inhomogeneities in thin films has a large influence on the optical transmission spectrum [1,2]. Particularly, the interference pattern at normal incidence corresponding to a wedge-shaped thin film is shrunk, and thus calculations based on the analysis of the transmission spectrum alone may lead to serious errors in the values derived for the refractive index and film thickness [3,4]. In this work, a procedure suggested by Swanepoel, which takes into account the profile of the layers, is applied to Ag-photodoped films of the $As_{30}S_{70}$ chalcogenide glass. The method is based on the transformation of the experimental envelopes of the transmission spectrum corresponding to a film of non-uniform thickness, into the envelopes of the spectrum of a uniform film whose thickness is equal to the average thickness of the non-uniform film. This procedure allows the accurate determination of the average thickness, thickness variation and refractive index of the film. It should be emphasized that using this optical method it is possible to obtain accurate information about thin films under study from a transmission spectrum that, otherwise, could become useless.

2. Experimental

The films studied were prepared by thermal evaporation in an Edwards coating unit, model E306A, onto cleaned substrates at a pressure $<10^{-6}$ torr. The evaporation sources for the $As_{30}S_{70}$ films were fragments of melt-quenched glasses, while 99.99% pure Ag wire was the source for the Ag layer depositions. The deposition rates used were ≈ 0.5 and 3–5 nm s^{-1} for the chalco-

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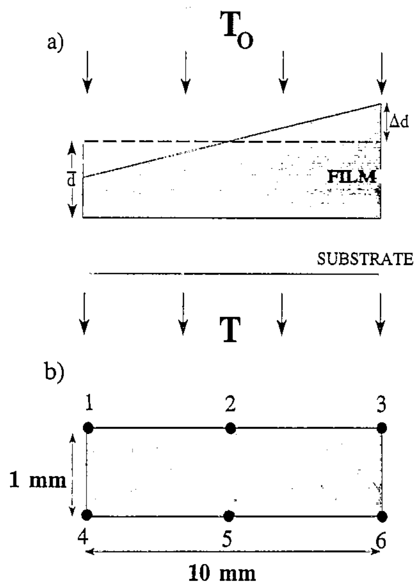

Fig. 1. (a) Wedge-shaped profile of the layer on the substrate. (b) Area of the layer illuminated by the spectrophotometer. The dots indicate the points where the mechanical measurements of thickness were carried out on the films.

genide and Ag layers, respectively. This quantity was continuously measured by the quartz-crystal microbalance technique. Photodoping of the films was achieved by illuminating the samples with a 500 W high-pressure mercury lamp through an IR-cut filter.

The optical transmission spectra at normal incidence were obtained over the 400–2000 nm spectral region by a double-beam UV/Vis/NIR spectrophotometer (Perkin–Elmer, model Lambda-19). It should be remarked that the transmission spectra show that the Ag-photodoped films have non-uniform thickness. This was confirmed by measurements of the film thickness with a surface-profiling stylus. These mechanical measurements were carried out by a set of three measurements on each longer edge of the illuminated area by the spectrophotometer — about 1 × 10 mm — to obtain a single transmission spectrum (see Fig. 1). All measurements reported were made at room temperature.

3. Calculation procedures

The relationships between the experimental envelopes T'_M, T'_m of the non-uniform film and the envelopes T_{M0}, T_{m0} of the uniform film, with a thickness equal to the average thickness of the non-uniform film, are shown by the expressions [5]

$$T'_M = \frac{(T_{M0}T_{m0})^{1/2}}{\chi}\tan^{-1}\left[\left(\frac{T_{M0}}{T_{m0}}\right)^{1/2}\tan\chi\right] \quad (1)$$

$$T'_m = \frac{(T_{M0}T_{m0})^{1/2}}{\chi}\tan^{-1}\left[\left(\frac{T_{m0}}{T_{M0}}\right)^{1/2}\tan\chi\right] \quad (2)$$

where

$$\chi = \frac{2\pi n\Delta d}{\lambda} \quad (3)$$

Δd being a parameter representative of the uniformity of the thickness of the film. It is assumed that the thickness of the non-uniform film varies linearly over the area illuminated by the spectrophotometer according to $d = \bar{d} + \eta\Delta d$, with $0 \leqslant \eta \leqslant 1$ and $\bar{d}$ the average thickness (see Fig. 1).

Eqs. (1) and (2) are two independent transcendental equations in T_{M0}, T_{m0} and χ. In the transparent region $T_{M0} \equiv T_s$ (see Fig. 2), and Eqs. (1) and (2) can thus be solved for T_{m0} and χ in this spectral region using a very fast-converging numerical method. On the other hand, it has been shown in a previous work [5] that the basic equation of interferences, $2n\bar{d} = m\lambda$, can be written as a function of the order number of the available longer-wavelength extreme, m_1, giving the equation

$$2n\bar{d} = \left(m_1 + \frac{l}{2}\right)\lambda \qquad l = 0, 1, 2, 3, \ldots \quad (4)$$

For the longer-wavelength extreme $l = 0$, so the orders of the following extrema are $m_1 + 0.5$, $m_1 + 1$, etc. (In Fig. 2, the longer-wavelength extrema are at $\lambda = 1298$ nm

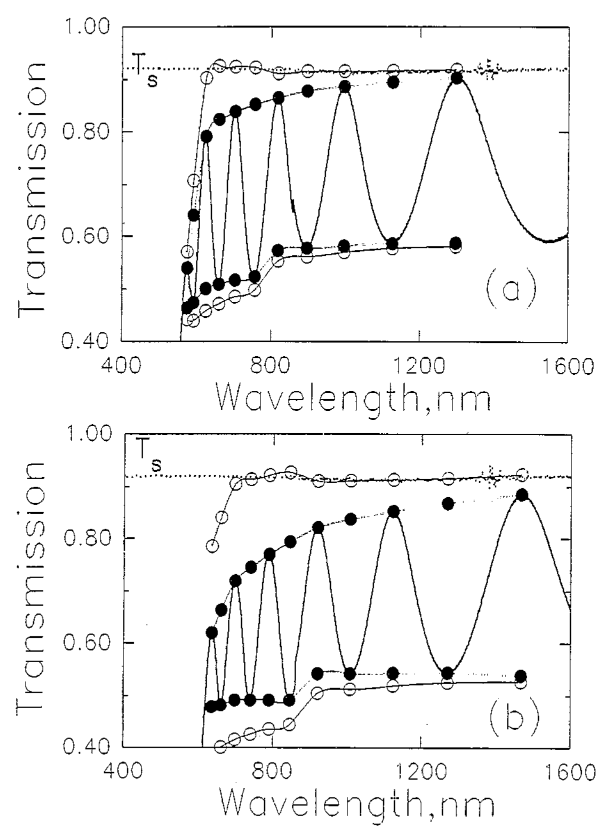

Fig. 2. Interference region of the transmission spectra of two a-$As_{30}S_{70}$ films: (a) photodoped with Ag content of 19 at.%; (b) photodoped with Ag content of 32 at.%. The filled symbols correspond to T'_M and T'_m. The points positioned between experimental interference extrema are calculated by parabolic interpolation. The hollow symbols correspond to T_{M0} and T_{m0}. The transmission spectra of the substrates alone are shown as T_s.

and $\lambda = 1467$ nm.) Next, by combining Eqs. (3) and (4), the following equation is obtained:

$$\frac{l}{2} = \frac{\bar{d}}{\pi \Delta d}\chi - m_1 \tag{5}$$

If $l/2$ is plotted versus χ, the slope and m_1 of Eq. (5) can

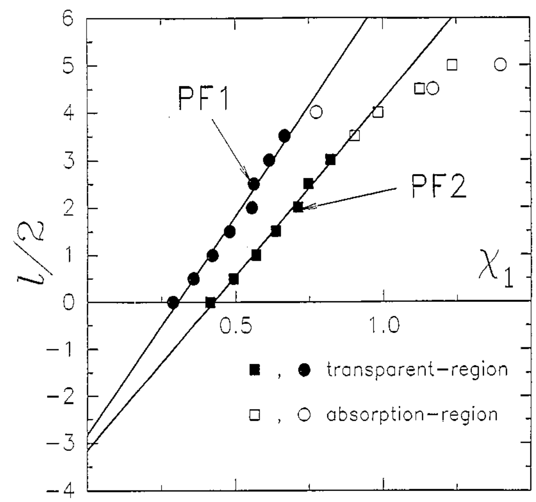

Fig. 3. Plot of $l/2$ against χ_1 in order to determine χ for the photodoped films.

Table 1
T'_M and T'_m are the optical transmittance for the interference extrema according to the envelopes of the shrunk transmission spectra of Fig. 2. T_{M0} and T_{m0} depict the same transmittance after being corrected for the shrinking effect. The values of the refractive index and $\bar{d}$ are simultaneously calculated from T_{M0} and T_{m0} using the uniform-film procedure. The values of $\Delta\bar{d}$-parameters are also shown

Film	λ (nm)	T'_M	T'_m	χ_1	χ	T_{M0}	T_{m0}	n
PF1	1298	0.903	0.588	0.29	0.30	0.919	0.582	2.665
	1127	0.894	0.587	0.36	0.36	0.916	0.578	2.700
	996	0.886	0.582	0.42	0.41	0.915	0.570	2.727
	897	0.878	0.577	0.48	0.47	0.915	0.561	2.762
	819	0.865	0.573	0.55	0.52	0.910	0.554	2.803
	756	0.852	0.524	0.56	0.57	0.922	0.498	2.846
	703	0.838	0.517	0.61	0.63	0.924	0.486	2.887
	660	0.823	0.509	0.67	0.68	0.925	0.472	2.936
	625	0.791	0.501	0.77	0.73	0.903	0.459	2.994
	592	0.641	0.475	1.17	0.79	0.708	0.440	—
	575	0.540	0.464	1.40	0.84	0.571	0.442	—
	$\bar{d} = 731 \pm 24$ nm				$\Delta\bar{d} = 25$ nm			
PF2	1467	0.885	0.541	0.41	0.42	0.922	0.528	2.890
	1270	0.868	0.544	0.49	0.49	0.916	0.526	2.919
	1124	0.853	0.543	0.57	0.56	0.913	0.520	2.953
	1008	0.837	0.543	0.64	0.63	0.911	0.513	2.979
	921	0.882	0.542	0.71	0.69	0.911	0.505	3.024
	846	0.794	0.492	0.75	0.76	0.927	0.444	3.056
	790	0.771	0.492	0.82	0.83	0.922	0.435	3.113
	740	0.746	0.492	0.90	0.90	0.914	0.425	3.159
	699	0.720	0.492	0.98	0.96	0.906	0.415	3.213
	661	0.664	0.482	1.12	1.03	0.841	0.401	3.256
	636	0.620	0.479	1.23	1.10	0.786	0.394	—
	$\bar{d} = 761 \pm 27$ nm				$\Delta\bar{d} = 33$ nm			

be obtained from the regression straight line across the transparent region, as is shown in Fig. 3. The values of χ are shown as χ_1 in Table 1. The deviation of the points for larger χ_1 from the straight line indicates the onset of absorption, and these points must be rejected. The value of χ at each extreme is now calculated from the expression which results from the appropriate rounding of the value of m_1 in Eq. (5). The new values of χ are shown in Table 1. Using these values, together with the values of T'_M and T'_m, T_{M0} and T_{m0} are calculated from Eqs. (1) and (2), and they are also shown in Table 1. These two last sets of values can now be used to derive $\bar{d}$ and $n(\lambda)$ using the optical method for uniform films, discussed in detail in our previous work [5]. Next, the spectral dependence of the refractive index is fitted to the Wemple–DiDomenico relationship [6], that is, the single-oscillator model

$$n^2(E) = 1 + \frac{E_0 E_d}{E_0^2 - E^2} \tag{6}$$

where E_0 is the single oscillator energy and E_d is the dispersion energy. These dispersion parameters can be obtained by the least-squares fit of $(n^2-1)^{-1}$ versus E^2.

4. Results and discussion

Table 1 shows the T_{m0} and χ_1 values obtained by solving Eqs. (1) and (2) for two photodoped films (PF1 and PF2) with Ag contents of 19 and 32 at.%, respectively. The straight lines of Eq. (5) for both films (see Fig. 3) are $l/2 = 9.30\chi - 2.83$ and $l/2 = 7.42\chi - 3.15$, respectively. The m_1 values associated with these equations are rounded to $m_1 = 3$. From T_{M0} and T_{m0}, by applying the method for uniform films, values of average thickness of 731 ± 24 nm and 761 ± 27 nm are obtained for the PF1 and PF2 films, respectively.

Table 2
Mechanical and optical measurements of thickness. The subindices indicate the position according to the pattern of Fig. 1

PF1 (thickness, nm)			
$d_1 = 719$			
$d_2 = 722$	$\bar{d}_{123} = 721$		
$d_3 = 721$		$\bar{d}_{mec} = 737$	$\bar{d}_{opt} = 731 \pm 24$
$d_4 = 743$		$\Delta d_{mec} = 17$	$\Delta d_{opt} = 25$
$d_5 = 766$	$\bar{d}_{456} = 753$		
$d_6 = 750$			
PF2 (thickness, nm)			
$d_1 = 739$			
$d_2 = 746$	$\bar{d}_{123} = 743$		
$d_3 = 744$		$\bar{d}_{mec} = 770$	$\bar{d}_{opt} = 761 \pm 27$
$d_4 = 792$		$\Delta d_{mec} = 27$	$\Delta d_{opt} = 33$
$d_5 = 799$	$\bar{d}_{456} = 797$		
$d_6 = 800$			

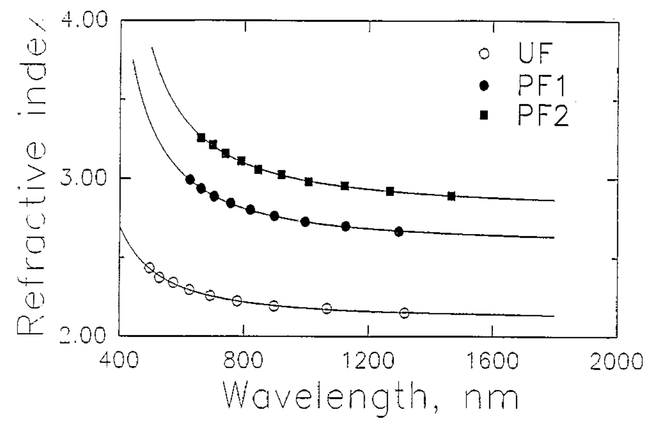

Fig. 4. Refractive index vs. wavelength for the two Ag-photodoped and undoped a-$As_{30}S_{70}$ films. Solids curves are determined according to the single-oscillator analysis.

Moreover, from the slopes corresponding to Eq. (5), once $\bar{d}$ is known, the values of Δd obtained are 25 and 33 nm, respectively. These results show an excellent agreement with the results of the mechanical average thickness measurements that are detailed in Table 2. The refractive indices are simultaneously determined with an accuracy of 3 and 4%, respectively, and they agree with those obtained by a different procedure [4]. Finally, the dispersion parameters obtained by the above-mentioned fits are $E_0 = 3.75$ eV and $E_d = 21.49$ eV for PF1 film, and $E_0 = 3.54$ eV and $E_d = 24.56$ eV for PF2 film. The dispersion curves of the refractive index are shown in Fig. 4, where the dispersion corresponding to an undoped film of a-$As_{30}S_{70}$ is also shown. It should be emphasized that, by making use of the Ag-photodissolution effect in As–S glass films, a substantial degree of control can be exercised over the magnitude of the refractive index and also the optical band gap [7]. In conclusion, the procedure used in this work to determine the magnitude of the thickness variation and the refractive index of wedge-shaped Ag-photodoped $As_{30}S_{70}$ layers has been found to be very efficient and accurate.

References

[1] D. Goldschmidt, *J. Opt. Soc. Am. A*, *3* (1984) 275.
[2] R. Swanepoel, *J. Phys. E: Sci. Instrum.*, *17* (1984) 896.
[3] J.B. Ramírez-Malo, E. Márquez, C. Corrales, P. Villares and R. Jiménez-Garay, *Mater. Sci. Eng. B*, *25* (1994) 53.
[4] E. Márquez, J.B. Ramírez-Malo, J. Fernández-Peña, R. Jiménez-Garay, P.J.S. Ewen and A.E. Owen, *Opt. Mater.*, *2* (1993) 143.
[5] E. Márquez, J.B. Ramírez-Malo, P. Villares, R. Jiménez-Garay and R. Swanepoel, *Thin Solid Films*, *254* (1995) 83.
[6] S.H. Wemple and W. DiDomenico, *Phys. Rev. B*, *3* (1971) 1338.
[7] E. Márquez, J.B. Ramírez-Malo, J. Fernández-Peña, P. Villares, R. Jiménez-Garay, P.J.S. Ewen and A.E. Owen, *J. Non-Cryst. Solids*, *164–166* (1993) 1223.