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On the influence of Ag-photodoping on the optical properties of As-S glass films

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Films of As-S glasses prepared by thermal evaporation were photodoped with Ag. The kinetics of Ag-photodissolution into As-S glass films have been investigated by monitoring the optical transmittance and electrical resistance of the Ag layer, simultaneously, during the process. The analysis proposed by Swanepoel, enabling the determination of the thickness variation, average thickness, refractive index and absorption coefficient of a wedge-shaped film, have succesfully been applied. The refractive-index behavior of the Ag-photodoped chalcogenide glasses under study is analyzed within the oscillator framework proposed by Wemple and DiDomenico.

1. INTRODUCTION

The chalcogenide glasses exhibit a remarkably wide range of photo-induced phenomena including photodarkening, photobleaching and photocrystallization [1]. Many chalcogenides exhibit a metal-photodissolution effect, also known as photodoping, in which illumination causes metal atoms to dissolve into the glass [2]. The mechanism is not fully understood, but it is thought to be a radiation-enhanced solid-state process, involving a three-dimensional intercalation reaction. Initial interest in photodissolution centered on its use as inorganic photoresist in the semiconductor industry and indeed, photo-induced effects on chalcogenides are still under study for applications in this area. Thus, by making use of all these photo-induced phenomena it is possible to produce diffractive optical elements [3].

This paper is concerned with the derivation of the optical properties of non-uniform (wedge-shaped) Ag-photodoped amorphous As-S films using only their optical transmission spectra; the chalcogenide glass compositions under study are $As_{30}S_{70}$ and $As_{40}S_{60}$ and the corresponding Ag-photodoped samples are almost saturated (the Ag/As-S thickness ratio is ≈ 0.3). This is a new approach to the systematic study of the influence of Ag-photodoping on the optical properties of chalcogenide films, based on a very appealing method proposed by Swanepoel [4], which takes into account the lack of uniformity of the undoped and photodoped film thicknesses.

2. EXPERIMENTAL DETAILS

The films used in the present work were prepared by thermal evaporation in a conventional coating unit (Edwards, model E306A) onto cleaned glass substrates at a pressure $< 10^{-6}$ Torr. The evaporation sources for the As-S films were fragments of melt-quenched glasses, while 99.99% pure Ag wire was the source for the Ag films. Electron microprobe analysis of the As-S films indicated that the stated composition is correct to ± 0.5 at.%. Moreover, it is known that the properties of both As-S [5] and Ag [6] layers are affected by the deposition rate: the rates used in this study were ≈ 0.5 and 3-6 nm/s for the As-S and Ag layers, respectively. This quantity was continuously measured by the quartz-crystal microbalance technique.

Photodoping of the chalcogenide films was achieved by illuminating the samples with a 500 W high-pressure mercury lamp through an IR-cut

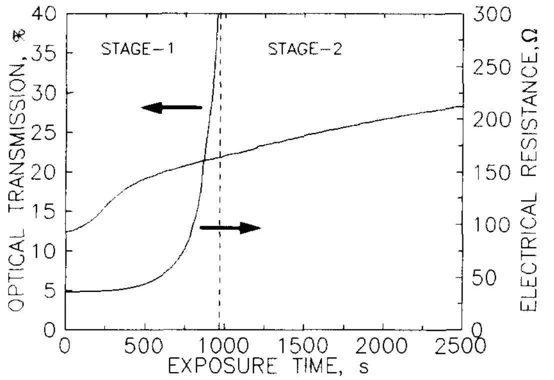

Figure 1. A typical plot of optical transmission and Ag electrical resistance versus illumination time for the photodissolution process in a As-S/Ag combination.

filter. It should be emphasized that the photodoping process does not stop when the Ag film is used up; on the contrary, under the influence of illumination, silver atoms are now supplied from the photodoped region itself. This is not necessarily surprising since it is known that Ag compounds can be used as the photodoping source. Figure 1 shows the electrical resistance of a Ag strip (see our previous work [7] for details) and the optical transmittance of the multilayer structure as a function of exposure time—these two typical plots were obtained using He-Ne laser light as the exciting and probing light of the photodissolution process and an intensity of ≈ 20 mW/cm^2, the initial thicknesses of the Ag and chalcogenide layers being ≈ 30 nm and 460 nm, respectively. It is the disappearance of the Ag layer that accounts for the very rapid increase in the electrical resistance. It is clear from Fig. 1 that the increase in the optical transmission continues after the Ag is consumed, so that photo-dissolution must still be occurring.

The optical transmission spectra were obtained over the 0.3 to 2.0 μm spectral region by a double-beam UV/VIS/NIR computer-controlled spectrophotometer (Perkin-Elmer, model lambda-19). It should be emphasized that the transmission spectra show that the Ag-photodoped As-S glass films have non-uniform thickness. This was confirmed by thickness measurements with a stylus-based surface profiler (Sloan, model Dektak IIA).

3. CALCULATION PROCEDURES

The transmission $T_{\Delta d}$ in the transparent region at a specific wavelength λ, for the case of non-uniform thickness, can be obtained by [4, 8]

$$T_{\Delta d} = \frac{1}{\varphi_2 - \varphi_1}\int_{\varphi_1}^{\varphi_2}\frac{A}{B - C\cos\varphi + D}\mathrm{d}\varphi \qquad (1)$$

where $A = 16n^2s$, $B = (n+1)^3(n+s^2)$, $C = 2(n^2-1)(n^2-s^2)$, $D = (n-1)^3(n-s^2)$, $\varphi = 4\pi nd/\lambda$ with $\varphi_1 = 4\pi n(\bar{d}-\Delta d)/\lambda$ and $\varphi_2 = 4\pi n(\bar{d}+\Delta d)/\lambda$. It is assumed that the thickness varies linearly over the illuminated area so that the thickness is: $d=\bar{d}\pm\Delta d$. Δd refers to the actual variation in thickness from the average thickness $\bar{d}$ and s is the refractive index of the substrate. The integral in eq. (1) yields

$$T_{\Delta d} = \frac{\lambda}{4\pi n\Delta d}\frac{a}{(1-b^2)^{1/2}}\left[\tan^{-1}\left(\frac{1+b}{(1-b^2)^{1/2}}\tan\frac{\varphi_2}{2}\right)\right.$$
$$\left.-\tan^{-1}\left(\frac{1+b}{(1-b^2)^{1/2}}\tan\frac{\varphi_1}{2}\right)\right] \qquad (2)$$

where $a = A/(B+D)$ and $b = C/(B+D)$.

The expression for the envelope around the interference maxima is the following

$$T_{Md} = \frac{\lambda}{2\pi n\Delta d}\frac{a}{(1-b^2)^{1/2}}\tan^{-1}\left[\frac{1+b}{(1-b^2)^{1/2}}\tan\left(\frac{2\pi n\Delta d}{\lambda}\right)\right] \qquad (3)$$

Furthermore, the expression for the envelope around the interference minima can be obtained by changing the sign of C in eq. (1). Thus, the expression for the envelope around the interference minima is

$$T_{md} = \frac{\lambda}{2\pi n\Delta d}\frac{a}{(1-b^2)^{1/2}}\tan^{-1}\left[\frac{1-b}{(1-b^2)^{1/2}}\tan\left(\frac{2\pi n\Delta d}{\lambda}\right)\right] \qquad (4)$$

The range of validity of eqs. (3) and (4) is: $0<\Delta d<\lambda/4n$. In addition, eqs. (3) and (4) are two independent transcendental equations with only two unknown parameters, n and Δd. They can be solved for experimental values using a standard computer method.

Moreover, in the region of weak and medium absorption ($\alpha>0$), the integration (1) should be done over both the film thickness variation and absorbance. This is prohibitively difficult analytically and an approximation would be to consider x to have an average value over the range of integration with respect to Δd. This is

Table 1. Values of λ, T_M and T_m for a typical transmission spectrum of the Ag-photodoped a-$As_{40}S_{60}$ films. The underlined values of transmittance are those calculated by suitable parabolic interpolation.

λ (nm)	T_M	T_m	n_2	Δd (nm)	n_3	x	α (cm^{-1})
1490	0.810	$\underline{0.482}$	3.173	51.0	2.817	0.925	1482
1208	$\underline{0.770}$	0.479	3.274	47.4	2.819	0.898	2045
1015	0.740	$\underline{0.461}$	3.423	41.2	2.894	0.884	2344
880	$\underline{0.716}$	0.445	3.546	36.3	2.968	0.877	2495
798	0.700	$\underline{0.432}$	3.659	32.5	3.072	0.880	2430

an excellent approximation provided $\Delta d << \bar{d}$. The constants a and b are now redefined asfollows: $a_x = Ax/(B+Dx^2)$, $b_x = Cx/(B+Dx^2)$, being $x=\exp(-\alpha\bar{d})$. The equations for the two envelopes now become

$$T_{Mx}=\frac{\lambda}{2\pi n\Delta d}\frac{a_x}{(1-b_x^2)^{1/2}}\tan^{-1}\left[\frac{1+b_x}{(1-b_x^2)^{1/2}}\tan\left(\frac{2\pi n\Delta d}{\lambda}\right)\right] \quad (5)$$

$$T_{mx}=\frac{\lambda}{2\pi n\Delta d}\frac{a_x}{(1-b_x^2)^{1/2}}\tan^{-1}\left[\frac{1-b_x}{(1-b_x^2)^{1/2}}\tan\left(\frac{2\pi n\Delta d}{\lambda}\right)\right] \quad (6)$$

These expressions are again two independent transcendental equations with two unknown parameters, n and x, since Δd is known from solving eqs. (3) and (4) in the transparent region. Equations (5) and (6) have again one unique solution for n and x in the range: $0<x\leq 1$.

4. RESULTS AND DISCUSSION

Firstly, the values of T_M and T_m belonging to an experimental transmission spectrum (the results corresponding to a photodoped $As_{40}S_{60}$ film are analyzed as a representative example) are used in eqs.(3) and (4) to determine the values of n and Δd, shown as n_2 and Δd in Table 1. From the values of Δd of Table 1 it seems reasonable to suggest a value for the thickness variation of $\approx$ 40 nm. The values of T_M and T_m are now used in eqs.(5) and (6) to calculate n and x, shown as n_3 and x in Table 1. In addition, the values of n_3 can be used to derived $\bar{d}$ from the basic equation for the interference fringes, $2n\bar{d}= m\lambda$ (m is the order number of the interference extremes), and also improved values for n as described in detail in a previous work [9]. If this is carried out the value of $\bar{d}$ obtained in this particular case is 526 ± 7 nm.

Next, the spectral dependence of the refractive index is fitted to the Wemple-DiDomenico dispersion relationship, that is, the single-oscillator model [10]

$$\epsilon_1(\nu) = n^2(\nu) = 1+\frac{E_oE_d}{E_o^2-(h\nu)^2} \quad (7)$$

where E_0 is the single oscillator energy and E_d is the dispersion energy. The refractive index for the saturated Ag-photodoped As-S films, along with those corresponding to the undoped chalcogenide films, are shown in Fig.2 as a function of wavelength. The full lines in Fig.2 represent the least-squares fits to eq.(7) and the dispersion parameters E_0 and E_d for the photodoped and undoped layers are presented in Table 2.

The value of $\bar{d}$ is now used to obtain the α-values from the x-values ($\alpha = -(1/\bar{d}) \ln x$). The α-values are listed in the last column of Table 1. Furthermore, the derivation of α in the strong absorption (interference-free transmittance) region is carried out using the Connell and Lewis formulae [11], that is

$$\alpha = -\frac{1}{\bar{d}}\, ln\left(\frac{1}{B}\,(A+[A^2+2BT(1-R_2R_3)]^{1/2})\right) \quad (8)$$

where $A=(R_1-1)\,(R_2-1)\,(R_3-1)$ and $B= 2T(R_1R_2 + R_1R_3-2R_1R_2R_3)$; R_1, R_2 and R_3 are the reflectances of the air-film, film-substrate and substrate-air interfaces, respectively. Next, the optical band gap, E_g^{opt}, has been determined from the α-values using the Tauc's procedure [12], i.e. from the relationship $\alpha(\nu)=K(h\nu-E_g^{opt})^2/h\nu$, where K is an energy-independent constant (see Fig. 3). This equation assumes that the densities of electron states in the valence and conduction bands near the band gap have a parabolic distribution and, also, that the matrix elements for interband

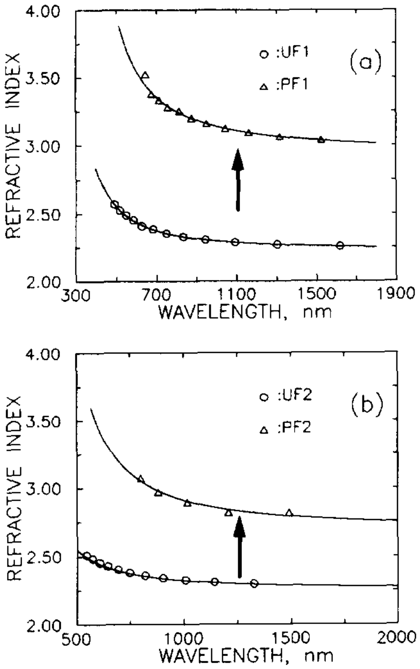

Figure 2. *n* vs. λ: (a) undoped and photodoped $As_{30}S_{70}$ films (UF1 and PF1) and (b) undoped and photodoped $As_{40}S_{60}$ films (UF2 and PF2).

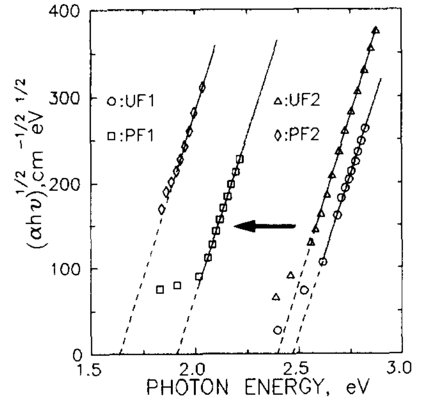

Figure 3. Determination of the optical gap in terms of the Tauc law for Ag-photodoped film samples.

transition associated with photon absorption are equal for all transitions. The value of E_g^{opt} for the glass compositions $As_{30}S_{70}$ and $As_{40}S_{60}$ decreased significantly with the addition of Ag (see Table 2). It is plausible that the photodoped Ag is incorporated with the chalcogen, in this case sulphur, in the chalcogenide layers, which may cause mainly an increase in the ratio of As-As bond in order to satisfy their bonding requirement. Therefore, a decrease in E_g^{opt} by the modification with Ag arise from the smaller binding energies of Ag-S and As-As bonds than that of As-S bonds. Finally, it should be emphasized that 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 optical band gap.

Table 2. Dispersion parameters and optical gap for the undoped and photodoped As-S films.

Sample	E_o (eV)	E_d (eV)	E_g^{opt} (eV)
UF1	4.78	19.03	2.47
PF1	3.58	27.95	1.91
UF2	4.82	19.83	2.39
PF2	3.19	20.23	1.64

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