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Optical reflectivity monitoring of the Ag-photodissolution kinetics in $As_{30}S_{70}$ chalcogenide glass films

E. Márquez *, J. Fernández-Peña, J.M. González-Leal, R. Jiménez-Garay

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz, Ap. 40, 11150 Puerto Real, Cádiz, Spain

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Abstract

The kinetics of the photo-induced solid-state chemical reaction of silver with $As_{30}S_{70}$ chalcogenide glass films in a conventional sandwich structure was measured by monitoring the change in the thickness of the undoped chalcogenide using a modified optical reflectivity technique. A knowledge of the optical constants is necessary for measuring the kinetics of the Ag-photodissolution effect using optical procedures. The kinetics data obtained show that there are two stages in the photo-reaction process: a first, very short one, and the second which goes on for about 94% of the total duration of the process. The latter corresponds to a diffusion-controlled process, leading to a $\sqrt{t}$ dependence for the decrease in the thickness of the undoped $As_{30}S_{70}$ layer.

The photo-induced solid-state chemical reaction between various metals (e.g. Ag, Cu, Zn) and amorphous chalcogenides has been extensively studied in numerous laboratories [1–4]. Interest in this effect (known also as photodiffusion, photodissolution or photodoping) has been stimulated partly by a desire to fully understand the mechanism of the photo-reaction process, and partly by its numerous potential applications in optical recording and, more recently, diffractive optics or optical integrated circuits for IR operation, which requires thick structures to be made in chalcogenide films.

The knowledge of the photo-reaction kinetics in such films is a crucial point in understanding the basic mechanism and its technological applications. Various methods have been used to study the kinetics of the photo-reaction, e.g. measurement of optical transmittance and reflectance, X-ray diffraction and electrical resistance monitoring. In the present study we have used the optical reflectivity technique, modified for measuring the photo-reaction processes in *thick* films of the $Ag/As_{30}S_{70}$ system. This system was chosen because for this combination the Ag-photodissolution effect results in a *homogeneous* glass and the speed of the photo-reaction is reasonably high.

Samples were prepared by evaporating in a coating unit (Edwards, model E306A) onto a cleaned glass substrate first an Ag layer and then an $As_{30}S_{70}$ layer. The $As_{30}S_{70}$ evaporation sources were powdered melt-quenched glasses and the Ag sources were sections of a high purity (99.99%) Ag wire. Electron microprobe analysis (using a Kevex 8000 instrument) indicated that the stated $As_{30}S_{70}$ composition was correct to ±0.5 at%. The $As_{30}S_{70}$ film thickness ranged from 1000 to 1500 nm and the Ag film thickness from 150 to 200 nm, the thicknesses being determined with a quartz-crystal monitor and checked using optical transmission measurements carried out with an UV/VIS/NIR spectrophotometer (Perkin-Elmer, model Lambda-19) and a mechanical stylus (Sloan, model Dektak IIA) with

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* Corresponding author.

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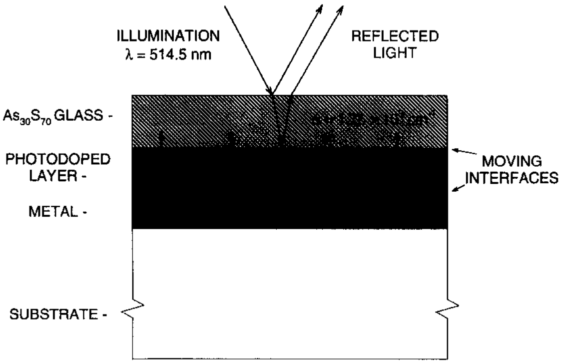

Fig. 1. A schematic cross section through a sample during the photodissolution process.

an accuracy of ±5 nm. During the preparation, care was taken to minimise exposure to light sources, and the samples were kept in complete darkness until required.

The technique used to measure the photodissolution rate has been described elsewhere [5] and is based on the periodic variation in the reflectivity of a thin weakly absorbing film with its thickness due to the interference between light reflected from the top and bottom surfaces of the film. Fig. 1 shows a schematic cross section through a sample during the photodissolution process: there is a *relatively* well-defined interface between the doped and undoped regions of the film and the doped region is generally highly absorbing, so that as the photodoped layer expands towards the top surface of the film, reflectivity changes will be observed due to the decreasing thickness of the undoped layer.

A typical plot of reflectivity as a function of exposure time during one of these experiments is shown in Fig. 2. The time between successive maxima or minima in the curve corresponds to the time required for the thickness of the undoped layer to decrease by $\lambda/2n$, where λ is the wavelength of the light and n is the refractive index of the $As_{30}S_{70}$ chalcogenide glass. At the end of the photodissolution process the thickness of the undoped layer is zero so that the maxima and minima occur when the $As_{30}S_{70}$ layer thickness is an integer multiple of $\lambda/4n$, this integer being 1 for the last minimum, 2 for the last maximum, and so on. In other words, there is an interference condition for the optical reflectivity in this particular case, $4nd = m\lambda$, where d is the layer thickness and m is an integer number, the order number, being odd for minima and even for maxima. This interference condition is based on the fact that the refractive index of the photodoped layer is higher than that belonging to the undoped layer. (It is worth mentioning that for $As_{30}S_{70}$ glass films the refractive-index difference between the more heavily photodoped and the undoped samples is >0.7 over the visible and infrared spectral regions [6].) Therefore, by noting the times corresponding to the maxima and minima it is thus possible to determine how the $As_{30}S_{70}$ layer thickness varies with exposure time.

On the other hand, the illumination of the samples was carried out by a tunable Ar ion laser (Omnichrome, model 543-AP; $\lambda = 514.5$ nm, light intensity ≈ 200 mW cm^{-2}). The angle of incidence was 10°, and the laser beam was chopped and a lock-in amplifier (EG&G, model 5104) was used to detect the reflected light. All the optical measurements reported in this Letter were made at room temperature.

Returning to the typical reflectivity–time trace shown in Fig. 2, it corresponds to a 195 nm Ag/1405 nm $As_{30}S_{70}$ combination and has a simple, almost sinusoidal form. It should be mentioned that the oscillations in the reflectance curves are much less pronounced in the case of the thicker samples. Previous work [5] suggests that if the Ag/$As_{30}S_{70}$ thickness ratio is greater than $\approx 1/3$, the Ag layer will not be entirely consumed when the chalcogenide film is completely photodoped. If this ratio is less than $\approx 1/3$ then the Ag layer will be used up at some point during the photodissolution process. Earlier studies suggested that the process stops

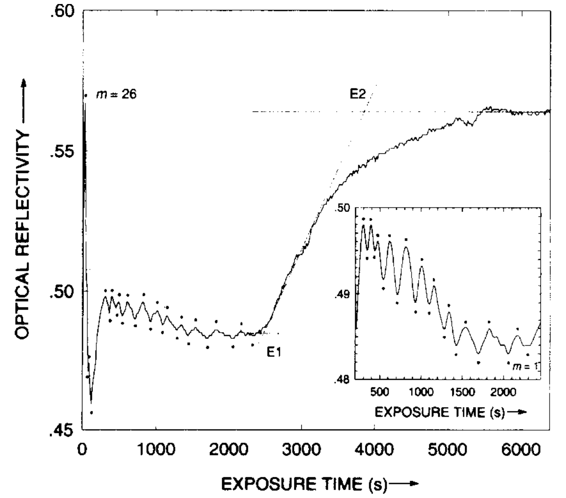

Fig. 2. A typical plot of reflectance versus exposure time for Ag-photodissolution in a 0.2 μm Ag/1.4 μm $As_{30}S_{70}$ combination. The E1 and E2 characteristic points are discussed in the text.

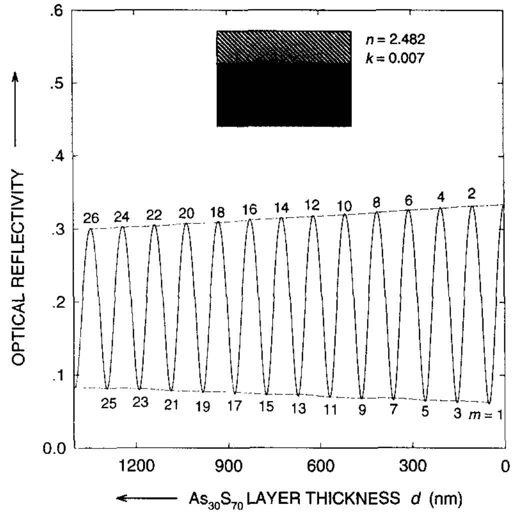

Fig. 3. Predicted reflectance versus *undoped* layer thickness for Ag-photodissolution in a 1.4 μm $As_{30}S_{70}$ film, assuming a perfectly step-like boundary between the photodoped and undoped material. The amplitude of the reflectance oscillations increases slightly as the undoped layer thickness decreases.

when the Ag is consumed, but our own results [6] indicate that the photo-reaction *continues* in this case, presumably using the photodoped layer as the Ag source. For the plot in Fig. 2, the Ag/$As_{30}S_{70}$ thickness ratio was ≈ 1/7 so that the Ag layer thickness decreases to zero at some point during the process.

Two features of the reflectance curve shown in Fig. 2 are difficult to account for, if the sample is regarded as a multilayer system with perfectly step-like boundaries between the different layers. Firstly, such an optical model [7] predicts that the amplitude of the oscillations should increase with time (see Fig. 3) because less light is absorbed in the undoped layer as its thickness decreases. We have derived the optical constants of the non-uniform (wedge-shaped) $As_{30}S_{70}$ glass films using only their transmission spectra and the very appealing and accurate optical procedure proposed by Swanepoel [8–10]; we have found that the values of the refractive index and extinction coefficient for $As_{30}S_{70}$ films at $\lambda = 514.5$ nm are 2.482 and 0.007, respectively. As is clear from Fig. 2, in fact the amplitude of the oscillations decreases notably with exposure time. Secondly, there should be a well-defined end-point in the reflectance curve corresponding to the exposure time at which the photodoped/undoped interface reaches the top surface of the film. In practice, after the oscillations have died out, the reflectance *increases* gradually to a new level. Two characteristic points, E1 and E2, at $t \approx 2480$ s and ≈ 3830 s, repectively, can be defined which approximately mark the onset of the increase in reflectivity, and the effective end-point of the process, respectively. Beyond E2 the reflectance essentially remains constant at the characteristic value of the photodoped material, ≈ 57 %. The gradual change in reflectance between E1 and E2, and the physical significance of the E1 point cannot be explained by this multilayer kinetics model.

In order to explain these optical results it is necessary to propose a more realistic model of the multilayer film structure: the transition from the photodoped to the undoped region is assumed to be *gradual* rather than step-like. This situation matches more closely the observed Ag profile in photodoped films [11] and would account for the gradual change in reflectance between the E1 and E2 points: at E1 the leading edge of the boundary region reaches the top surface of the film and the Ag concentration at the surface then gradually increases (thereby increasing the reflectance) until the trailing edge of the boundary region reaches the surface at time E2 and photodoping is essentially complete. In order that the usual multilayer calculations could be used to determine the reflectance of the system, the Ag concentration was made to vary in discrete steps across the boundary region (made up of 10 layers), and reflectance was found to increase 33% between the characteristic points E1 and E2 [12].

As to the nature of the time dependence of the Ag-photodissolution process, it should be noted that at least five different rate laws have been observed for the kinetics of solid-state chemical reactions and in many cases combinations of these laws apply [13]. In the case of the metal photodissolution effect, previous studies generally report either a linear dependence on time, t, or a square-root time dependence. A linear time dependence indicates that the speed of the process is controlled by a chemical reaction, whereas a $\sqrt{t}$ dependence implies that the diffusion of the metal ions through the reaction product is the rate-limiting step.

Fig. 4 shows the variation of undoped $As_{30}S_{70}$ layer thickness as a function of the square-root of exposure time; it is clear from this figure that after a very short period of time (from $t \approx 300$ s onwards), the undoped layer thickness is proportional to $\sqrt{t}$, indicating that after a first stage there is another, long stage (lasting about 94% of the total duration of the process) in which

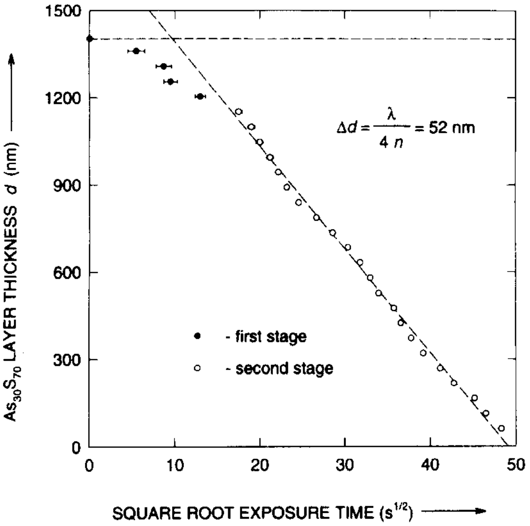

Fig. 4. Undoped layer thickness versus square root of exposure time for a 0.2 μm Ag/1.4 μm $As_{30}S_{70}$ combination.

there is a *diffusion-controlled* process. The gradient of the line corresponding to the second stage is what we define as the "rate" of the process and the value of this parameter for the plot shown in Fig. 4 is 35.5 nm $s^{-1/2}$ (the value of the correlation coefficient corresponding to the least-squares fit for this set of data is 0.996) and the corresponding diffusion coefficient is 1.26×10^{-11} $cm^2\ s^{-1}$.

Regarding the dissolution-limiting step, when the process is diffusion-limited, various workers have pointed out the importance played by the electronic conductivity as the limiting parameter when it is smaller than the ionic conductivity in the photodoped chalcogenide [1]. In this case, consideration of the diffusion equations when mixed (electronic and ionic) conduction occurs (as in the motion of Ag^+ ions through a photodoped layer) leads to a "parabolic" kinetics for the photodissolution reaction with the electronic photoconductivity of the photodoped material being the crucial parameter. In this picture, for the electroneutrality to be maintained during the process, a flux of the electronic carriers through the photodoped region must compensate that due to metal ions. Thus it has been suggested [14] that, if the photodoped material is a p-type semiconductor (and it is reasonable to assume that the Ag-photodoped material should be p-type, as is the case for all undoped chalcogenide glasses [15]), with the holes as the dominant carriers, the actinic light should be absorbed at the photodoped/undoped interface, since the holes can then flow from this region towards the metal in the counter-direction to that of the Ag^+ ions (the electrons are injected into the undoped chalcogenide to assist bond breaking which causes the formation of bonds between metal and chalcogen).

Finally, this investigation has demonstrated that optical reflectivity monitoring is a simple and versatile technique for studying the kinetics of the metal photodissolution effect in chalcogenide glasses.

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