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On the Ag-photodissolution phenomenon in $As_{0.35}S_{0.65}$ chalcogenide glass films

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Abstract

The results of a systematic study of the photodissolution of silver in $As_{0.35}S_{0.65}$ chalcogenide glass films are reported. The silver and chalcogenide glass films were prepared by thermal evaporation. The kinetics of the photodoping process have been investigated in detail by monitoring the time dependence of the electrical resistance of the Ag layer, under illumination by He–Ne laser light, with a view to the determination of the dependence of the electrical resistivity of the silver film on its thickness. In contrast with the behaviour found in other amorphous chalcogenide materials, an induction period was not observed before the onset of the photodissolution effect; instead, the process consisted of a phase of acceleration, followed by one of deceleration. The maximum photodissolution rate and duration of acceleratory period were studied as a function of the light intensity and of the temperature of the sample.

1. Introduction

Photodissolution is a phenomenon observed in metal/chalcogenide layer structures, in which light illumination induces a fast diffusion of metallic species [1]. At the present time, it is accepted [2–4] that this phenomenon involves a photo-stimulated solid-state reaction between the metal and the amorphous chalcogenide. It seems that the kinetics of the PD process, during a short initial period of time, are limited by the rate of the chemical reaction between them, and later, during the longer period, by the rate of the diffusion process of the metallic ions through the product of the reaction [5].

In this work, a systematic study is carried out into the kinetics of the PD process of thin silver films within a-$As_{0.35}S_{0.65}$ layers. First, the photodissolution rate is determined according to the technique proposed by Goldschmidt and Rudman [6], which is based on measuring variation in the electrical resistance of the silver film. The dependence of the electrical resistivity of the silver film on its thickness has been determined experimentally by a novel method based on simultaneous measurements of optical transmittance and electrical resistance. Finally, the influence on the process of both the intensity of the actinic light and the temperature of the sample has been studied.

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2. Experimental

The substrates used during the process were glass microscope slides. Pure strips of powdered silver (99.999%), with physical dimensions of about 2 mm width, 2 cm length and thickness ranging from 25 to 35 nm, were first deposited by thermal evaporation in a conventional coating unit (Edwards E306A) at a pressure of $< 10^{-6}$ Torr onto the substrate, and over these, a second layer of amorphous chalcogenide of ≈ 110 nm was equally deposited by thermal evaporation. The starting material for the chalcogenide film was an ingot of the stoichiometric composition, As_2S_3, prepared by the 'melt-quenching' technique. The rates of deposition used to prepare the samples were 3–5 and 0.5–1 $nm\,s^{-1}$, respectively, for the silver and chalcogenide. By means of a compositional analysis of the glass films (EDAX), it was established as $As_{0.35}S_{0.65}$, to an accuracy of $\pm 0.5\%$.

The light beam used in the PD process was from a He–Ne laser generator, $\lambda = 632.8$ nm (Siemens LGK 7626-S). The maximum possible light intensity was ≈ 60 $mW\,cm^{-2}$. The sample was illuminated at normal incidence, in the spectral range of 0.4–2.0 μm, with a UV/VIS/NIR double beam spectrophotometer (Perkin-Elmer Lambda-19). The electrical resistance of the silver strips was measured with a micro-ohmeter (Keithley 580).

3. Determination of the electrical resistivity of the silver film during the photodissolution process

During the PD process, as the thickness of the silver film decreases, obviously its electrical resistivity increases [7]. In the course of this process, the dependence between the electrical resistivity and the thickness of the silver film can be determined experimentally from the variations of the electrical resistance, ΔR, and the thickness, d, by the expression

$$\rho(d) = \left(\frac{\Delta R w}{l} + \frac{\rho_0}{d_0} \right) d \tag{1}$$

where l and w are the length and width of the photodoped area of the silver strip, ΔR is the difference between the initial resistance and the resistance in any time, and where ρ_0 and d_0 are, respectively, the initial values of the electrical resistivity and of the thickness of the silver film. Both of these can be determined beforehand [8,9]. Next, the rate of change of the silver thickness is determined from the evolution of the optical transmittance during the process [10] by the expression

$$d = d_0 - \frac{1}{\alpha_{Ag}} \ln\left(\frac{T}{T_0} \right), \tag{2}$$

where α_{Ag} is the absorption coefficient of the silver film at the wavelength of the actinic light, and T_0 is the optical transmittance through the sample at the initial moment of the process.

In using expression (2), it has been assumed as a working hypothesis that the time dependence of the optical transmittance in the multi-layer optical system (silver/doped chalcogenide/undoped chalcogenide) depends essentially on the variation of the silver thickness during the PD process. This hypothesis is justified by the fact that, within the spectral range of 0.4–2.0 μm, the absorption coefficient of the silver, α_{Ag}, is significantly greater than that of both the undoped amorphous chalcogenide, α_c, and the doped amorphous chalcogenide α_{dc}. In this experiment, the PD process was performed with discontinuous illumination of the sample, for discrete periods of 180 s. Between each of the consecutive periods, a spectral analysis of the sample by spectrophotometer was performed and, simultaneously, the change of the electrical resistance of the silver film was measured. The experimental results obtained are shown in Figs. 1 and 2. In Fig. 1, it can be observed that the optical transmittance during the process is affected by interference-fringes, which

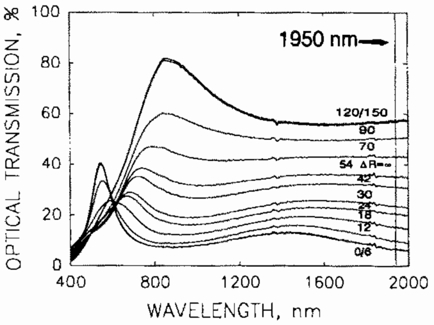

Fig. 1. Evolution of the optical transmission for a photodoped thin film. The illumination time is given in minutes.

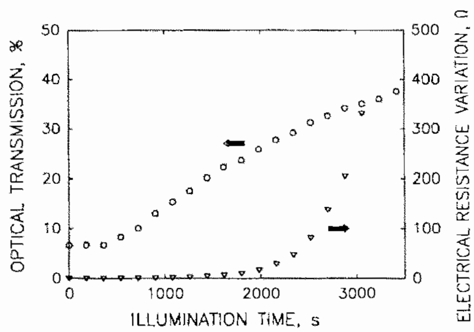

Fig. 2. Dependence of optical transmission and electrical resistance variation on illumination time during the PD process.

gradually vanish as the wavelength increases; this is the reason why the wavelength of 1950 nm was selected for determination of the silver thickness. At this wavelength, the values of the absorption coefficients for the three materials are: $\alpha_{Ag} = 9.2 \times 10^5$ cm^{-1} [11], $\alpha_c = 6.0 \times 10^2$ cm^{-1} [12]. In Fig. 2, the values obtained for the optical transmittance at this wavelength and the variation of the electrical resistance, both as a function of the illumination time, can be observed.

Next, once the initial values of the electrical resistivity and of the thickness of the silver film are known, it is possible to determine the value of the electrical resistivity of the silver film with respect to its thickness according to expression (1). The values obtained for the electrical resistivity in this experiment are plotted vs. thickness in Fig. 3. Appropriate regression curves, for thicknesses greater and less than 12 nm, have been fitted to the data, yielding

(a) $d > 12$ nm,

$$\rho_1(d) = -0.005d'^3 + 0.16d'^2 - 1.32d' + 10.40,$$
$$r = 0.995, \qquad (3)$$

where $d' = d - 10.51$ (d in nm, ρ in ΩW cm).

(b) $d < 12$ nm,

$$\rho_2(d) = \frac{3353.87}{d''^{3.75}} + 0.09d''^2 - 2.60d'' + 23.84,$$
$$r = 0.97, \qquad (4)$$

where $d' = d - 4.43$.

It is noteworthy that the results obtained are similar to those found by Rennie and Elliott [13] for the Ag–GeSe$_2$ system and by Oldale and Elliott [7] for the Ag–GeS$_2$ system, both using an X-ray diffraction technique.

4. Results

Once the dependence of the resistivity of the silver as a function of the thickness, $\rho(d)$, is known, it is possible to establish the kinetics of the PD process by carrying out only measurements of the electrical resistance vs. time while the sample is illuminated.

From Eq. (1), the time-dependence of the silver thickness is obtained. The PD rate of the process is simply given by the derivative of the thickness; the results are shown in Fig. 4. The characteristic periods of acceleration and deceleration [4], together with the absence of the induction period, are clearly

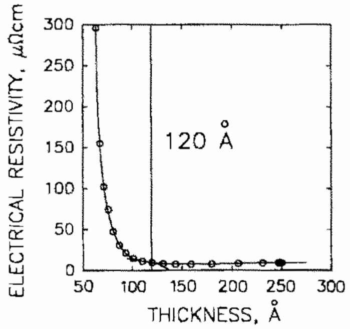

Fig. 3. Computed electrical resistivity as a function of the thickness for thin Ag layers.

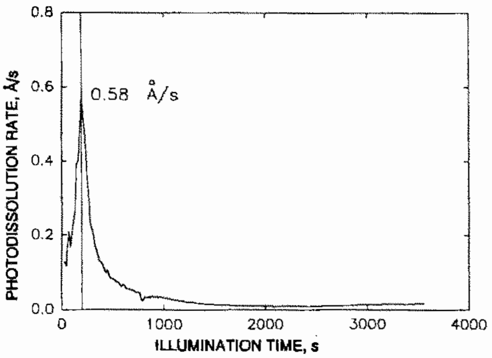

Fig. 4. Photodissolution rate as a function of the illumination time, showing the division into acceleratory and deceleratory phases of the reaction.

observed in the curve. For more detailed information about the process, see Ref. [14].

In order to study the process, two significant quantities have been chosen: the maximum value of the PD rate, $v_{\max}$, and the duration of the acceleration phase, $t_{\max}$.

4.1. Dependence of the kinetics of the PD process on the intensity of the illuminating light beam

The kinetics were studied by varying the beam intensity within the range of 10–50 mW cm^{-2}. The PD process was performed as previously described, at room temperature, in samples having a silver film thickness between 29 and 35 nm and a chalcogenide film thickness of 120 nm. The curves for $v_{\max}$ and $t_{\max}$ as a function of the light intensity are shown in Fig. 5. In both curves, a supralinear dependency of values, $I^{1.45}$ and $I^{-1.57}$, respectively, can be observed.

4.2. Dependence of the kinetics of the PD process on the temperature of the sample

To study this aspect, several experiments were performed, in each of which the sample was held at a constant temperature whose value ranged between 40 and 90°C. The process was performed as already described, in samples with thicknesses between 27 and 29 nm for the silver film and ≈ 108 nm for the chalcogenide film, which were illuminated with a laser beam of 10 mW cm^{-2}. The values of $v_{\max}$ and $t_{\max}$ with respect to the inverse of temperature are plotted in Fig. 6. In both curves, the data can be fitted to an Arrhenian temperature dependence and values of 0.41 and 0.94 eV, respectively, are obtained for the energy of activation.

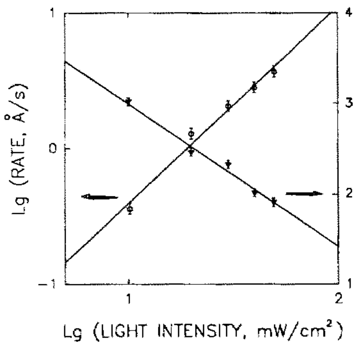

Fig. 5. Influence of the light intensity on the maximum process rate and on the duration of the acceleratory phase.

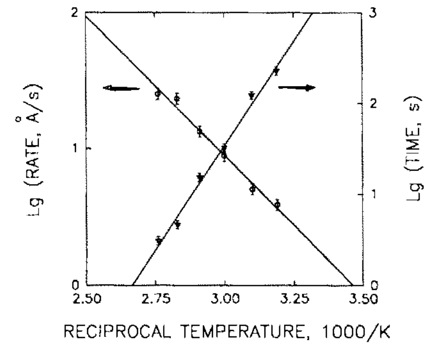

Fig. 6. Influence of the temperature on the maximum process rate and on the duration of the acceleratory phase.

5. Discussion

The data shown in Fig. 5 are comparable to these obtained by Buroff and Baeva [1] for the same combination Ag/As–S but differ from the linear dependency found in other studies [1,6]. This tendency, found for the electrical conductivity of the doped chalcogenide under different conditions of illumination, is similar to that reported by Elliott as a phenomenon of photoconductivity in semiconductor materials [4].

On the other hand, the values of the energy of activation corresponding to $v_{\max}$ and $t_{\max}$, found in the present work, are similar to those obtained by Kostyshin and Minko [15] for the same glassy system. The obtained values of the energy of activation seem to indicate that the kinetics of the PD process is dependent on the temperature. This dependence seems to be a characteristic of solid-state reactions, in which their kinetics are controlled by a process of diffusion. However, it is possible that this is not the only cause, since the doped chalcogenide behaves like a type-p semiconductor [4], as it is known that, as the temperature of these glassy materials increases, so does their electrical conductivity, as a result of the thermal generation of electron-hole pairs. Finally, the difference existing between the values obtained for the energies of activation, according to Rennie [13], seems to indicate the existence of two different processes taking place simultaneously.

6. Conclusions

Based on the kinetic data, $v_{\max}$ and $t_{\max}$, two analyses were carried out, which have enabled the dependence of the kinetics of the process on the intensity of the light beam and on the temperature of the sample to be established. From the first analysis, we conclude that the process of PD in the Ag–$As_{0.35}S_{0.65}$ system is photostimulated, for relatively low values of light intensity (< 50 mW cm^{-2}). Based on the second analysis, the process is strongly thermally activated, when the sample is under conditions of illumination.

References

[1] A.V. Kolobov and S.R. Elliott, Adv. Phys. 40 (1991) 625.

[2] V. Honnig, V.A. Fedorov, G. Liebmann and P. Suptitz, Phys. Status Solidi A96 (1986) 611.

[3] G. Kluge, Phys. Status Solidi A101 (1987) 105.

[4] S.R. Elliott, J. Non-Cryst. Solids 130 (1991) 85.

[5] K. Tanaka, J. Non-Cryst. Solids 137&138 (1991) 1021.

[6] D. Goldschmidt and P.S. Rudman, J. Non-Cryst. Solids 22 (1976) 29.

[7] J.M. Oldale and S.R. Elliott, J. Non-Cryst. Solids 128 (1991) 255.

[8] E. Marquez, R. Jimenez-Garay, A. Zakery, P.J.S. Ewen and A.E. Owen, Philos. Mag. B63 (1991) 1169.

[9] S.G. Tomlin, Br. J. Appl. Phys. 2 (1968) 1667.

[10] T. Kawaguchi and K. Masui, Jpn. J. Appl. Phys. 26 (1987) 15.

[11] P.B. Johnson and R.W. Christy, Phys. Rev. B6 (1972) 4370.

[12] E. Marquez, J. Ramirez-Malo, J. Fernandez-Peña, P. Villares, R. Jimenez-Garay, P.J.S. Ewen and A.E.,Owen, J. Non-Cryst. Solids 164–166 (1993) 1223.

[13] J.H.S. Rennie and S.R. Elliott, J. Non-Cryst. Solids 77&78 (1985) 1161.

[14] J. Fernandez-Peña, E. Marquez, J.B. Ramirez-Malo, C. Corrales, P. Villares, R. Jimenez-Garay and P.J.S. Ewen, An. Fís. 91 (1995) 36.

[15] M.T. Kostyshin and V.I. Minko, Ukr. Fiz. Zh. 29 (1984) 1560.