

# Effect of temperature on the photodissolution of silver in arsenic threesulphide

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**Abstract** — The influence of temperature on the photodissolution of Ag into glassy As<sub>2</sub>S<sub>3</sub> films has been studied by monitoring the changes that occurs in transmission of weakly absorbed broadband light. It was shown that besides of a low induction period, the photodissolution kinetics consists of two linear steps with different activation energies, followed by a parabolic tail. The transitions between photodissolution steps was found to be not monotonous and explained in terms of Elliott's model, which asserts a simultaneous ionic and electronic charge transport controlled by chalcogenide properties, illumination and temperature.

**Index Terms** — Chalcogenides glasses, Dissolution, Kinetics, Photoinduced effects

## I. INTRODUCTION

The phenomenon of photodissolution (synonymously called photodoping or photodiffusion) of certain metals (e.g. Ag) in chalcogenide glasses (ChG) discovered by Kostyshin et al. [1] is of great scientific interests (see an extensive review in ref. [2]).

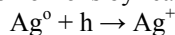
This is due to its application in light, electrons or ions lithography and Programmable Metallization Cell (PMC) technologies (reviews ref. [3] and [4] respectively). Arsenic threesulfide (As<sub>2</sub>S<sub>3</sub>) was the first ChG in which the photodissolution (PD) of metals was observed and, being a typical glassy compound, so far remains the most attractive for investigation of this unique phenomenon.

The experimental investigations of photodissolution [5-7] and migration [8] of silver in glassy As<sub>2</sub>S<sub>3</sub>, ionic conductivity of Ag photodoped As<sub>2</sub>S<sub>3</sub> [9] and electrostatic potential at the Ag-As<sub>2</sub>S<sub>3</sub> interface [10] led to development of a unified mechanism for metal PD in chalcogenide materials [11, 12].

The mechanism suggested for the PD of silver in ChG comprises at least three processes:

1) A solid state chemical reaction between Ag and the chalcogenide, which results in formation of a superionic conductor, that is a ternary Ag-containing ChG with high ( $10^{-5} - 10^{-3} \text{ Ohm}^{-1}\text{cm}^{-1}$ ) ionic conductivity

2) Photo-creation of free holes at the superionic / electronic (doped / undoped) chalcogenide interface, followed by their drift through superionic chalcogenide to Ag layer and production of ions by reaction



3) Motion of Ag ions in opposite direction i.e. towards the boundary doped / undoped chalcogenide through the doped (superionic region)

These processes occur simultaneously and it is not easy to distinguish between them. At the same time they together control the kinetics of PD (plot of Ag layer thickness change versus time), which usually consists of four stages: (I) induction period; (II) linear dependence; (III) square-root dependence and (IV) cessation of PD when Ag layer is exhausted or when the photodoped front has penetrated the entire thickness of the ChG layer. That is why knowledge of the kinetics of photodissolution is essential to distinguish between stages of the PD process and to understand the mechanism of this phenomenon for its applications, particularly in PMC devices [13, 14].

In the present paper we report some new results concerning the influence of temperature on PD of silver in glassy As<sub>2</sub>S<sub>3</sub> measured by monitoring the optical transmittance of a broadband light weakly absorbed in As<sub>2</sub>S<sub>3</sub>.

## II. EXPERIMENTAL PROCEDURES

The samples were prepared by subsequent evaporation of As<sub>2</sub>S<sub>3</sub> and silver in a vacuum of  $10^{-5}$  Torr onto Pyrex glass substrates with a thickness of 1mm. The film thicknesses were kept constant from sample to sample at  $10^3$  nm and 60 nm for the As<sub>2</sub>S<sub>3</sub> and Ag layers respectively.

The effect of temperature on PD was studied by placing the multilayer structure on a resistive electrical heater but a platinum resistance detector Pt-100 close to sample has been used for assisting the temperature control

The PD of silver onto As<sub>2</sub>S<sub>3</sub> was performed by illumination the Ag film, lying on the top of the multilayer structure, through substrate and chalcogenide glass, using the light of a halogen 100W lamp focused by a quartz lens. The integral intensity of applied illumination was  $250 \text{ mW} / \text{cm}^2$ .

The PD rate was measured by monitoring the changes that occur in the transmittance of the sample of weakly absorbed in As<sub>2</sub>S<sub>3</sub> broadband light ( $\lambda > 0.65\mu\text{m}$ ) as photodissolution proceeds. For this purpose a cut filter (KC-15) with transparence range 650-3000 nm was placed behind the sample, i.e. in front of photomultiplier, which served as light detector. A PC with a data acquisition board manufactured by National Instruments Inc. was used for processing.

Figure 1a shows schematically the multilayer structure of the sample. There are three well-defined boundaries: 1) substrate / undoped As<sub>2</sub>S<sub>3</sub>; 2) undoped As<sub>2</sub>S<sub>3</sub> / photodoped material (solid electrolyte); 3) photodoped material / Ag. During the photodissolution the boundary between photodoped material and undoped As<sub>2</sub>S<sub>3</sub> propagates towards the substrate, but the boundary between photodoped material and Ag propagates in opposite direction i.e. towards surface, so that the thickness of both Ag layer and undoped As<sub>2</sub>S<sub>3</sub> glass decrease with time.

The movement of the boundary between photodoped and undoped As<sub>2</sub>S<sub>3</sub> was used to measure the photodissolution rate by technique based on monitoring the changes that occur in reflectivity of the sample [7] but the movement of the boundary between photodoped material and Ag was

used for the same purpose by technique based on continuous measurement of silver layer resistance [9, 11]. In the present work we tracked the movement of boundary between photodoped material and Ag layer measuring the transmission of weakly absorbed in ChG light with PD of silver in progress. This method allows to track the evolution of transmission spectra of the two-layer structure as PD proceeds, which can give information about the last stage of PD when the Ag layer exhausts.

### III. RESULTS AND DISCUSSIONS

Figure 1b shows the optical transmission of the two-layer structure  $As_2S_3 / Ag$  (broadband light  $\lambda > 0.650 \mu m$ ) versus exposure time as PD proceeds, at several temperatures. The dot line indicates the transmittance of pure  $As_2S_3$  film without Ag layer. It is seen that independent on temperature the transmission in the region of weakly absorbed light recovers to that of  $As_2S_3$  before Ag evaporation with increase of the exposure time. Obviously this is due to a decrease of Ag layer effective thickness: the absorption coefficient of Ag film in this region of spectrum, being of about  $10^5 cm^{-1}$  [15], is much higher than absorption coefficient of doped / undoped  $As_2S_3$  double layer, which is less than  $10^2 cm^{-1}$  [16].

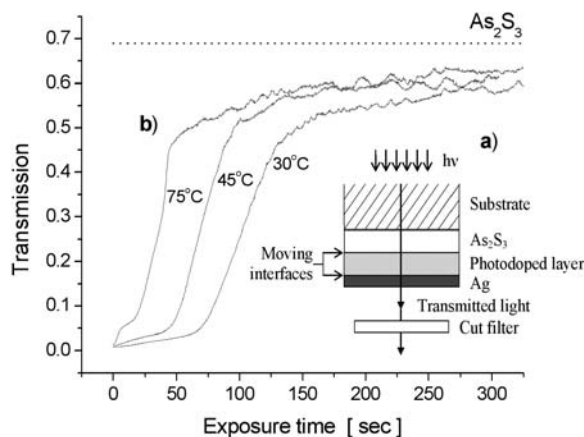


Fig.1 a) Schematic cross section through a sample during the photodissolution process; b) Transmission of a broadband light  $\lambda > 0.65 \mu m$  of two-layer structure vs. exposure time

Hence, the PD rate of Ag can be estimated by measuring the recovery rate of optical transmission of two-layer structure  $As_2S_3 / Ag$  in IR region of spectrum if the thickness dependence of Ag film transmittance is a priori known. The instantaneous transmission of unreacted Ag layer ( $T_{Ag}$ ) and that of the whole two-layered  $As_2S_3 / Ag$  structure ( $T$ ) are interdependent as  $T_{Ag} = T / T_0$ , were  $T_0$  is the transmission of pure  $As_2S_3$  layer on glassy substrate.

We have calculated and plotted the thickness of unreacted Ag film versus exposure time (PD kinetics) applying our experimental data ( $T_{Ag}$ ) to the thickness dependence of transmission spectra of silver films measured by X. Sun et al. [17]. The error of such a method is mainly due to progressive light absorption in doped layer during PD. The relative error of transmission, being minimal at the beginning of PD process, becomes maximal of about 5-10% closely to its finish. However, the transmission of Ag layer below 20 nm increases very rapidly with decrease of its thickness [17]. Therefore the

error in Ag thickness determination below 20 nm, by 10% error in transmission of unreacted Ag film, is assessed to be of about 1 nm.

Figure 2 shows the unreacted Ag layer thickness vs. exposure time for different temperatures. Several steps of PD kinetics can clearly be distinguished: (I) the relatively slow step observed only at curve measured at 30°C; (II) the second one, where the thickness of Ag layer linearly decreases with exposure time, but the slope (the PD rate) is strongly influenced by temperature; (III) the third step that is also linear but with a slope only slowly dependent on temperature; and a final step (IV), which exhibits a sub linear dependence of thickness change of Ag layer on time, particularly observed at low (less than 60°C) temperatures.

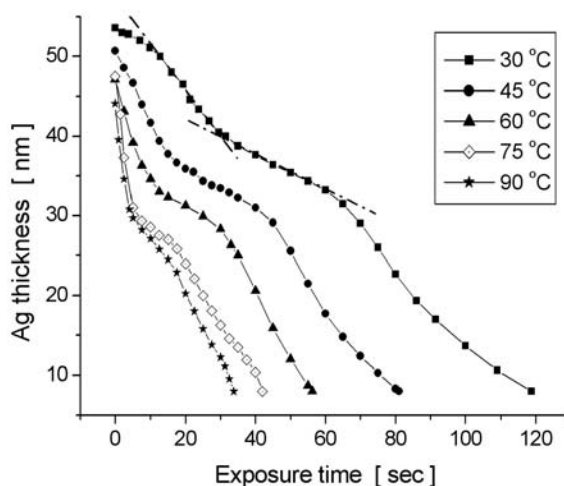


Fig.2 Decrease of Ag film thickness versus exposure time at various temperatures

The segmentation of PD kinetics curve into several distinct sections is of course not new and has been done by everybody studying PD process [2, 9, 12]. None the less, here we observed some new peculiarities of PD kinetics, which can play an important role in further understanding the PD mechanism. First it should be mentioned that the kinetics can be divided into four distinct sections instead of three or even two sections usually observed. Secondly, with exception of transition between the first and second steps, the transitions between other steps are not monotonic but rather sharp. We suppose that the reason for these peculiarities of PD kinetics is due to the special conditions of our experiment, which imply the high intensity of illumination applied ( $250 mW/cm^2$ ), the thick films of silver ( $\sim 60nm$ ) combined with a direct measurement of optical transmission of the sample as the photodissolution proceeds. Our results are consistent with unified model for metal PD in amorphous chalcogenide materials proposed by Elliott [12] and, what is more, they bring to light the experimental confirmation of some theoretical predictions underlined in this model.

The first step of PD kinetics, were the PD is very slow (in our experiments observed only at 30°C), is ascribed to so called "induction period" generally observed in solid state photoinduced reactions between metals and chalcogenide glasses [2]. The origin of the induction period was suggested [12] to be the lateral diffusion of metal in ChG between dendritic nuclei of reaction product. It depends on intensity and wavelength of illumination [18]

and strongly decreases with temperature increase [9]. Namely the last explains why the induction period observed on the kinetic profile (Figure 2) measured at 30°C disappears on the curves measured at higher temperatures.

The second step is a period during which the reaction proceeds at an approximately constant rate for each temperature, but this rate strongly increases with temperature increase. Figure 3a shows the temperature dependence of PD rate at this stage plotted in Arrhenius coordinates. The slope of the obtained line exhibits a rather high value of 0.34 eV that indicates a high effect of temperature on PD process. The constant rate of photodissolution is generally agreed to be determined by reaction between metal and ChG, which occurs simultaneously in two different spatial regions of the sample: (I) absorption of photons by breaking As–S bonds that results in a simultaneous producing of non-bridged chalcogen atoms with a single unpaired electron (dangling bond) and generation of free holes at or near the doped / undoped interface, and (II) creation of Ag<sup>+</sup> ions at the Ag / doped As<sub>2</sub>S<sub>3</sub> interface were photogenerated holes, after the drift through doped layer react with neutral Ag atoms. In turn, Ag<sup>+</sup> ions after the drift towards the doped / undoped interface accept the unpaired electron from chalcogen dangling bond and a photodoped ternary Ag–As–S compound is created. Thus, the reaction limited step of PD depends either on electronic (hole) photoconductivity of doped layer  $\sigma_{ph}$  or its ionic conductivity  $\sigma_{Ag^+}$ .

Investigation of the effect of temperature on the PD kinetics allows in principle to distinguish between effects of photoconductivity  $\sigma_{ph}$  and ions conductivity  $\sigma_{Ag^+}$  of doped layer on reaction rate. To date was found that PD process of Ag into As<sub>2</sub>S<sub>3</sub>, being thermally activated, exhibits activation energy of 0.1 – 0.2 eV [9, 11, 19]. Such a relatively weak temperature dependence of PD kinetics is usually ascribed to photoconductivity and the solid state reaction is assert to be limited by the holes flux under condition  $\sigma_{ph} \ll \sigma_{Ag^+}$ .

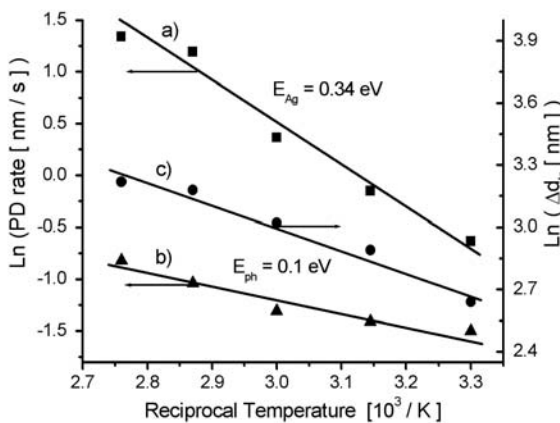


Fig.3 Arrhenius plot for the second (a) and third (b) stages of PD kinetics; c) Temperature dependence of thickness of Ag layer photodissolved before transition between two linear steps of PD occurs

The opposite situation, that is  $\sigma_{ph} \gg \sigma_{Ag^+}$ , means the reaction rate limitation by Ag<sup>+</sup>-ion conductivity. It has not been observed experimentally so far, but was predicted by

Elliott [12] to exhibit the activation energy in the range of 0.3÷0.5 eV. We suppose that our experiment confirms this prediction. The high temperature dependence observed on the second step of PD process, which exhibits activation energy E<sub>Ag</sub> = 0.34 eV indicates that Ag<sup>+</sup> ion conductivity becomes rate-limiting. It is interesting to note that the activation energy of “superionic conductor” Ag<sub>2.6</sub>As<sub>2</sub>S<sub>3</sub> synthesized by I. Plocharscki and coworkers [9] was found to be the same, i.e. 0.34 eV that confirms our assert.

The third step of PD kinetics shows also a linear dependence of the change of Ag thickness on time, but its slope only slowly increases with temperature increase. Figure 3b illustrates the photoreaction rate estimated from third step of PD kinetics versus temperature in Arrhenius coordinates. The slope of this line exhibits a relatively low value of 0.1 eV, which as mentioned above, should be attributed to activation energy of photoconductivity, i.e. E<sub>ph</sub> ≈ 0.1eV. In fact, the photoconductivity of photodoped As<sub>2</sub>S<sub>3</sub> thin layer exponentially increases with temperature increase, but the activation energy depends both on light intensity and temperature regime. At high intensities and temperatures 300-370K (applied in present work) the activation energy was found to be of 0.9 – 0.14 eV [20], which comprises estimated from the third step of PD value E<sub>ph</sub> ≈ 0.1eV. Thus, the PD kinetics on the third step is a reaction limited process, but it is controlled by photoconductivity  $\sigma_{ph}$  under condition that

$$\sigma_{ph} \ll \sigma_{Ag^+}.$$

The transition from the ion conductivity limiting to photoconductivity limiting is probably due to increasing in time both of the concentration C<sub>Ag<sup>+</sup></sub> and mobility μ<sub>Ag<sup>+</sup></sub> of Ag<sup>+</sup> ions in doped region, but the first reason seems to be the main. The transition point corresponds to situation when

$$\sigma_{Ag^+} \approx \sigma_{ph} \sim \exp\left(-\frac{E_{ph}}{kT}\right) \quad (1)$$

where k is the Boltzman’s constant and T – is the thermodynamic temperature. On the other hand, assuming the homogeneity of silver ion concentration in the doped layer,

$$\sigma_{Ag^+} \sim C_{Ag^+} \sim \Delta d_{tr} \quad (2)$$

where Δd<sub>tr</sub> is the thickness of the photodissolved Ag layer until the transition to photoconductivity limiting occurs (transition point). Consequently, the proportionality as:

$$\Delta d_{tr} \sim \exp\left(-\frac{E_{ph}}{kT}\right) \quad (3)$$

should be expected. The ln(Δd<sub>tr</sub>) versus reciprocal temperature is plotted in figure 3c. The slope of the presented line is approximately 0.1 eV which coincides with activation energy E<sub>ph</sub> calculated from temperature dependence of photoreaction rate, related to third step of PD process. Obviously, this coincidence confirms our suggestion concerning the nature of a sharp transition between the second and the third steps of PD kinetics.

The final (fourth) step of PD kinetics is a deceleratory stage of the process, particularly visible at low

temperatures. It appears to be a quasi-parabolic step, i.e. with a square-root dependence of Ag thickness on time.

Figure 4 shows the thickness change of Ag layer as a function of square root of exposure time for different temperatures related to the last step of PD kinetics. One can see that each of curves is a straight line that characterizes a diffusion controlled process. Such a PD process is consistent with model [12] wherein both ionic and electronic charge transport occur simultaneously by the condition that the flux of ions  $j_{Ag^+}$  balances that of holes  $j_h$  in reverse direction:

$$j_{Ag^+} = -j_h \quad (4)$$

Each of curves from Figure 4 can be described by relation:

$$\Delta d_T = A_T t^{\frac{1}{2}} \quad (5)$$

The coefficient of proportionality  $A_T$  seems not much to depend on temperature and was assessed [12] as:

$$A_T = (2K_T)^{\frac{1}{2}} = \left( \frac{2\sigma_{ph} \Delta\mu_{Ag}}{C_{Ag^+} F^2} \right)^{\frac{1}{2}} \quad (6)$$

where  $\sigma_h$  is the electronic (hole) conductivity of doped ChG,  $\Delta\mu_{Ag}$  is the difference between the chemical potentials of Ag at Ag / doped  $As_2S_3$  and doped / undoped  $As_2S_3$  interfaces (Figure 1a),  $F$  is the Faraday constant.

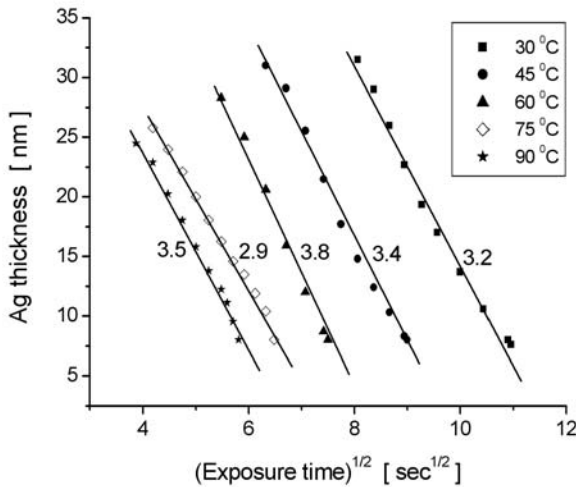


Fig.4 Decrease of silver thickness vs. exposure time at fourth (quasi-parabolic) step of PD. The number by each curve shows the photodiffusion coefficient  $K_T$  multiplied by  $10^{13} \text{ cm}^2\text{s}^{-1}$

The values of coefficient  $K_T$  can be estimated from the slope of these curves. One can see that the slope of the lines in Figure 4 does not vary essentially no monotonically with temperature. The values of the coefficient  $K_T$  (shown in Figure 4 by each curve) are in the range of (2.9 – 3.8)  $\cdot 10^{13} \text{ cm}^2\text{s}^{-1}$ . These values are with three orders of magnitude higher than either the thermodiffusion coefficient of Ag in  $As_2S_3$  determined experimentally [9] or its value estimated by indirect calculations [12]. An essential increasing of parabolic constant  $K_T$  in a PD process comparative with its dark value in a thermodiffusion process was predicted by Elliott [12] and

obviously is due to a high photoconductivity of Ag doped ChG. Namely the photoconductivity  $\sigma_{ph}$  is involved as electronic conductivity in equation (6), but as shown in [20], the photoconductivity of doped  $As_2S_3$  layer ( $As_2S_3Ag_{0.15}$ ) is much higher than its dark conductivity, particularly at low temperatures and high light intensities.

#### IV. CONCLUSION

The kinetics profile of Ag photodissolution in glassy arsenic threesulphide comprises two linear steps followed by a parabolic tail. The temperature strongly influences only the first linear step, which is ascribed to ion conductivity limiting solid-state reaction. The second linear step is ascribed to photoconductivity limiting, but the parabolic tail appears to be derived from diffusion controlled processes respectively. The diffusion coefficient varies not essentially no monotonically with temperature, being of about  $(2.9 - 3.8) 10^{13} \text{ cm}^2\text{s}^{-1}$ .

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