

PHOTODOPING OF GLASSY ARSENIC CHALCOGENIDE FILMS BY ZINC

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Thermo- and photodoping of glassy As_2S_3 , As_2Se_3 and $As_{50}Se_{50}$ films by Zn is investigated. Zn dissolution and Zn diffusion processes were studied separately. Threshold temperatures for beginning of the photodissolution and thermodissolution were determined for all three types of chalcogenide films. The study of the etching rate of doped chalcogenide films in some liquid etchants and of Zn depth profile by the method of Auger spectroscopy clearly showed the existence of photo- and thermoinduced diffusion of Zn in the chalcogenide materials under investigation. The difference between these two processes was pointed out.

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1. Introduction

The photodoping of chalcogenide glassy semiconductors by silver has been the subject of numerous investigations (see the review papers [1, 2] and the more recent articles [3, 4]). On the contrary, the photodoping of these materials by Zn is very poorly studied in spite of several features of the process, which are important for practical applications [5-7]. It is known that the effect of photodoping can be divided into two phenomena: photodissolution of the metal and photodiffusion of the metallic atoms in chalcogenide glass [1]. In the case of photodoping by silver both of these phenomena are studied while for the Zn photodoping, only Zn photodissolution was investigated. Besides, many characteristics of Zn and Ag photodissolution in glassy As_2S_3 films were shown to be distinctly different [5-7].

In the present paper we demonstrate some characteristics of Zn photodissolution in glassy films of several arsenic chalcogenides and report the first results of study of Zn photodiffusion in these films. We used two main methods: the recording of a rate of chalcogenide films etching in some liquid etchants and the Auger Electron Spectroscopy (AES) analysis combined with Ar sputtering depth profile, allowing to record the in-depth Zn distribution in the doped samples.

2. Samples preparation and experimental technique

The samples for experiments on etching of doped films were prepared by the sequential vacuum deposition ($\sim 5 \times 10^{-6}$ Torr) of a thin chalcogenide film ($d = 0.05 \mu\text{m}$), a Zn layer ($d = 100 - 300 \text{ \AA}$) and a second chalcogenide film ($d = 0.5 - 2.0 \mu\text{m}$) onto transparent microscope slides under a pressure $\sim (1-3) \times 10^{-6}$ Torr. All three films were prepared without breaking vacuum by using two different heated crucibles for chalcogenide glass and for Zn. The first thin chalcogenide film was used since Zn could not be condensed uniformly onto oxide glass substrate.

The samples for AES measurements contained a first very thin Ni layer ($d = \sim 50 \text{ \AA}$) deposited onto microscope slide, followed by a film of chalcogenide glass ($d = 0.5 - 2.0 \mu\text{m}$), a Zn layer

($d = 100 - 300 \text{ \AA}$) and a second very thin Ni layer. The Ni layers were used in order to avoid charging of the samples when they were bombarded by Ar ions in the process of determination of the depth profile of Zn and other elements. The same samples, but not containing Ni layers were used for the study of Zn photo- and thermodissolution in chalcogenide films. The films of As_2S_3 , As_2Se_3 and $\text{As}_{50}\text{Se}_{50}$ chalcogenide glasses were investigated in this research.

The data about the zinc thermo- and photodissolution in chalcogenide films were obtained from kinetics of optical transmission changes in the sample, and for this aim the two He-Ne laser beams installation [8, 9] was used. One weak beam (probing beam) allowed to determine transmission of the sample and the second, more intense beam caused the Zn photodissolution

The rate of etching of the non-irradiated and irradiated samples in some etchants was studied using a thin film interference technique [10, 11]. Our installation of interference etching contained a semiconductor laser working at $\lambda = 910 \text{ nm}$. This light is very weakly absorbed in all studied films, what is important for interpretation of obtained results. The laser beam passes through the sample placed in the bath with etching solution and then it is received by the Si-photodiode. Changes of photocurrent in the process of etching were recorded by a computer.

The elemental composition of the samples at the surface and in-depth concentration distributions ("sputter depth-profiling") were estimated by PHI 549 SAM/AES/XPS apparatus with usual pressure of 1×10^{-9} Torr in the chamber and CMA (cylinder mirror analyzer). Quantitative analysis was based on atomic sensitivity factors [12] and was done from the general survey spectra. Sputtering procedure was done by the differential pumped small-spot ion gun (IQE 12/38) under Ar pressure 1×10^{-7} Torr and power supply 3 kV with the sputtering yield of $\sim 20 \text{ \AA}/\text{min}$.

3. Results and discussion

3.1. Zn dissolution in chalcogenide films

Fig. 1 shows the typical temperature dependence of the Zn- As_2S_3 structure transmission both in darkness and with irradiation of the sample. It is seen that the substantial change of transmission (it means, the dissolution of the Zn layer in the As_2S_3 film) in darkness starts at $115 - 120 \text{ }^\circ\text{C}$, while under the action of light, the beginning of the transmission increase is observed at $70 - 75 \text{ }^\circ\text{C}$. We can conclude that in the temperature range $80 - 110 \text{ }^\circ\text{C}$ the Zn photodissolution proceeds without any participation of dark dissolution. In the next research, when the Zn photodoping (both photodissolution and photodiffusion) was studied, the samples were kept at 90°C , while the thermodoping (both thermodissolution and thermodiffusion) was investigated at temperatures $> 120 \text{ }^\circ\text{C}$. The similar temperature dependences were obtained for the Zn- As_2Se_3 and Zn- $\text{As}_{50}\text{Se}_{50}$ structures. In these cases, the Zn dissolution started at temperatures $85 - 95 \text{ }^\circ\text{C}$ and $55 - 70 \text{ }^\circ\text{C}$ in the darkness and at the laser irradiation, respectively.

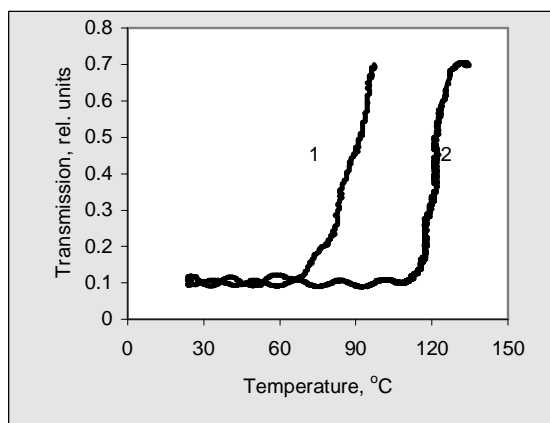


Fig. 1. Temperature dependence of optical transmission of the As_2S_3 -Zn- As_2S_3 sample in darkness (2) and with irradiation by the He-Ne-laser light (1).

Typical kinetics of Zn photodissolution at constant temperature 90 °C for the Zn-As₂S₃ structure is represented in Fig. 2. This characteristic clearly shows three stages of the Zn photodissolution process, namely initial induction period, the stage of effective dissolution and the final stage, the saturation of dissolution (probably connected with exhaustion of Zn) just as well as it was observed at the Ag photodissolution in various chalcogenide glassy films [1].

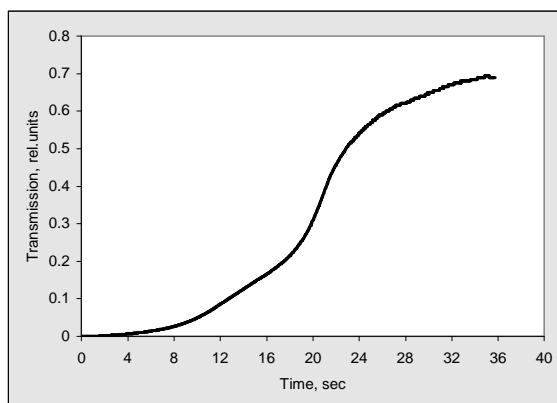


Fig. 2. Kinetics of change in optical transmission of the As₂S₃-Zn-As₂S₃ sample irradiated with the He-Ne-laser light ($\lambda = 633$ nm) of intensity 2.75 W/cm² at temperature 90 °C.

3.2. Rate of chalcogenide films etching in liquid etchants

Typical curves, characterizing etching of the As₂S₃-Zn-As₂S₃ structure in etchant on the base of isoamylamine are shown in Fig. 3. It is seen that if the studied structure was neither heated nor irradiated, the etching curve contains 7 periods and indicates the uniform etching of the whole As₂S₃ film (Fig. 3a). The similar form of the etching curve (7 periods) was recorded for this structure heated in darkness at 90°C during 30 min. After irradiation of the structure at 90 °C during 20 s, only 4 periods can be recorded (Fig. 3b), and we can conclude that an essential part of the As₂S₃ film was doped by Zn (we know that doping of chalcogenide film by Ag results in strong decrease of the etching rate [1], and probably the same effect is characteristic also for the Zn doping). The curves shown in Fig. 3 permit to obtain the real etching characteristics if we know the initial thickness of the sample (1.6 μ m), the refractive index of the chalcogenide film (2.3) and the wavelength of the light (0.91 μ m).

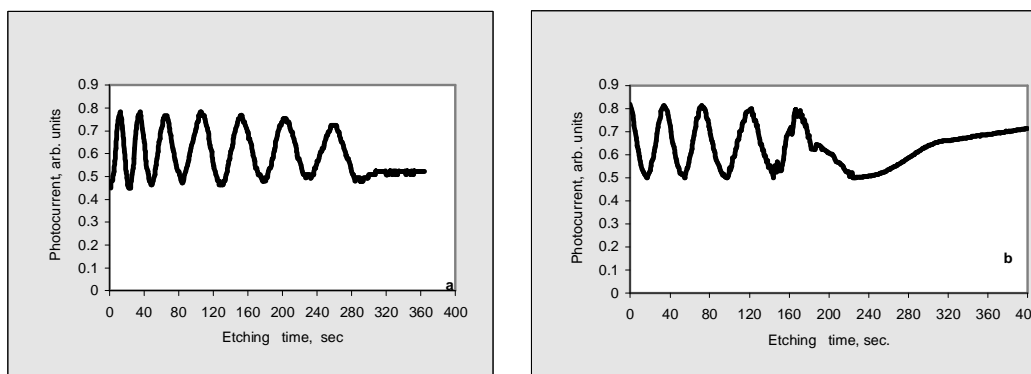


Fig. 3. Interferograms obtained at etching of non-treated As₂S₃-Zn-As₂S₃ structure (a) and of the same structure irradiated from halogen lamp during 20 s at 90 °C (b).

Such characteristics for the As₂S₃-Zn-As₂S₃ structure, irradiated at 90 °C by light of halogen lamp during different periods of time, are demonstrated in Fig. 4. These characteristics show the film

thickness etched for the certain time. It is important to stress that the initial parts of characteristics at small time of irradiation coincide with the dissolution curve obtained for the non-irradiated structure. The deviation from this curve of the initial part of characteristics at larger irradiation time (20 s) is due to effect of photostructural transformations in the As_2S_3 film which are accompanied by the change of the etching rate.

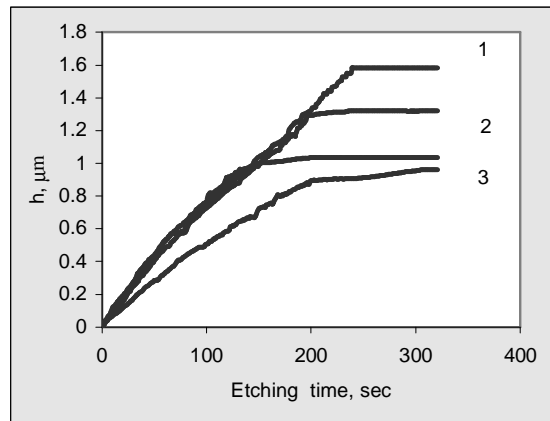


Fig. 4. Characteristics of etching of non-treated As_2S_3 -Zn- As_2S_3 structure (1) and of the same structure irradiated from halogen lamp during 5 s (2), 10 s (3) and 20 s (4) at 90 °C.

The characteristics of etching for the $\text{As}_{50}\text{Se}_{50}$ -Zn- $\text{As}_{50}\text{Se}_{50}$ structure in etchant on the base of ethylenediamine are shown in Fig. 5. They are similar to that for the As_2S_3 -Zn- As_2S_3 structure, but in this case much larger time is necessary in order that Zn could diffuse to the same thickness of the chalcogenide film. Big deviation of the curves for irradiated structures from the curve of the non-treated structure in this case is probably due to strong photoinduced structural transformations in the $\text{As}_{50}\text{Se}_{50}$ film.

The obtained results allow to conclude that we really record the Zn photodiffusion into chalcogenide glassy films and it is the first case of the direct confirmation of the Zn diffusion process. Unfortunately, from these data we can not say anything about the Zn distribution inside the sample and can only record the appearance of Zn in certain areas of the chalcogenide film. This conclusion is based on a drastic decrease of the etching rate even at a minor amount of Zn in chalcogenide glass (this opinion was confirmed by our special experiments). Information about the Zn distribution inside the chalcogenide film was obtained using the method of Auger spectroscopy.

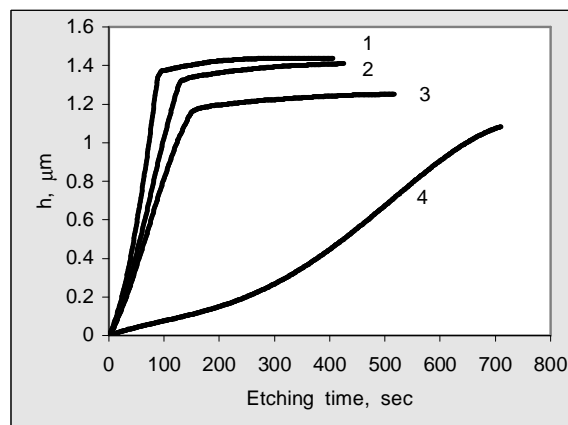


Fig. 5. Characteristics of etching of non-treated $\text{As}_{50}\text{Se}_{50}$ -Zn- $\text{As}_{50}\text{Se}_{50}$ structure (1) and of the same structure irradiated from halogen lamp during 10 s (2), 2.5 min (3) and 30 min (4) at 65 °C.

3.3. AES studies of Zn in-depth distribution

AES study of the Zn depth profile was performed for the Ni-As₂S₃-Zn-Ni samples treated both optically and thermally. Fig. 6 represents the Auger depth profile of Zn and other components of the sample for various periods of the Ar ion sputtering. In the very initial and final periods of Ar sputtering we see only Ni, and in the other periods, all constituent elements are recorded. For the non-treated sample (Fig. 6a) and also for the samples annealed at 90 °C, Zn is recorded only in the first 5 minutes of sputtering. For the samples, irradiated at low temperature (Fig. 6b,c), and for the sample annealed at 130°C in darkness (Fig. 6d), we recorded the appearance of Zn in the depth of the sample. The change of the metallic front position with variation of the irradiation and annealing time testifies to the gradual penetration of Zn atoms from a surface deep into the As₂S₃ film.

The data of Fig. 6 permit us to suppose that in the case of photodiffusion, the amount of Zn is more or less constant along whole diffusion area and that the sharp step-like profile of Zn concentration exists in this case just as it was shown for the Ag or Cu photodiffusion into different chalcogenide glassy films [1, 13]. At the same time, for the case of thermodiffusion, instead of distinct diffusion front we see the "tail" of the diffused Zn.

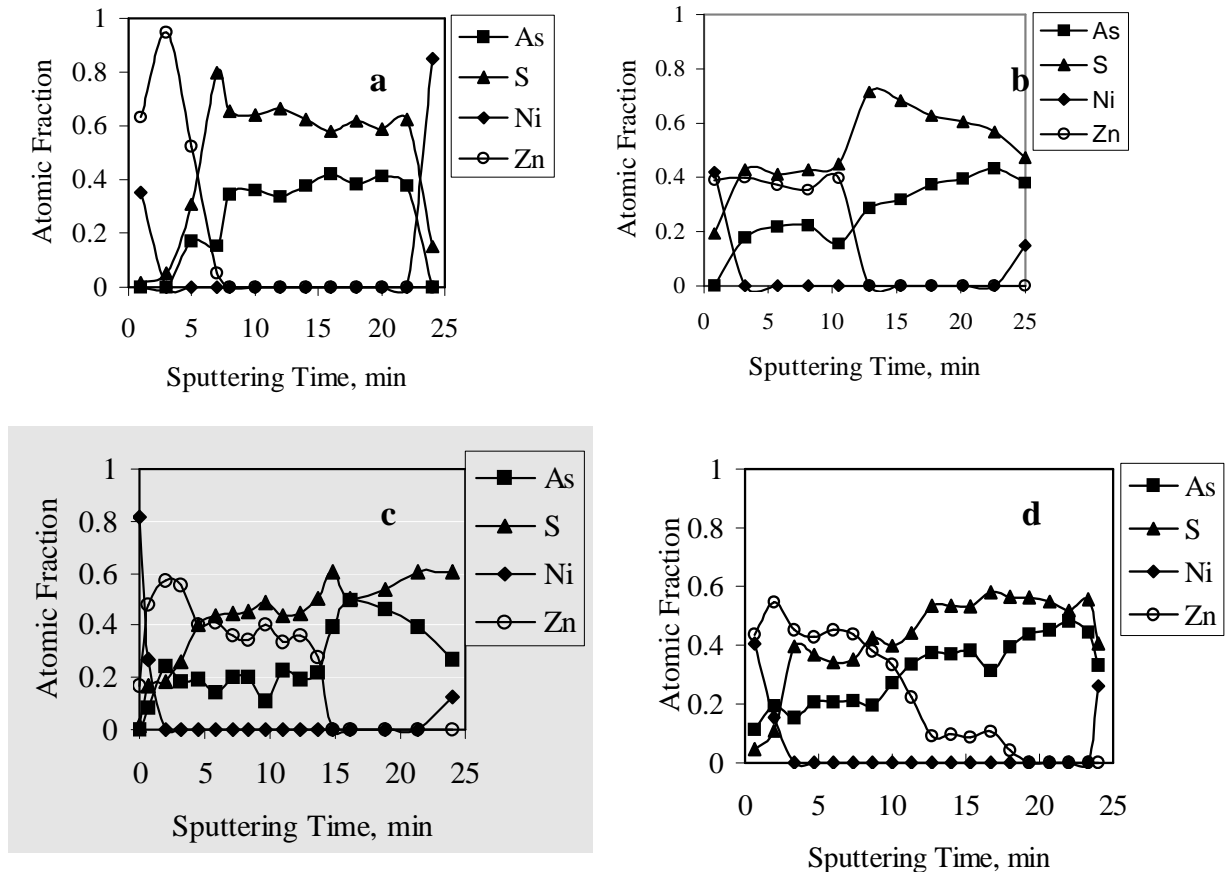


Fig. 6. Temporal variations of concentration of elements present in the non-treated Ni-As₂S₃-Zn-Ni sample (a) and in the same sample irradiated during 30 min (b) and 60 min (c) at 90 °C and annealed in darkness during 30 min at 130 °C (d).

4. Conclusion

We confirmed the photoinduced dissolution of Zn in chalcogenide films only after heating of all studied structures containing As₂S₃, As₂Se₃ and As₅₀Se₅₀ films to certain temperature. We determined these threshold temperatures of the beginning of Zn photodissolution and, also, the

temperatures of the beginning of Zn thermodissolution in all three types of chalcogenide films studied. Kinetics of Zn dissolution process is shown to be qualitatively similar to the same for the Ag dissolution, demonstrating an identity of the dissolution mechanism in both cases.

By studying the rate of etching of chalcogenide films in some liquid etchants and the Zn depth profile with the method of AES, we clearly demonstrated for the first time the existence of photo- and thermoinduced diffusion of Zn and the differences between these two processes in the arsenic chalcogenide films.

The observed peculiarities of Zn photodissolution and Zn photodiffusion are qualitatively analogous for all three types of films studied and we can assume that these peculiarities will be typical also for all other chalcogenide glassy films.

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