

PHOTOPLASTIC PHENOMENA IN CHALCOGENIDE GLASSES

M. L. Trunov^{*}, V. S. Bilanich^a

Uzhgorod National University, Department of Engineering, 13 Kapitulna str., Uzhgorod, 88000, Ukraine

^aUzhgorod National University, Department of Physics, 13 Kapitulna str., Uzhgorod, 88000, Ukraine

The brittle-to-ductile transition observed in As-S(Se) films under the action of light has been investigated. In this transition, the bandgap light, incident on the chalcogenide film causes a reversible transition from brittle to ductile state (the photoplastic effect) produced by successive on-off cycles of band-gap illumination. A macroscopic model is proposed, which explains this effect in terms of photosoftening phenomena of glass structure, which causes an essential decrease in the viscosity of glasses to the level close to 10^{12} - 10^{13} Poise under the bandgap illumination. This effect is electronic, not thermal in origin and consists of two parts, namely negative (sharp decreasing in viscosity down to 1×10^{12}) and positive (its increase up to 1×10^{13}) stages. All parts are temporary and exist under irradiation only. We assume that the first part is general and causes all photostructural and related phenomena in chalcogenide glasses.

(Received July 25, 2003; accepted August 28, 2003)

Keywords: Chalcogenide glass, Photoplastic effect, Viscosity, Photoinduced phenomena

1. Introduction

It has been known for a very long time that inorganic glasses are typically brittle materials at ambient temperature and this is due to the relatively low hardness as compared to their flow limit. By applying *in-situ* stress measurement to photostuctural changes in chalcogenide films based on As-S(Se) we have found essential dynamic changes in films plasticity, i.e. a reversible photoinduced transition from brittle to ductile state in chalcogenide glasses (the photoplastic effect) produced by successive on-off cycles of band-gap illumination [1,2]. A macroscopic model is proposed, which explains this effect in terms of the viscous flow of glasses under irradiation with the viscosity near 10^{12} - 10^{13} Poise (see, for example, a review in English in [3]). This phenomenon was confirmed later by Hisakuni and Tanaka [4], as photoinduced fluidity of chalcogenide glasses for sub-gap illumination. In subsequent papers the effect was considered as discovered by Hisakuni and Tanaka. Actually, this effect is part of the photoplastic effect in chalcogenide glasses and was published as early as three years before their communication. Indeed, in his subsequent review [5], K. Tanaka did cite one of our publications [6], although this reference and his comments in [5] do not reflect the full content of our previous works. In his later articles [7-9] even this reference was omitted.

The photoplastic effect has been employed to fabricate refractive lenslets in As_2S_3 glasses as was demonstrated in [10] and may be used for other applications in which the surface shape modification is necessary.

In this paper we present new details of our experimental results devoted to the photoplastic effect. A review is given on these topics through the recently obtained results on the positive and negative photoplastic effects for As-S (Se) films.

^{*} Corresponding author: stm@tn.uz.ua

2. Experimental

Two groups of samples were investigated: As-S and As-Se thin films were prepared by thermal evaporation of bulk glasses onto cleaned mica or glass strips 15-30 mm long, 2-5 mm wide and 0.05-0.3 mm thick (for stress relaxation measurement in films) and onto quartz substrates with the thickness of 10 mm (for viscosity measurements) at a pressure of 1×10^{-3} Pa and deposition rate of about 0.2 $\mu\text{m}/\text{min}$. The substrate temperature in all cases was close to ambient. The thickness of the films varied within the limits of 0.5 to 4 μm and was controlled by a laser interferometer.

The stress relaxation was measured with the original measuring laser dilatometer which allows for the continuous determination of the film stress during the film deposition process and during heating and/or irradiating the sample. The cantilever with a film on one side is illuminated with bandgap light (as a light source we used Ar^+ - laser for As-S system with the intensity of 50-300 mW/cm^2 and He-Ne or Kr^+ - laser for As-Se system with the intensity of 5-150 mW/cm^2) and the displacement of the cantilever is detected by a laser interference measuring equipment described in detail earlier [3]. The initial stress values during deposition and after annealing were calculated from Stoney's formula. For a strip of length L , thickness d , and Young's modulus Y , clamped on one end, the deflection δ of its center due to stress σ of the film with the thickness t is given by

$$\delta = \frac{3L^2t}{d^2Y} \cdot \sigma \quad (1)$$

The microhardness tests for viscosity evaluation were performed by the method described in [2,6] by the microhardness tester PMT-3 with a Vickers' diamond pyramid as an indenter. The indentation depth was measured by an interferometer technique with an accuracy of better than $\pm 0.01 \mu\text{m}$. The viscosity η is estimated by

$$\eta = \frac{P}{h_0 \cdot dh/dt}, \quad (2)$$

where dh/dt is the rate of the indentation depth change, h_0 is the "instantaneous" value of the indentation depth at the moment when a load P is applied.

3. Results

The starting level of internal stresses for as-deposited (σ_1) and annealed (σ_2) As-S(Se) films was calculated and the dependences of the internal stress relaxation process as a function of illumination time for each coating/substrate system were obtained (quantitative data are given in [11]). Fig. 1a presents typical σ -t (or, more exactly, δ -t) stress/deflection relaxation curves for as-deposited (1) and annealed (2) A-S (Fig. 1 a) and As-Se (Fig. 1b) films. Curve 3 on both Fig. 1 a, b shows the internal stress changes during reiteration laser on-off periods. A positive value of σ or δ corresponds to tensile stress and the film volume V (or thickness d) decrease.

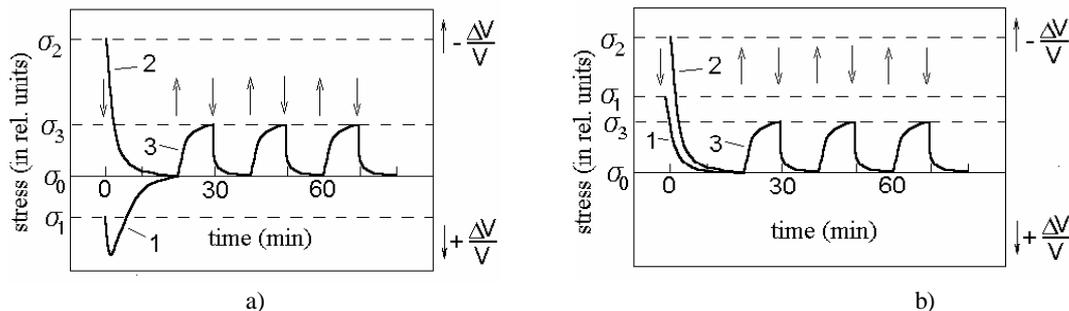


Fig. 1. Kinetics (in relative units) of internal stress relaxation (1,2) and generation (3) for 1 μm As-S (a) and As-Se (b) films under the action of laser light. The arrows show the beginning (\downarrow) and the end (\uparrow) of exposure. See the text for details.

It is shown that as-deposited As-S films are characterized by compressive stresses but the process of film annealing results in the emergence of tensile stress. The films of As-Se system are characterized by tensile stresses only irrespectively of films prehistory.

For both film systems, the stress reaches the value σ_0 , which approximately equals zero (the first equilibrium position of a cantilever) under illumination. It does not remain constant with the illumination turned off and approaches another equilibrium level σ_3 in the dark period. With reiteration laser on-off periods, reversible changes in the internal stress from level σ_3 to zero level σ_0 occur in the films. The magnitude of the internal stress in a dark period (σ_3) depends on the darkness period duration.

Note that the above data were confirmed later by Teteris [12] and used for development of holographic gratings in amorphous As_2S_3 films [13].

The typical kinetics of the indenter penetration (see Fig. 2) for As_2S_3 and As_2Se_3 thin films tested in darkness (I) and for those tested under illumination at variable illumination power (II, III) shows that the indentation depth in the latter cases is much greater than that one in a dark period (i.e. before or after the process of illumination). The kinetics of the indenter penetration for films after irradiation and tested in darkness is qualitatively the same to line I and has differences only in size of impression.

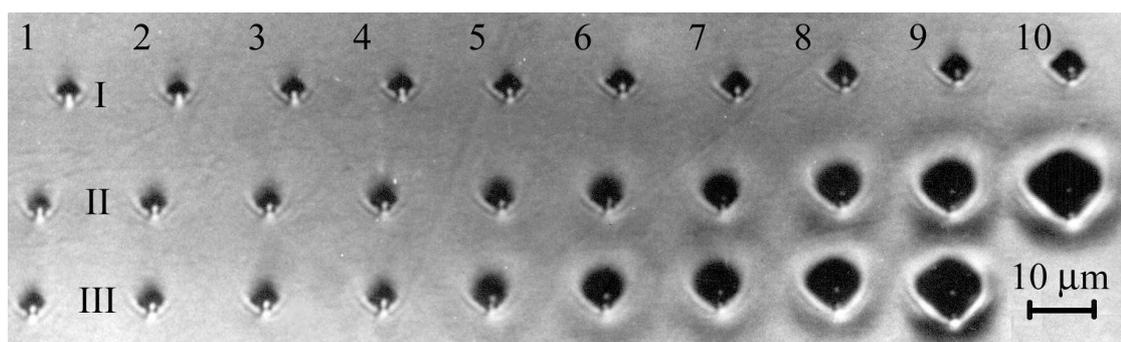


Fig. 2. The indentation depth as a function of the loading time (for $P=0.02$ N) for $3 \mu m$ As_2Se_3 film: line I - film tested by Vickers' indenter in darkness; line II - under the action of laser light with the power density of 5 mW/cm^2 ; line III - the same with the power density of 10 mW/cm^2 . Time of loading is: 1 - 1 s; 2 - 30 s; 3 - 1 min; 4 - 3 min; 5 - 5 min; 6 - 10 min; 7 - 20 min; 8 - 30 min; 9 - 40 min; 10 - 50 min.

As follows from Fig. 2 the change in indentation depth linearly depends on the time under illumination (appropriate Fig. 2 dependence was published in [2]) and in that article we estimated the film viscosity level. The calculated value was close to 10^{16} in darkness and 10^{13} during illumination.

The above level of viscosity is average and correct only if the value does not change with time and remains constant during the whole process of illumination. We have checked this supposition by using the test procedure which is associated with the measurement of the indenter penetration through an equal test interval (time of loading is $\Delta t = 20$ s). As follows from the data obtained (see Fig. 3) the photsoftening of the $As_{50}Se_{50}$ film increased drastically at the beginning of the process of illumination while the prolonged laser illumination decreases the indentation depth and leads to saturation of the level of film microhardness. The value of viscosity is about 1×10^{12} Poise in the initial part of the process and close to 10^{13} Poise at the end.

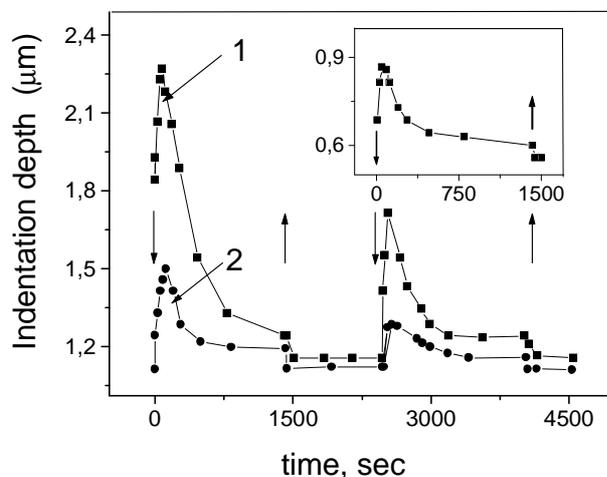


Fig. 3. The indentation depth as a function of the illumination time (for $P=0.02$ N) of $3 \mu\text{m}$ $\text{As}_{50}\text{Se}_{50}$ (curve 1) and As_2Se_3 (curve 2) film tested by using an equal test interval (loading time is 20 s) under the action of laser light with the power density of $130 \text{ mW}/\text{cm}^2$. In inset – the same for annealed $\text{As}_{50}\text{Se}_{50}$ film. The arrows show the beginning (\downarrow) and the end (\uparrow) of exposure.

The investigation of the viscosity behavior under illumination in As-Se chalcogenide films of another composition yields the results similar to those given above and differs only quantitatively (Fig. 3, curve 2).

4. Discussion

So, the laser irradiation causes the stress (σ) relaxation close to zero level irrespective of the initial stresses in films and thermal prehistory (Fig. 1) and this is due to the photsoftening phenomena (the photoplastic effect) (Fig. 2) which lead to a reversible transition from brittle to ductile state in chalcogenide glasses produced by successive on-off cycles of band-gap illumination. The basic relaxation mechanism involves a viscous flow under simultaneous action of illumination and applied external forces. The value of viscosity is approximately equal to 10^{13} Poise and very close to the viscosity at the glass transition temperature. This result was confirmed later in [4] from the experiment of fiber elongation under the combined action of sub-gap light illumination and external loading. This effect was called “photoinduced fluidity” of chalcogenide glasses by authors [4].

Very interesting is the fact that the impression shape under illumination differs essentially, because the plastic zone size under the indenter is comparable with the impression diagonal length (Fig. 4a). On the contrary, the plastic deformation for non-irradiated material (or after the incident laser illumination is switched off) is highly localized. This is due to the difference in the plastic deformation mechanisms in amorphous chalcogenide films under the action of laser light and in darkness. Note, that this effect is not thermal, because the indentation shape for heated films is very small and has cracks on the edges of the impression diagonal (Fig. 4b). This phenomenon is typical for brittle materials and may be explained by the process of increasing in tensile stress for films during heating.

As follows from Fig. 3 the process of photsoftening has a fine structure and consists of two parts: sharp decreasing in viscosity at a first second of illumination (the negative part) and its subsequent increasing with prolonged laser illumination (the positive part). These parts are characterized by the viscosity levels close to 1×10^{12} and to 1×10^{13} Poise, respectively.

Note, that the negative part of the effects is not thermal either because as we can see from Fig. 3 during the repeated laser on-off periods and for illumination of annealed films (which are characterized by much greater absorption than as-deposited films) the intensity of decreasing the

viscosity is much smaller. We assume that the first part is general and causes all photostructural and related phenomena in chalcogenide glasses. This property is currently under investigation.

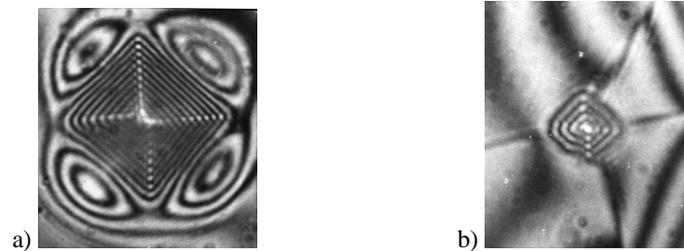


Fig. 4. The interference pictures of the indentation shape for As_2Se_3 films: a) microhardness test under the action of laser light with the power density of 10 mW/cm^2 ; b) the same in darkness at a temperature of $80 \text{ }^\circ\text{C}$. The loading time for $P = 0.02 \text{ N}$ was 50 min.

The experimental results can be interpreted at the atomic scale in terms of the model of repulsion and slip motion of layered structure [14]. However we think that not enough experimental data are obtained for the development of a microscopic model of the photoplastic effect. Taking into consideration the results shown in works [15,16] we could only predict some features, in particular, the presence of temperature hindering of the photoplastic effect causes its anomalous temperature dependence [17]. We have predicted the anomalous temperature dependence of viscosity of chalcogenide glasses under irradiation taking into account the following facts: In the paper [15] the light effect is investigated on As_2S_3 viscosity within the temperature range $80 - 210 \text{ }^\circ\text{C}$ (see Fig. 5 curve 1, 2). According to our results the viscosity of As_2S_3 thin films under irradiation at room temperature decreases to $10^{12}-10^{13}$ Poise. If we combine this point and the points on curve 2 (see Fig. 7) we will obtain the curve describing the anomalous temperature dependence of photo-viscosity with a maximum within the region of $10^4/T = 28-30$ ($60-85 \text{ }^\circ\text{C}$). The real experimental points (Fig. 7, curve 3) show a good qualitative correlation with the general aspect of photo-viscosity dependence on temperature but they do not correlate quantitatively with Nemilov's data. To evaluate the viscosity dependence we used the method of microindentation [2]. Our method differs from Nemilov's one whose accuracy is much higher. Besides, to measure the viscosity of bulk glass is much easier than to measure it in films. The conditions under which we conducted experiments differ, that is why it is difficult to expect a good correlation of our results. But the general aspect of anomalous temperature dependence of photo-viscosity is very close to the data obtained in [18].

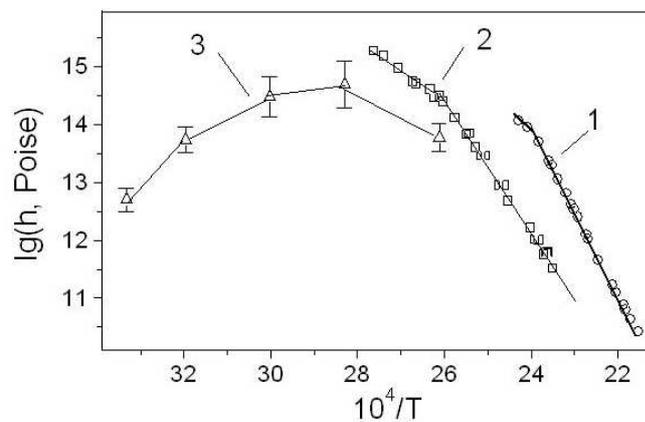


Fig. 5. The photoinduced viscosity dependence of temperature in the region from ambient to T_g in chalcogenide glasses. Curve 1 and 2 show dependence for bulk As_2S_3 in darkness and under laser irradiation, respectively (after Ref. 15). Curve 3 gives a good correlation with predicted anomalous temperature dependence of photo-viscosity in [17] and confirmed the results obtained in [18].

Note that all the results concerning the photoplastic effect were obtained by using band gap illumination with the intensity power within 5-300 mW/cm², that is why we can neglect the role of the temperature effect. As we can see we do not need to use 1000 W/cm² or more as it happens if the intense sub-bandgap light illumination is used [4]. Moreover, in our experiments we have found a fine structure of the photoplastic effect which is hindered under sub-band gap illumination.

We emphasize that the influence of light on materials plasticity was observed for crystalline semiconductors by Osipian and Savchenko for the first time [19]¹, who called this effect photoplastic. We consider this term to be more correct than photo fluidity, opto-mechanical effect² and others since it exactly reflects the essence of the phenomena observed. The use of the term “photofluidity” does not reflect the essence of the phenomenon. In reality chalcogenide glasses do not flow under irradiation. For “glass flow” the simultaneous irradiation and application of external forces is necessary. Thus it is more reasonable to use the term “photosoftening” or “photoplasticity”³. That is why in our article in 1995 [6] we use the name photoplastic effect.

5. Conclusion

We claim that for chalcogenide films under illumination the negative and positive photoplastic effect occurs. The main mechanism is the two - stage transformation of film materials from elastic to viscous state with the viscosity levels close to 1×10^{12} and 1×10^{13} Poise, respectively,

Acknowledgements

We appreciate participation of A.G. Anchugin in manufacturing the devices for stress measurement and discussions of the results received earlier. The authors are grateful to Dr. N. D. Savchenko for his assistance and stimulating discussion.

References

- [1] M. L. Trunov, A. G. Anchugin, *Sov. Technical Physics Letters* **18**, 37 (1992) and references therein.
- [2] M. L. Trunov, A. G. Anchugin, *Sov. Technical Physics Letters* **18**, 78 (1992).
- [3] M. L. Trunov, A. G. Anchugin, N. D. Savchenko, V. M. Rubish, *Proc. SPIE* **2113**, 183 (1994).
- [4] H. Hisakuni, K. Tanaka, *Science* **270**, 274 (1995).
- [5] K. Tanaka, *Current Opinion in Solid State & Materials Science* **1**, 567 (1996).
- [6] M. L. Trunov, *J. Non-Cryst. Solids* **192&193**, 431 (1995).
- [7] K. Tanaka, N. Yoshida, *Solid State Commun.* **55**, 153 (1997).
- [8] K. Tanaka, *Philos. Mag. Lett.* **79**, 25 (1997).
- [9] K. Tanaka, *C. R. Chimie* **5**, 805 (2002).

¹ Very old results devoted to the influence of light on the speed change of elongation for vitreous selenium fibers [20] are known. But in this paper the kind of deformation observed (elastic or viscous) and its origin (thermally or optically) is not investigated.

² For instance, according to [21], the opto-mechanical effect is the displacement of a cantilever with a film under the action of light. Indeed, this displacement is a result of films internal stress relaxation or generation caused by increase or decrease in its plasticity that are photoplastic effect. If the film does not have the initial stress we do not observe any displacement of the cantilever under the action of light (maybe from laser heating only if film and substrate linear expansion are not equal). That is why the stress value for film irradiated to saturation, and its change induced by polarized light cannot be calculated by Stoney's formula, because it is true only for elastic materials. So, the photoinduced stress change in the film given in [21] does not seem to be correct. Real opto-mechanical effect for As-S films was reported in [22].

³ In [18] the term photo-induced ductility for fiber elongation is suggested because this term reflects the presence of the combined effect of illumination and the application of external stresses.

-
- [10] S. Ramachandran, J. C. Pepper, D. J. Brady, S. G. Bishop, *J. Lightwave Technol.* **15**, 1371 (1997).
- [11] M. L. Trunov, V. S. Bilanych, Extended Abstracts of the XIII-th International Symposium on Non-Oxide Glasses and New Optical Glasses, Pardubice, Czech Republic, September 9-13, 2002, part I, p. 401.
- [12] J. Teteris, O. Nordman *J. Opt. Soc. Am. B* **14**, 2498 (1997).
- [13] A. Ozols, O. Nordman, N. Nordman *J. Opt. Soc. Am. B* **15**, 2355 (1998).
- [14] K. Shimakawa, N. Yoshida, A. Ganjoo, Y. Kuzukawa, J. Singh, *Philos. Mag. Lett.* **77**, 153 (1998).
- [15] S. V. Nemilov, D. K. Tagantsev, *Sov. Glass. Phys. and Chem.* **7**, 195 (1981).
- [16] D. K. Tagantsev, S. V. Nemilov, *Sov. Glass. Phys. and Chem.* **13**, 677 (1987).
- [17] M. L. Trunov, A. G. Anchugin, Proceedings of the 5-th Ukrainian Conference in Physics and Technology of Complex Semiconductors Thin Films, Uzhgorod, Ukraine, June 24-26, 1992, p.38.
- [18] D. T. Kastrissios, G. N. Papatheodorou S. N. Yannopoulos, *Phys. Rev. B* **65**, 165211-1 (2002). For a recent general review on the subject see S. N. Yannopoulos "Photo-plastic effects in chalcogenide glasses: Raman scattering studies", in: A. V. Kolobov (Ed.), *Photo-induced metastability in amorphous semiconductors*, Wiley-VCH, Germany 2003 (Chapter 8)
- [19] Yu. A. Osipyany, I. B. Savchenko, *JETP Letters* **7**, 130 (1968).
- [20] O. U. Vonwiller, *Nature* **104**, 347 (1919).
- [21] P. Krecmer, A. M. Moulin, R. J. Stephenson, T. Rayment, M. E. Welland, S. R. Elliott, *Science* **277**, 1799 (1997).
- [22] B. V. Deryagin, Yu. A. Toporov, K. I. Merzhanov, N. M. Galyvidish, I. N. Aleinikova, L. N. Burta-Gapanovich, *Sov. Phys.-Solid State* **16**, 1155 (1974).