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## LIGHT-INDUCED PLASTICITY IN CHALCOGENIDE GLASSES: EVOLUTION OF PLASTIC PROPERTIES UNDER IRRADIATION

M. L. Trunov<sup>\*</sup>

Uzhgorod National University, 13, Kapitulna str., Uzhgorod 88000, Ukraine

The evolution of the plastic properties of chalcogenide glasses of  $As_xSe_{1-x}$  system irradiated by band-gap light has been studied using a micro- and nanoindentation methods. The photoinduced variation of plasticity (photo-plastic effect) exhibits a two-stage character, whereby an intermediate metastable phase is formed in the first stage. The plasticity of this phase is higher than that of the light-stable phase formed under prolonged irradiation. The most pronounced negative photo-plastic effect (giant photo-softening) is observed in  $As_{20}Se_{80}$ films while their photo-induced optical constants change are the lowest.

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## 1. Introduction

Recently, the research activities have been focused on photo-induced modifications of mechanical properties of chalcogenide glasses. It has been found that thin films of chalcogenide glasses exhibit a variety of intriguing phenomena caused by both band-gap and sub-gap light irradiation. In [1-3] we reported the photo-plastic effect induced by band-gap irradiation and noted the reversible influence of light on the flow stress and hardness of glasses. A negative light effect, that is, the decrease of these characteristics of material has been found. It has been shown from stress relaxation and microindentation kinetic measurements that the viscosity  $\eta$  decreases from  $\eta \ge$  $10^{16}$  P in the dark to  $10^{12}$  -  $10^{13}$  P under irradiation both for glasses of As-S and As-Se systems [1, 2]. These values of viscosity were close to that of initial glasses near their glass-formation temperature  $T_{\rm o}$ . The same results were obtained for the films of chalcogenide glasses of other compositions that allowed supposing the general character and unique mechanism of the phenomenon revealed [3, 4]. One of the facets of photo-induced plasticity was observed in As<sub>2</sub>S<sub>3</sub> fibers and flakes when the subband-gap light and elongation stresses were applied [5] (the so-called photo-induced fluidity of chalcogenide glasses). The necessary condition for the effect to be observed in this case was a considerable (more than 100 W/cm<sup>2</sup>) power density of the light incident upon the samples. The viscosity evaluated for such conditions of irradiation falls down from dark value of  $\eta \ge 10^{14}$  Poise to  $\sim 5 \times 10^{12}$  P that is in good agreement with previously published data [2], which is evidence of the universal character of these phenomena and a common mechanism, responsible for the observed behavior. However, this mechanism has not been clear so far, though it is being investigated both theoretically [6,7] and experimentally [4,8-12].

This paper presents the results of investigation of the kinetics of a photo-plastic effect in thin films of chalcogenide glasses of the As-Se systems using a micro- and nanoindentation technique.

# 2. Experimental

The experiments were performed on 1–to 3- $\mu$ m thick films prepared by thermal evaporation of As<sub>x</sub> Se<sub>1-x</sub> glasses (for x = 0, 10, 20, 30, 40 and 50) from quasi-closed effusion cells and deposition

<sup>\*</sup> Corresponding author: stm@tn.uz.ua

at a rate of 2-5 nm/s onto unheated glass substrates. The samples were exposed to radiation of a laser diode operating at a wavelength of 630 nm. The radiation power density at the sample surface did not exceed 100 mW/cm<sup>2</sup> under microindentation tests and 30 mW/cm<sup>2</sup> under nanoindentation ones. This power density did not cause any heating of the film [13]. Therefore all effects described below have an athermal (electronic) nature.

The films were irradiated from the bottom of samples through transparent substrates. The mechanical properties of the deposited films were studied by the method of cyclic indentation. During the experiment, several indentations on the irradiated sample were made. After each load-unload cycles, the sample was moved so that each subsequent cycle was performed in a new region of the film. The indented volume of films is much smaller than that affected by the laser irradiation; hence the changes in plasticity reported here were caused by the influence of light only. We have neglected the role of temperature increase due to irradiation and assumed that no micro structural changes in the film material take place as the result of the high pressure created on the indenter tip. Five samples prepared in one deposition cycle were tested. The diameter of samples was 15 mm and allowed us to carry out multiple measurements to obtain reliable and reproducible results.

The microindentation measurements were performed on a PMT-3 micro hardness tester using a Vickers indenter (a tetrahedral diamond pyramid with a 136° angle between opposite faces) and a Knoop indenter (a rhombohedral diamond pyramid; the pyramid shape employed has an included longitudinal angle of  $172^{\circ}$  30' and included transverse angle of  $136^{\circ}$ ) under a load of P=20-50 mN. In the first set of experiments, the exposure in each subsequent cycle was increased from 10 s to 2 h; in the second series, the exposure time was fixed at 20 s.

Nanoindentation measurements were performed using a depth-sensing nanohardness tester (model Nanoindenter II, MTS Systems) with a Berkovich diamond pyramid as an indenter (a trigonal diamond pyramid with a  $65^{\circ}30$ 'angle between opposite faces). The details of instruments and methods are given in [14]. For the set of experiment the load schedules comprised first a load ramp to the peak load of 2 mN with a rate of 0.7 mN/s, followed by holding at the peak load for a duration of 120 s, then unloading with a same rate and followed by holding at the zero load for a duration of 120 s. The nanohardness (H) and Young's modulus (E) were calculated from the load–displacement curves according to the Oliver and Pharr procedure [15] with a typical error of  $\pm 0.1$  GPa and  $\pm 1$  GPa, respectively.

### 3. Results and discussion

Figure 1 (rows I-IV) shows the typical interferograms of indenter imprints obtained in the first series of microindentation experiments (at a load of P = 20 mN) with as-deposited As<sub>50</sub>Se<sub>50</sub> films. The measurements in these experiments were performed in the dark (row I), during the first exposure (row II), after switching off the laser (row III), and during repeated exposure (row IV). As can be seen from the experimental data, the depth of indenter penetration in the dark only very slightly increases with the time of indenter loading (Fig. 1, row I) in the sequence of micro indentations on a freshly prepared film and is virtually independent of this time in the sequence of measurements performed in the dark after exposure of the film (Fig. 1, row III). The pattern is significantly different for the measurements in the course of irradiation whereby the indenter penetration nonlinearly varies with the time: in the initial stage, the indenter imprint rapidly increases to reach a maximum size after a 120-s exposure; then, the penetration depth exhibits a decrease followed by new growth in proportion to the time of exposure (Fig. 1, row II). During the second exposure after holding in the dark, the depth of indenter penetration virtually linearly increases with time from the very beginning (Fig. 1, row IV). The interferograms of the indenter imprints measured using a Michelson microinterferometer showed that the initially brittle glass becomes soft and fluid under the action of light and stress. This is manifested by a significant increase in the indenter penetration depth and the appearance of fluidity zones appearing as a broad black-and-white contour along the perimeter. Such zones are typically observed during microindentation testing of plastic materials such as metals. It should be noted that certain plasticity is also inherent in the as-deposited films (Fig. 1, row I). However, the observed increase in the indenter penetration depth with the loading time is mostly related to a reduced initial density of packing in the film and the presence of a free volume (voids, pores, and other micro-defects destroyed by high pressure at the indenter tip).

It was demonstrated previously [2] that the rate of the indenter penetration into chalcogenide glasses in the course of exposure is controlled by viscous flow in the material. For this reason, the observed no monotonic variation of the indenter print size during the first exposure (Fig. 1, row II) is indicative of the photo-induced variation of the glass viscosity. This is confirmed by the results of the second series of experiments during microindentation studies, in which the films were subjected to microindentation at a fixed time ( $\Delta t$ = 20 s) of indenter loading (Fig. 1, row V). In this case, the kinetics of indenter penetration reflects variation of the viscosity drops to a minimum level within the first 50 s of exposure, then gradually increases, and eventually ceases to change with the duration of exposure.



Fig. 1. Interferograms of sequential microindentations in a  $3-\mu$ m - thick as-deposited As<sub>50</sub>S<sub>50</sub> film. The duration of every next load-unload cycle in rows I-IV increases with the number, amounting to 10 s (1), 30s (2), 1 min (3), 3 min (4), 5 min (5), 10 min (6), 30 min (7), and 120 min (8). In row V, the time of each cycle is fixed (20) s and the exposure increases with the number, amounting to 20 (1), 50 (2), 80 (3), 140 (4), 200 (5), 300 (6), 600 (7), and 1200 s (8); imprint 9 was obtained immediately after switching off the laser. A Vickers indenter was used in all the tests.

Fig.2 shows quantitative data characterizing the entire process of microindentation in the second series of experiments with P=20 mN for  $As_{50}Se_{50}$  films with thickness of 1 and 3 µm. As can be seen, the intermediate stage of increased plasticity is observed both during the first cycle of irradiation and in the course of repeated exposures. Similar behavior, although less pronounced, was also observed in the experiments with As–Se films of other compositions, for example for  $As_{20}Se_{80}$  and  $As_{30}Se_{70}$  films (see the inset in Fig. 2). Thus, the results of our experiments show that the process of microindentation in all cases has two stages. In the first stage (during the initial exposure), the film is characterized by a higher plasticity than in the second stage corresponding to prolonged irradiation.

Fig. 3 (curves 2-4) shows an example of nanoindentation obtained in the first series of experiments (at a load of P = 2 mN) with as-deposited  $As_{40}Se_{60}$  films. The measurements were performed in the dark (2), during the first exposure, which is started with loading simultaneously (3), and during prolonged irradiation (4). The second series of experiments were performed with irradiated sample of  $As_{40}Se_{60}$  film after holding in the dark during 24 h (Fig. 3, curves 5 - 7). The measurements in these experiments were performed in the dark (5), during the second exposure (6) and multiply repeated series of measurements with the laser switched on and off on the different parts of load-unload cycle (7). In these series of nanoindentation under illumination the light was

turned on during hold period at maximal loading and after unloading. In both cases it corresponds to 60 s on the hold-time curve after the application or removal of the indenter load.



Fig. 2. Plots of the imprint depth *h* versus exposure time *t* for 1  $\mu$ m – thick (1) and for 3  $\mu$ m – thick (2) as-deposited As<sub>50</sub>Se<sub>50</sub> films at a load of P=20 mN. The inset shows the same data at a load of P=20 mN for the (1) As<sub>20</sub>Se<sub>80</sub>, (2) As<sub>30</sub>Se<sub>70</sub>, (3) As<sub>40</sub>Se<sub>60</sub> and (4) As<sub>50</sub>Se<sub>50</sub> films (all films were 2  $\mu$ m thick). The time of loading at each point was  $\Delta t = 20$  s. Arrows indicate the moments of laser switching on ( $\uparrow$ ) and off ( $\downarrow$ ). The second cycle of irradiation for curves on inset and for curve 1 on Fig.2 is not shown. A Knoop indenter was used in all the tests.



Fig. 3. Load - time (curve 1) and displacement - time curves during nanoindentation tests of  $As_{40}Se_{60}$  film: tested in the dark (2); during initial part of irradiation (3); during prolonged illumination, intermediate part (4); tested after irradiation and holding in the dark during 24 hrs (5); under second irradiation, initial part (6); after second irradiation and under repeated cycle of light switch on-off (7). The arrows show the beginning ( $\uparrow$ ) and the end ( $\downarrow$ ) of exposure for the curve 7.

As can be seen from the experimental data, the depth of indenter penetration in the dark only very slightly depends on holding the indenter under constant load and the depth recovery is defined by elastic components  $h_e$  during fast unloading (Fig. 3, curve 2). Really, the total relative value of recovering the depth of imprint  $D = (h_e + h_r)/h_t$  equals in this case 38 % and mainly is formed from elastic part  $\beta = h_e/h_t$  of recovery, which is dominant (35 %) while the contribution of the visco-elastic part  $\gamma = h_r/h_t$  is illegible and makes up 3 % only.

For the measurements in the course of irradiation the pattern is significantly different, whereby the indenter penetration nonlinearly varies with time. In the initial stage the indenter penetration depth increases sharply (Fig. 3, curve 3). Then during prolonged irradiation the penetration depth is decreasing (Fig. 3, curve 4). During the second exposure (Fig. 3, curve 6) after holding and testing in the dark (Fig. 3, curve 5) and during exposure on the different parts of load-unload cycle (Fig. 3, curve 7) the results are similar to those presented in Fig. 3 (curves 2 - 4). As it can be seen from curves 5 and 7 (see Fig. 3) the photo-softening state in the film is still active after the light has been turned off.



Fig. 4. The components of the deformation processes during nanoindentation tests of  $As_xSe_{1-x}$  films. The exposure increases with the number, amounting to 120 (2), 420 (3) and 820 (4) s; the values for the numbers of 1 and 5 was obtained in permanent darkness before irradiation and immediately after switching off the laser. See text for details.

We calculate all components of deformation in relative units (the plastic  $\alpha = h_p/h_t$ , elastic  $\beta = h_e/h_t$ , and visco-elastic, or retarded  $\gamma = h_r/h_t$  where  $h_t$ - total value of indenter penetration before unloading,  $h_e$  – elastic recovery of imprints;  $h_p$  – residual depth of imprint after completing of relaxation processes;  $h_r$  – visco-elastic component of imprint recovery- see example for curve 3 in Fig. 3) and plot them for all investigated compositions of the films in Fig. 4 as diagrams. In the course of irradiation the essential redistribution of these components was observed upon load removal. From the obtained data it can be deduced that the visco-elastic component ( $\gamma$ ) of the film deformation increases with light switching on. Indeed, it depends non-monotonic on the irradiation time. However, testing the films under the light illumination we observe that the plastic component  $\alpha$  rises sharply at first seconds of illumination and further reaches the maximal value, but elastic component  $\beta$  reduces at the same time proportionally to the sample exposure (see Fig. 4).

The value of  $K = H^3/E^2$  was used to estimate the ability of the film material to resist plastic deformation [16]. The results show that at the initial stage of irradiation this ability decreases by a factor of 20 in comparison with a dark sample for As<sub>20</sub>Se<sub>80</sub> and As<sub>30</sub>Se<sub>70</sub> films. However, for the film of other composition this ability decreases much less, for example the latter is changed by a factor of 1.5 to 5 for As<sub>10</sub>Se<sub>90</sub> and As<sub>40</sub>Se<sub>60</sub> films, respectively. We also used a ratio of  $S_i = \beta^{dark} / \alpha^{dark} - \beta_i^{irrad} / \alpha_i^{irrad}$  (where i is the number of nanoindentation tests under irradiation

which corresponds to the number of 2 to 4 on diagrams in Fig. 4; the values of  $\alpha^{dark}$  and  $\beta^{dark}$  correspond to the nanoindentation test in the permanent darkness before irradiation, i.e. to point 1 in Fig.4) as a value of light-induced plasticity of the films. This value is plotted in Fig.5. A strong negative correlation of this value with the degree of light – induced changes in optical constants (e.g. optical gap changes,  $\Delta E_{\alpha}$ ) of the films is found.



As concentration, %

Fig. 5. Evolution in plasticity S(x) in  $As_x Se_{1-x}$  films versus exposure time (indicated for each curve as a number of nanoindentation tests). Curve 1 shows the changes in optical gap for the  $As_x Se_{1-x}$  films under irradiation (see Ref. [17]).

As shown in Fig. 5 the highest changes of plasticity induced by light irradiation are observed for  $As_{20}Se_{80}$  films (the giant photo-softening). On the other hand, the light-induced optical changes for these films are the lowest. It may be noted that in  $As_{29}Se_{71}$  bulk glasses the transition from floppy to intermediate phase occurs [18] and  $As_{20}Se_{80}$  film is near to these compositions. That is why we suggest that the stress-free phase presence (close to the mean-field rigidity percolation transition) is the main condition for the giant photo-softening observation in chalcogenide glasses. This suggestion is in agreement with those published earlier in [19].

## 4. Conclusions

The mechanical response to the light irradiation of  $As_xSe_{1-x}$  films has been investigated by micro and nanoindentation tests. There have been found essential changes in plasticity (a negative photo-plastic effect, i.e. the light-induced softening) and we have shown that compositional trends in this light-induced softening are the highest for  $As_{20}Se_{80}$  films (while their photo-induced optical transformations are the lowest) and they do not practically change in a consecutively repeated series of exposure. This light-induced softening effect is still active during a few seconds after the light is turned off (the photo-plastic after-effect) and proved to be a static effect because the alteration of penetration depth has been found when changing the irradiation state in films during holding under a constant load.

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