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The non-Hookian behavior of chalcogenide glasses under irradiation: A nanoindentation study

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Abstract

The combination of nanoindentation and band-gap irradiation has been used to study the photoplastic effect in vitreous semiconductors. It has been shown that a non-linear (non-Hookian) mechanism of the formation of the strain response is realized in the As–Se chalcogenide films subjected to the combined action of light and external mechanical loading, simultaneously with opposite changes in Young's modulus and nanohardness. These observations have been considered in the frame of the two-phase model of glasses in which each of the phases has a time-dependent character of the mechanical response subjected to an external perturbation. We have confirmed this assumption by experiment with irradiation of the film surface by linearly polarized light and give a simple mechanical model for explanations of the obtained results.

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1. Introduction

The negative photoplastic effect was observed previously [1–3] in As–S(Se) vitreous semiconductor films irradiated by light from the region of the absorption edge. A macroscopic model of this phenomenon was based on the assumption of the athermal decrease in the viscosity of the films during irradiation to 10^{12} Poise, which is close to the viscosity of vitreous semiconductors near their glass-transition temperature T_g . This assumption was directly confirmed in the experiment [2]. Further observations of a manifestation of the negative photoplastic effect at low temperatures in amorphous selenium (optical melting [4]), photoinduced fluidity [5], which was discovered when vitreous semiconductor fibers were irradiated by slightly-absorbed light, as well as the presence of the tem-

perature hindering of the negative photoplastic effect [5,6], show that the phenomena found in [1,2] are universal and general. In this work, we explore the nanoindentation method for investigating the photoplastic effect of chalcogenide films on a nanoscale. The results show that the opposite changes in major nanoindentation characteristics (Young's modulus and nanohardness) were observed under irradiation. Moreover, the elastic response of the films was changing essentially in time, i.e. the non-Hookian behavior takes place. We give a simple macroscopical model for these results in terms of rigid and floppy clusters formations and modifications with light.

2. Experiments

Chalcogenide glasses of As–Se composition were synthesized in evacuated quartz ampoules in a standard procedure from elemental pure components (99999). The experiments were performed on 2- μ m thick films prepared

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by thermal evaporation of $\text{As}_x\text{Se}_{100-x}$ glasses (for $x = 10, 30, \text{ and } 40$) from quasi-closed effusion cells and deposition at a rate of 2–5 nm/s onto unheated quartz or K-8 glass substrates. The film thickness in the deposition process was controlled by the interference method.

The photomechanical response of films to the irradiation by light from the region of the absorption edge was studied by the method of nanoindentation of samples on a Nanoindenter II (MTS Systems) nanohardness meter. The instrument is equipped with a sharp indenter (a three-sided diamond Berkovich pyramid with a vertex angle of 65.3° and a tip curvature radius of about 200 nm) and allows investigation of samples with various loading application schemes. The characteristics of the instrument and the nanohardness test procedure were described in [7]. The nanohardness (H) and Young's modulus (E) were calculated from the load–displacement curves according to the Oliver and Pharr method [8] directly from NanoIndenter II software and a typical error did not exceed of ± 0.1 GPa and ± 0.5 GPa, respectively. In order to accumulate statistics and to estimate the reproducibility of the results, tests were carried out with three samples obtained in one technological deposition cycle. In contrast to the load scheme commonly accepted for nanoindentation [7], a very steep loading and unloading sequence was used in our load scheme followed by longer holding periods to reveal the regime of the viscoelastic recovery of the indented region. Each nanoindentation test consisted of four time segments: the steep loading segment (1 or 2 s), the holding segment (20 or 60 s), the steep unloading segment (1 or 2 s), and a second holding period at nearly zero load to measure the creep process during the recovery of the indented region (20 or 60 s); see approximate load programs in the bottom part of Fig. 1 (line 1). The maximum load P in each cycle was equal to 2 mN. During the experiment, several pricks (test cycles) of a sample were performed at the same test parameters and with the lateral displacement of the indenter after each test. Thus, a new test cycle was conducted in the following (clean) film sec-

tion. The distance between sections was equal to $25 \pm 0.5 \mu\text{m}$. The total area of the tested section was much less than the area of the laser spot (2 mm^2) that was further focused on the sample. Each sample was subjected to 12 test cycles: two cycles in darkness (before and after irradiation) and 10 cycles during light irradiation, which allowed investigation of the dynamics of the mechanical properties of films on nanoscale upon irradiation. To reduce the effect of relaxation processes upon the stabilization of the structure, freshly deposited films were kept in darkness for three months. The irradiation was carried out by means of a 633-nm He–Ne laser whose radiation energy ($E = 1.90 \text{ eV}$) is close to the gap width of the films under investigation ($E_g \approx 1.78\text{--}1.90 \text{ eV}$ at absorption $\alpha = 10^3 \text{ cm}^{-1}$), and the radiation power did not exceed 60 mW/cm^2 .

3. Results

Fig. 1 shows the characteristic time dependences of the penetration depth of a Berkovich indenter for an $\text{As}_{30}\text{Se}_{70}$ film. Qualitatively similar dependences were observed for the films of other compositions. By analogy with investigations of the retarded elasticity in glasses by the strain relaxation method [9], the total penetration depth h_t of the indenter at the unloading time can be represented as the sum $h_t = h_e + h_r + h_p$ of the elastic h_e , the relaxation h_r , and the plastic h_p components (see line 3 in Fig. 1). As it is seen in Fig. 1, the indenter penetration depth in the nanoindentation of the film in darkness varies only slightly during the indenter exposure to loading and the recovery of the indented region is primarily determined by the elastic component h_e at the step unloading (line 2 in Fig. 1). Upon irradiation, the ratios of the components h_e , h_r , and h_p , as well as h_t , sharply change. The dynamics of these changes is correlated with the previously obtained results for variation in the micro- and nanohardness of the As–Se films during irradiation [10–12]. In particular, when loading is combined with the simultaneous irradiation of the sample (line 3 in Fig. 1), a sharp increase in the indenter penetration depth, as well as a pronounced viscoelastic increase in the indented-region depth, is observed. Unloading is accompanied by a step decrease in the indented-region depth by h_e and by a further recovery of the indented region due to the h_r component. The results obtained in the next nanoindentation cycle (line 4 in Fig. 1) represent the dynamics of the photoinduced redistribution of the components h_e , h_r , and h_p , which depend on the chemical composition of the samples under investigation. This dependence (excluding the relaxation component, h_r which slightly depends on the composition), as well as the changes in the nanohardness and the Young's modulus upon light irradiation for all the test cycles, is shown in Figs. 2 and 3, respectively. The strain components are determined using the indenter unloading curve for each test cycle (see line 3 in Fig. 1). It is seen that dynamical changes are observed not only for the (line 1) h_p and (line 2) h_e , (see

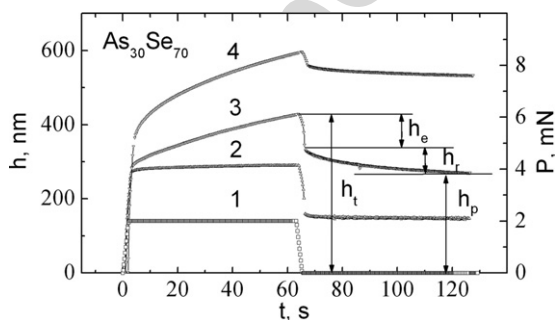


Fig. 1. Time dependence of the indenter penetration depth in nanoindentation of $\text{As}_{30}\text{Se}_{70}$ films (2) in darkness and in the (3) second and (4) third cycles of tests upon continuous light irradiation by He–Ne laser, along with the (1) loading application scheme in the test process. Light intensity is 30 mW/cm^2 and average exposure time are 120 s (for line 3) and 500 s (for line 4). Lines just connect the experimental points.

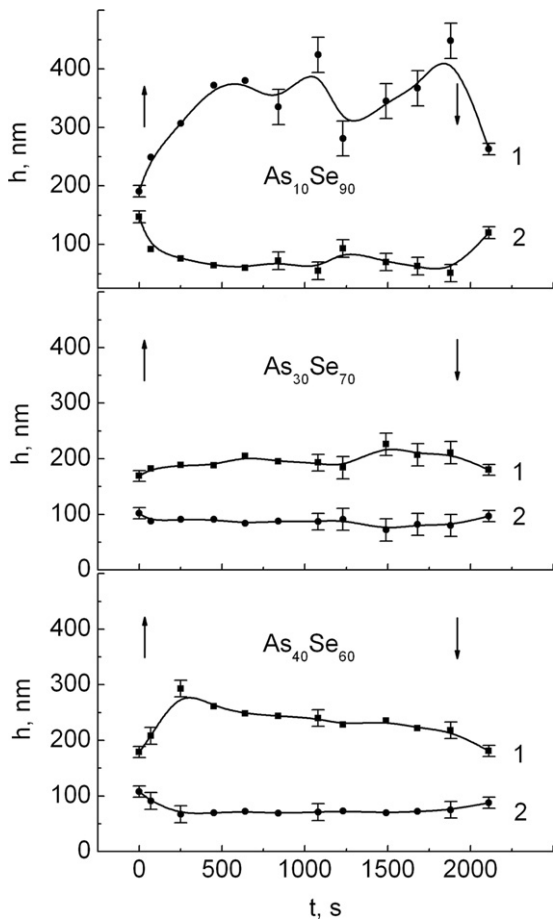


Fig. 2. Dynamics of the photomechanical response of As_xSe_{100-x} films upon indentation: the (1) plastic h_p and (2) elastic h_e components of the total strain of the films. Light source is He–Ne laser with intensity 60 mW/cm^2 . Arrows indicate the moment of light switching on (\uparrow) and (\downarrow) off. Lines are b-spline fits to the experimental data.

Fig. 2) components but also for the nanohardness H and (Fig. 3(a)) and the Young's modulus E (Fig. 3(b)).

A light-induced change in the mechanical parameters of the films indicates that the films become more compliant and plastic; maximum changes occur in the $As_{10}Se_{90}$ film. At the initial stage of irradiation, a steep increase in the (line 1 in Fig. 2) plastic component and (Fig. 3(b)) Young's modulus, as well as a simultaneous decrease in the (line 2 in Fig. 2) elastic component and (Fig. 3(a)) nanohardness, are observed. In particular for the $As_{10}Se_{90}$ film, the plastic component h_p increases in twice, whereas the nanohardness is halved. Figs. 1 and 2 also show that, for the same loading on the indenter, the change is observed in (lines 3 and 4 in Fig. 1 and line 2 in Fig. 2) the elastic strain component h_e upon unloading, which testifies to the non-Hookean character of the film deformation process upon irradiation. These processes are maximal at the moment if the irradiation starts and more pronounced for Se richer films. Furthermore the opposite changes in nanohardness and Young's modulus take place: elastic modulus increases while nanohardness decreases, whereas usually these two

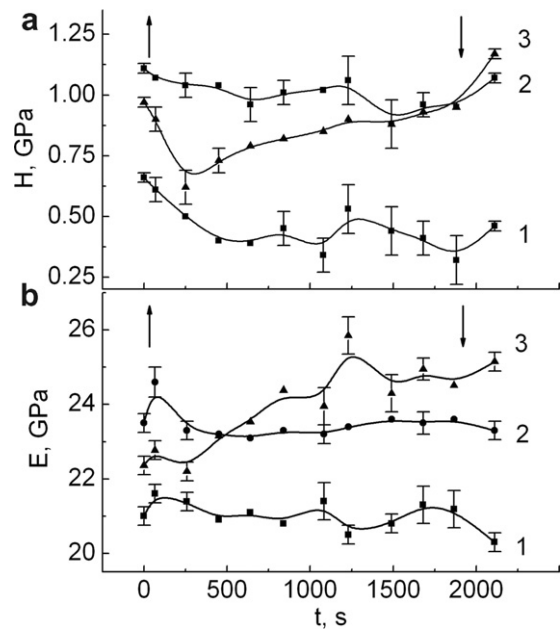


Fig. 3. Dynamics of nanohardness (a) and Young's modulus (b) changes in (1) $As_{10}Se_{90}$, (2) $As_{30}Se_{70}$, (3) and $As_{40}Se_{60}$ films under irradiation of 633 nm light with an intensity 60 mW/cm^2 . The arrows show the beginning (\uparrow) and the end (\downarrow) of exposure. Lines are b-spline fits to the experimental data.

parameters are in direct correlation. It can be assumed that this can be the evidence of the two-phase model of glasses [13], in which each of the phases has a time-dependent character of the mechanical response subjected to an external perturbation. In our case a coupled external perturbation field was applied, that is, the light irradiation and simultaneous application of mechanical field (mechanical load).

4. Discussion

Let us discuss the possible process leading to the observed softening of the films and simultaneous increase of their rigidity. Macroscopically these two phenomena reveal themselves as the reduction of nanohardness and increase of Young's modulus. First of all it should be noted that although the average temperature of the film rises for several degrees only under irradiation [14] the film softens and becomes viscous just as it were observed upon heating near or even above the glass-transition temperature T_g [2]. Since the latter equals 360–450 K for the compositions to have been investigated the plasticity state is not caused by heating but it is purely athermal. So, upon heating, Young's modulus of the chalcogenide glasses drops in two orders of magnitude [15]. Under irradiation we obtain an opposite situation: if the irradiation starts the elastic modulus generally increases by 10–20% and slightly decreases during prolonged exposure. For some film compositions the Young's modulus rises continuously (see Fig. 3(b), line 3). The high value of the elastic modulus and at the same time the presence of a low viscosity under

irradiation directly indicate that different mechanisms take responsibility in the case of light-induced and heat-induced plasticity (softening) of the film.

Note, that we use the term plasticity or softening, but not fluidity, because in the last case, i.e. if the material behaved under irradiation like a viscous fluid, we would observe: (i) a complete disappearance of the region with elastic response under step unloading (it follows from Hook's law for elastic solids) and, (ii) the negative value of the derivative dP/dh in the initial portion of an unloading curve during routine nanoindentation procedure. Indeed, this value is positive for all film compositions under study though the slope of an unloading curve decreases essentially under irradiation [16,17]. Moreover, the fluid substances would be characterized by a lower Young's modulus value in the fluid state than in the solid one.

Phenomenological explanation of the effect can be given within a frame of the conception of local rearrangements [18,19] due to the heterogeneity (or polydispersity) of the microscopic structure of disordered solids. It means that deformation in amorphous materials occurs at special sites where the molecules are able to rearrange themselves in response to applied stresses.

We assume that such a conception may be successfully applied to chalcogenide glasses. So, considering the approach given in [13] we can find a weak and tensile zones (shear transformation zones (ShTZ), according to [18] or rigid domains separated by softer interfacial zones, according to [19]) in the force network embedded within a rigid repulsive matrix. As suggested by [18] these ShTZ might consist of groups of four or more relatively loosely bound molecules surrounded by more rigid 'cages'-molecules. A

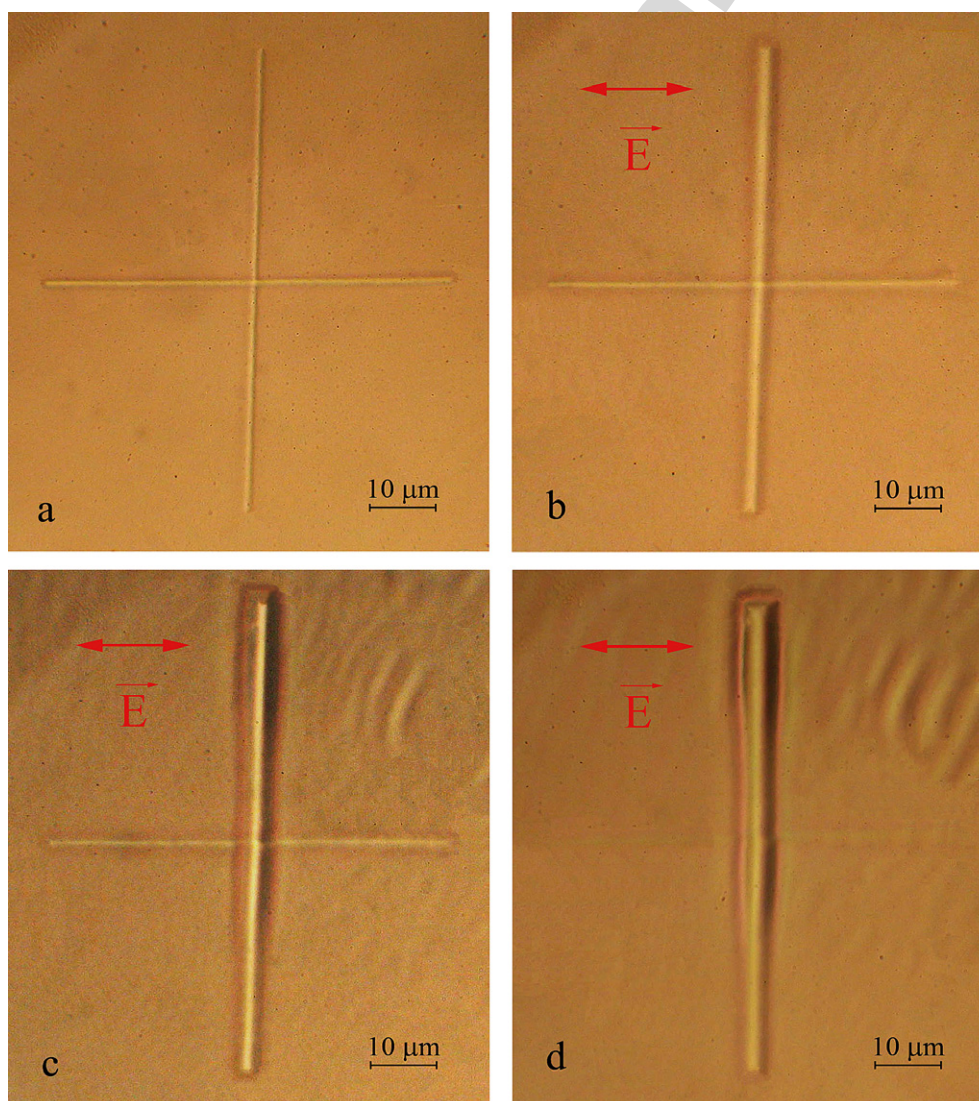


Fig. 4. Direct observation of light-induced anisotropic plasticity in $\text{As}_{20}\text{Se}_{80}$ film due to the presence of floppy and rigid phases in the film structure: (a) image of non-irradiated film surface and (b–d) images of this surface under 5 h, (b) 12 h (c) and 16 h (d) irradiation by unfocused ($d \sim 2$ mm) linearly polarized laser with $\lambda = 633$ nm and $P = 60$ mW/cm². The orientation of the polarization of the laser light is indicated on the images (b–d).

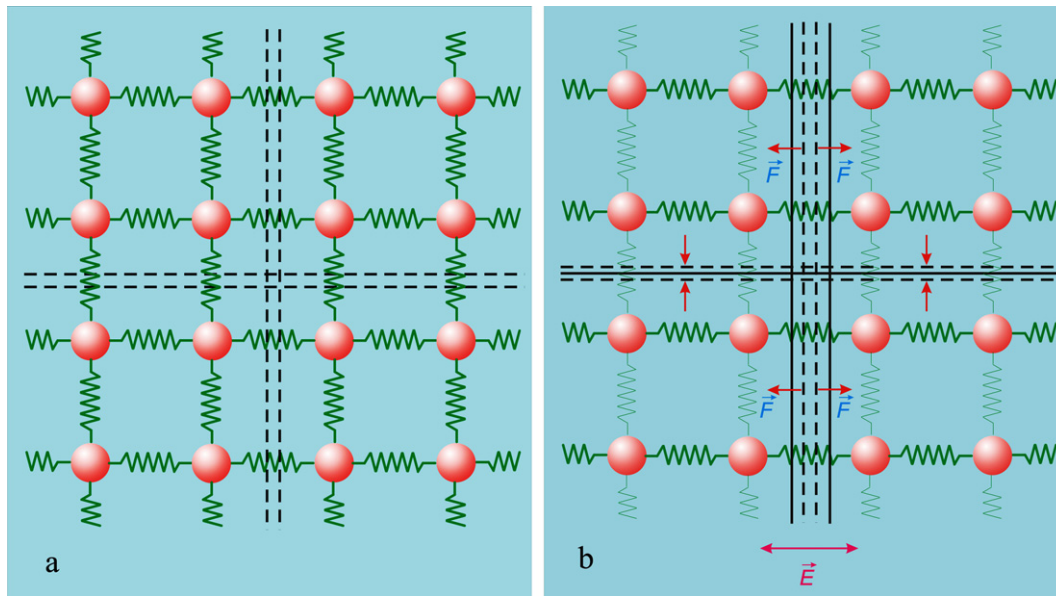


Fig. 5. Mechanical model of anisotropic plasticity in chalcogenide films (a) initial state and (b) under irradiation (see text for explanations).

conventional thermal heating of such disordered heterogeneous structure results in the isotropic state and this is due to random orientation of ShTZ. During irradiation with band-gap light due to electron–hole pair excitation we obtain continuous modification of the floppy (soft) phase which is responsible for the plastic flow and continuous modification of the rigid phase. The latter defines the change (increase) in Young's modulus of the material on a nanoscale and consequently takes responsibility for non-Hookean behavior of the film under irradiation in the course of nanoindentation. We supposed that the selective excitation of floppy (soft) phase makes its orientation parallel to the light polarization and also introduces reorientation in rigid phase.

From the very general point of view and considering the results published previously by different authors [14,20,21] we expected that the mechanical behavior of such ShTZ strongly depends on the state of polarization of the incident light. To check this supposition we produced by microlithography technique two orthogonal scratches on the surface of the film and then illuminated this surface by non-focused He–Ne laser with a linear polarized light. We studied the changes in surface topography by optical microscopy after a long-term (a few days) irradiation with intensity 60 mW/cm^2 , so, all the effects described below are of athermal (electronic) nature.

The initial picture in the case of the As–Se film is shown in Fig. 4(a). After prolonged irradiation the canal of the scratch which had the perpendicular direction to the light polarization increases essentially but at the same time the canal of the scratch which is along the electric field of light fills up (Fig. 4(b)–(d)). By performing the same experiment with circularly polarized light we observed that the canals in both scratches fill up. We performed these experiments in other composition of $\text{As}_x\text{Se}_{100-x}$ films (from pure Se

to $\text{As}_{50}\text{Se}_{50}$ films) with the step of x by 5 at.%. The results were reproducible well and differ only quantitatively. However the analysis of the compositional dependence is beyond the scope of the present work. It should be noted only that we have not confirmed this result for a thin film of pure amorphous selenium. After more than one-day of irradiation the canals of scratches did not change, but the film was crystallized.

Thus we found that plasticity of the films strongly depends on the orientation of the electric field vector of the light. These observations directly confirmed our previous results which were devoted to investigation of the polarization-dependent photoplastic effect in vitreous semiconductors [21]. We found there that band-gap polarized light produces hardness anisotropy at the surface of chalcogenide films.

We propose a simple mechanical model for explanation of this phenomenon (Fig. 5(a) and (b)), where the process of anisotropic softening consists in the weakening of mechanical compliance (it is pointed out as elastic elements in the Fig. 5) in the direction to be orthogonal to the light polarization. Taking into account the results of investigation of photo-induced anisotropic deformation in As_2S_3 [14] and $\text{As}_{50}\text{Se}_{50}$ [20,21] thin films we assume that microscopically the origin of these phenomena is similar to the described above. Since the latter were observed under irradiation only, they may be considered as a reversible part of long-term anisotropic structural changes caused by irradiation of linearly polarized light.

5. Conclusions

The compositional dependence of the photoplastic effect in $\text{As}_x\text{Se}_{100-x}$ has been investigated by nanoindentation test with the step-loading protocol. The non-monotonic

and opposite changes of the Young's modulus and nanohardness have been found. The pronounced non-linear (non-Hookian) mechanism of the formation of strain response in the films has been detected by the tests under irradiation and this behavior has been described in terms of shear transformation zone conception which assumes that the heterogeneous (two-phase) structure of chalcogenide glasses undergoes the modification with light. We have shown that compositional trends in these modifications are the highest for Se-enriched films (with As concentration near 10%). We have confirmed our suggestions directly by experiment with irradiation of the film surface by linearly polarized light. A simple mechanical model was proposed for explanation of the obtained results.

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