POLARIZATION - DEPENDENT PHOTOPLASTIC EFFECT IN As$_{50}$Se$_{50}$ CHALCOGENIDE GLASSES

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The band-gap linear polarized light has been shown to produce the hardness anisotropy of the surface of As$_{50}$Se$_{50}$ films, i.e. this is the result of a light-induced decrease or increase in the plasticity of glasses which depends on the polarization states of the incident light (the polarization – dependent photoplastic effect).

1. Introduction

In [1] the photoplastic effect in chalcogenide glasses has been described. This effect comprises two parts – negative and positive, which are accompanied by the two - stage transformation of film materials from the elastic to viscous state with different viscosity levels close to $1 \cdot 10^{12}$ and $1 \cdot 10^{13}$ Poise, respectively (for the illumination power of 100 mW|/cm^2). As a result the plasticity of chalcogenide glasses essentially increases under the band-gap illumination. In the present communication we report the observation of band-gap light polarization – dependent plasticity changes in As$_{50}$Se$_{50}$ thin films.

2. Experimental

The As$_{50}$Se$_{50}$ thin films with different thickness (1 - 3 μm) were prepared by thermal evaporation of bulk As$_{50}$Se$_{50}$ glass in vacuum of 10^{-4} Pa at the evaporation rate of 2-5 nm/s. Two groups of samples were investigated. To measure the stress in films they were deposited onto a clamped cantilever as the substrates (glass strips from microscope slides, 30 mm long, 2mm wide and 0.3 mm thick or muscovite strips, 30 mm long, 2mm wide and 0.03 mm thick) and to test the microhardness the films were deposited on quartz substrates with the thickness of 10 mm. Only fresh-deposited samples were used for our investigations.

A scheme of the experimental setup used to measure the stress relaxation σ in As$_{50}$Se$_{50}$ films during deposition and subsequent action of the light is given in [2,3]. The substrate was fixed as a cantilever. The displacement of the free end of the cantilever during deposition and subsequent illumination of the film with the band-gap light was measured by a laser dilatometer. This technique is based on the laser interference method intended to measure the thin substrate deflection which occurs during deposition and illumination of the film and is proportional to the internal stress in the film. The stress sensitivity of the dilatometer was near 10^5 Pa/μm and the accuracy in stress measurements was ±15%.

The microhardness tests were performed by the microhardness tester PMT-3. The indenter was a home-made sapphire knife with an angle of ≈ 100° and was held against the tested sample at a

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longitudinal angle of $\approx 10°$. We estimated the microhardness of the film H_0 and its change under illumination ΔH by measuring the length of imprints (where H_0 is the length of imprints for a non-illuminated film). The length of imprints was measured by an optical microscope. The scatter of 3-5% for imprints more than 15 μm was observed. For the smallest imprints ($\approx$ 3-5 μm) the scatter increased to 15-20%.

A sequence of succesive loading-unloading cycles for different lateral positions at the same load on the indenter was performed during one experiment. We moved the sample after each loading-unloading cycle so that a new area of the sample surface would have been tested during a new cycle. It enabled us to estimate hardness changes in the films during illumination. In all these cycles a loading time was equal to 20 s. The whole area of the sample for all cycles under test was much smaller than that affected by the laser spot ($\sim$ 2 mm). To obtain a reasonably good accuracy and reproducibility of the results five samples with the films obtained in one evaporation cycle were tested.

To measure the stress relaxation under illumination the $As_{50}Se_{50}$ films were excited by the band-gap light from 50 mW- He-Ne (633 nm) laser with a beam expanding system for uniform intensity. To test the microhardness we used a non - focused beam (diameter $\sim$ 2 mm) of the same laser with the attenuation system to reduce the resulting intensity. In both cases the beam intensity was within the range of 80 – 130 mW/cm^2.

Half - wave and quarter - wave plates were used to change the polarization state of the laser beam.

3. Results and discussion

The tensile stress $\sigma_1 \approx + 4 \times 10^7$ Pa in $As_{50}Se_{50}$ films deposited at the substrate temperature of $T \approx 300$ K was observed. Fig. 1 shows the effect of the polarization state of the incident light on the stress relaxation. For the as-evaporated film during the light illumination with a circularly polarized light ($\circlearrowright$), the initial tensile stress decreased from σ_1 to zero (level σ_0, Fig. 1), i.e. the photo-induced expansion of the film volume was observed but after the light having been switched off the tensile stress arose again (level σ_2, Fig. 1). These results are in agreement with those presented earlier in [4]. Similarly, the illumination of the film with a linearly polarized light, oriented along the axis of the cantilever ($\parallel$) was accompanied by the disappearance of the initial tensile stress which also decreased to zero (level σ_0, Fig. 1). In fact, no difference was observed between kinetics of the stress relaxation in films during the illumination with a circularly ($\circlearrowright$) or linearly ($\parallel$) polarized light. We suppose that this difference was much smaller than our accuracy of stress measurements. However, the light illumination of the film with a linearly polarized light, oriented orthogonally to the axis of the cantilever ($\perp$) significantly changes the situation, - the tensile stress disappears slower and reaches the level of σ_3 which is not equal to zero for the same illumination time as previous direction ($\parallel$) of polarization (Fig. 1).

According to Fig. 1, the stress relaxation kinetics and its magnitude during illumination of the film depend on the polarization state of the incident light. The illumination of the film with a linearly polarized light, oriented along the axis of the cantilever ($\perp$) results in a stronger stress relaxation in the film than that oriented orthogonally to the direction of the cantilever axis. The reversible change of these directions of polarization causes the reversible changes in the stress relaxation magnitude from level σ_3 to zero level σ_0.

It is seen from Fig. 1 that kinetics of the stress relaxation or generation is rather prolonged during illumination with a linearly polarized light oriented orthogonally to the direction of the cantilever axis, while the same process is much greater during illumination with a linearly polarized light having an opposite direction. We showed earlier [5-7] that the stress in chalcogenide films is closely connected with its microhardness and viscosity. Considering the results presented above, we assume that these parameters must depend on the direction of a linearly polarized light, too.
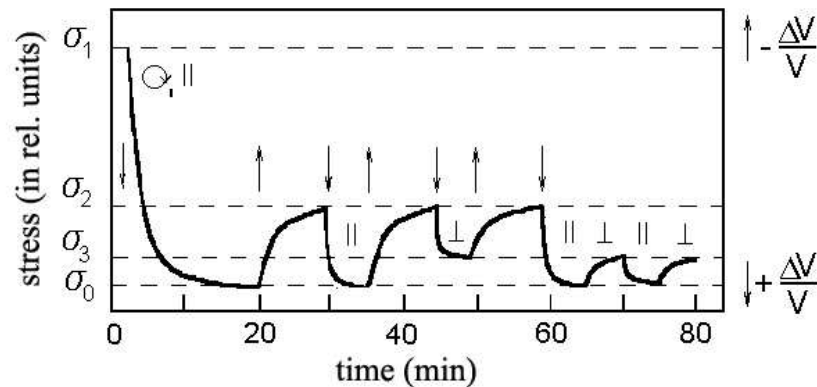
Fig. 1, Kinetics (in relative units) of stress relaxation and generation for 3 μm - As$_{50}$Se$_{50}$ film under the action of a circularly polarized ⟲ and/or linearly polarized laser light with two orthogonal directions of an electrical vector, oriented along (∥) or orthogonally (⊥) to the direction of the cantilever axis. The arrows show the beginning (↓) and the end (↑) of exposure and increase (↓) or decrease (↑) in the film volume.

According to [5-7] the viscosity glass material during illumination by the band-gap light decreases up to 10^{12}-10^{13} Poise. That is why under the action of the band-gap light the viscous flow of glasses can be observed. This viscous flow can be detected by the microindentation technique. We used this technique to investigate possible polarization dependences of microhardness in As$_{50}$Se$_{50}$ thin films.

As it was published earlier [1] for these films by using the Vickers indenter we found the giant photosoftening during the first stage of illumination followed by the increase in their microhardness during the second stage, - i.e. when the illumination is prolonged (the negative and positive parts of the photoplastic effect). We obtained the same results by using a home-made sapphire knife as an indenter (Fig. 2).
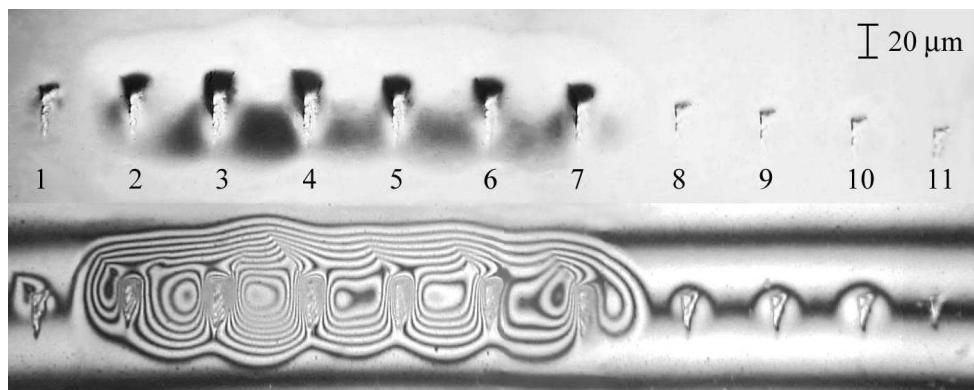

Fig. 2. The imprints and their interference pictures after microindentation (P=0.02N) for 3 μm-As$_{50}$Se$_{50}$ film (the test time for each imprint is equal to 20 s): 1 – as-evaporated film tested in the dark; 2 - 10 – tested during illumination with a linearly polarized light, oriented along the indenter tip; 11 – tested immediately after the incident laser is switched off. Total exposure of the film increases from imprint 2 to 10 as follows: 2 – 20 s; 3 – 50 s; 4 – 80 s; 5 – 110 s; 6 – 180 s; 7 – 240 s; 8 – 440 s; 9 – 760 s; 1 0 – 1380 s. See the text for details.

The imprint 1 on the Fig. 2 shows the result of indentation test in the dark and corresponds to the initial microhardness of the film. The small pileups detected around the imprint 1 can be explained by the presence of pores and voids in the as-deposited film which reduce the film viscosity to 10^{16} Poise [6] and annihilate under indentation. The imprints 2-10 manifest the changes in microhardness

of the film during illumination. The imprint 11 shows the result when the indentation starts after the light having been switched off.

There appeared a prompt dramatic increase in total depth of imprints at the initial stage of illumination (Fig. 2, imprints 2-7). We observed a large surface relief modulation caused by the giant photosoftening in the glass. As a result, during the simultaneous action of the surface photo-expansion and indenter penetration, the formation of dips with pillups in the illuminated and indented area takes place. When the laser illumination was prolonged the surface relief became much smaller (see the interference pictures for imprints 8 – 10) and disappeared completely after the light having been switched off (imprint 11). In the last case no pile-up was detected around the dip (Fig. 2, the interference picture for imprint 11).
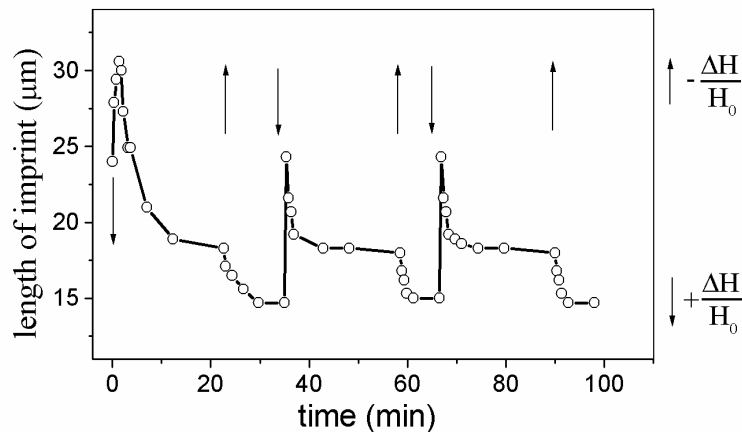

Fig. 3. Kinetics of microhardness changes as the change in the length of imprints obtained under illumination with a linearly polarized light oriented along the indenter tip (for P=0.02N) of 3 μm - $As_{50}Se_{50}$ film. The test time for each imprint is equal to 20 s. The arrows show the be ginning ($\downarrow$) and the end ($\uparrow$) of exposure and increase ($\downarrow$) or decrease ($\uparrow$) in the film microhardness.

The quantitative data of the whole process of microindentation, including successive on-off cycles of illumination are presented in Fig. 3. As follows from it, the photosoftening of the film increased drastically not only for the first illumination but for the repeated laser switching - on periods, too. In all the cases during illumination we observed two parts of the process; the first of them is characterized by a more pronounced photo-softening compared to the other one.

That is why we investigated the kinetics of the indenter penetration for the initial stage of illumination of the films with a linearly polarized light. This experiment showed that a linear polarized light produced hardness anisotropies of the film surface (Fig. 4).

The curve of relative changes in the hardness induced by illumination with a linearly polarized light oriented orthogonally to the indenter tip had a sharp maximum (Fig. 4, curve 1). This curve showed one and a half times increase in the plasticity of the film in comparison with that which was illuminated with a linearly polarized light in an opposite direction (along the indenter tip) (see Fig. 4, curve 2).

Note that we can't get such clear results for another composition of As-Se films, namely, for As_2Se_3 ones. We assume that in this case we need more sensitive equipment (e.g. nanoindentation technique), because the initial photosoftening for As_2Se_3 films is smaller than for $As_{50}Se_{50}$ ones.
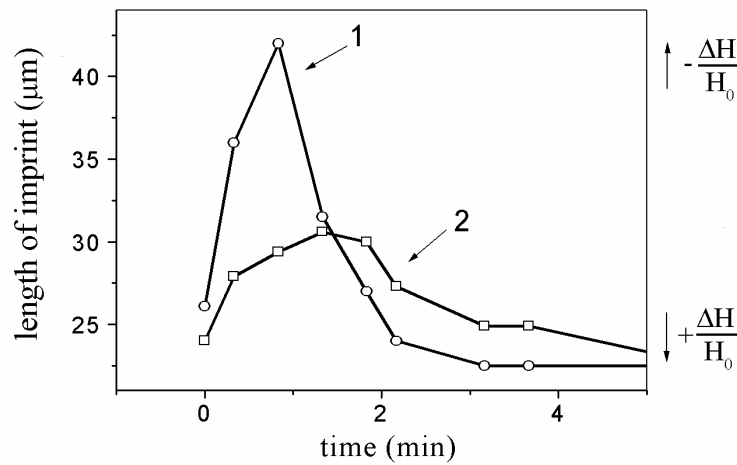
Fig. 4 The same as in Fig. 3 but at the initial stage of illumination: curve 1 – during illumination with a linearly polarized light, oriented orthogonally to the indenter tip; curve 2 – during illumination with a linearly polarized light, oriented along the indenter tip. The arrows show the beginning ($\downarrow$) of exposure and increase ($\downarrow$) or decrease ($\uparrow$) in the film microhardness.

Summarizing the results presented above, we can make a conclusion that during illumination of $As_{50}Se_{50}$ film by a linearly polarized light the internal stress will relax more along the polarization direction of the light than along the perpendicular direction (Fig. 1)[2] and as a result the hardness anisotropy of the surface caused by the polarized light takes place.

We emphasize that the influence of a linearly polarized light on the internal stress was observed for $As_{50}Se_{50}$ film for the first time in [9,10]. However, in these papers only some parts of the whole process were presented. Many details of the whole stress relaxation curve including the initial stress level and the sign of the relaxation process are not understood. Nevertheless, the authors in [6,7] supposed that an optical nanocontraction or expansion in the films of chalcogenide glasses were induced by the polarized light, resulting in the displacement of the free end of the clamped cantilever onto which the film was deposited.

As follows from our experiments we cannot expect any reversible expansion or compression of the film material. We assume that the band-gap linearly polarized light - dependent decrease or increase in the plasticity of glasses accompanied by the stress relaxation or generation (the polarization – dependent photoplastic effect) leads to the displacement of the cantilever.

The microscopic mechanism of the above- reported polarization-dependent plasticity may be similar to those presented in [11,12] and the initial giant photosoftening seems to be confirmed by the intra-molecular model proposed recently in [13][3]. In these models the presence of As_3Se_4 clusters or As_4Se_4 cage-molecules (using the terminology of [13]) is necessary. However, in our case we deal with the changes in macroscopic properties in non-crystalline material (viscosity, microhardness, etc.) which are caused by the structural changes of medium-range order. Thus, such macroscopic phenomena as the changes of viscosity, microhardness or increase/decrease in the volume can only be explained by complex structural changes, which take place at the short-range- and medium-range-orders. These structural modifications must involve all the atoms but not specific clusters, or cage-molecules only. In this connection we draw attention to the initial stage of the photoplastic effect in which the fall in viscosity is maximal and the photo-induced plasticity of glasses is maximal, respectively. As follows from the results given in this paper and obtained by us earlier [1], this stage

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[2] This result is in agreement with those predicted earlier by Fritzsche in [8].

[3] In the paper [13] the probable model of photoinduced plactisity was given, based on effective unfolding of As_4S_4 cage-like molecules realized by the combined action of light and stress. Similarly, the unfolding of As_4Se_4 - type cage-like molecules originally presented and dominated in as-deposited $As_{50}Se_{50}$ films, probably causes the giant photo-induced plasticity observed by us at the initial stage of illumination.

is to some or other extent observed under illumination of chalcogenide films having different compositions (for As-S(Se) systems, at least). The study of this stage will probably furnish the clue to better understanding of the nature of photo-induced transformations in these materials.

4. Conclusions

There was shown that band-gap polarized light produces hardness anisotrpy at the surface of $As_{50}Se_{50}$ films. This effect was ascribed to light-induced modification of the plasticity of the glass, which depends on the polarization state of the incident light.

References

[1] M. L. Trunov, V. S. Bilanich, J. Optoelectron. Adv. Mater. **5**, 1085 (2003).

[2] M. L.Trunov, A. G.Anchugin, N. D. Savchenko, M. A.Shakhaida, Sov. J. Opt. Techn. **2**, 76 (1993).

[3] M. L.Trunov, A. G.Anchugin, N. D. Savchenko, V. M. Rubish, Proc. SPIE **2113**, 183 (1994).

[4] M. L.Trunov, A. G.Anchugin, N. D. Savchenko, Sov. J. Sci. Appl. Photogr. Cinem. **5**, 384 (1991).

[5] M. L. Trunov, A. G.Anchugin, Sov. Tech. Phys. Lett. **18**, 37 (1992).

[6] M. L. Trunov, A. G.Anchugin, Sov. Tech. Phys. Lett. **18**, 78 (1992).

[7] M. L.Trunov, J. Non-Cryst. Solids **192&193**, 431 (1995).

[8] H. Fritzsche, Fizika I Tekhnika Poluprovodnikov (russ.) **32**, 952 (1998).

[9] P. Krecmer, A. M. Moulin, R. J. Stephenson, T. Rayment, M. E. Welland, S. R. Elliott, Science **277**, 1799 (1997).

[10] M. Stuchlik, P. Crecmer, S. R. Elliott, J. Optoelectron. Adv. Mater. **3**, 361 (2001).

[11] G. Chen, H. Jain, M. Vlcek, S. Khalid, J. Lee, D. A. Drabold, S. R. Elliott, NSLS Activity Report 2-22 (2001).

[12] G. Chen, H. Jain, M. Vlcek, S. Khalid, J. Lee, D. A. Drabold, S. R. Elliott, Appl. Phys.Lett. **82**, 106 (2003).

[13] S. N. Yannopoulos, Phys. Rev. B **68**, 064206 (2003).