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Photo-thermoinduced changes of transmission spectra of $As_{40-x}Sb_xS_{60}$ amorphous layers

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Abstract. The results of investigation of the $As_{40-x}Sb_xS_{60}$ (x = 0-10) thin films transmission spectra depending on exposure and heat treatment conditions are given. It was established that illumination and annealing of films leads to the absorption edge shift into the longwave spectral region. The values of pseudogap width E_g are determined. Optical characteristic changes of films are caused by photo-thermostructural transformations taking place in them under irradiation and annealing.

Keywords: amorphous film, arsenic chalcogenides, transmission spectra, photo-thermostructural transformations, information optical recording.

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1. Introduction

Due to their high sensitivity, amorphous films of arsenic chalcogenides are widely used as media for information optical recording, in creation of highly efficient holographic gratings, optical diffraction elements for various applications [1-7]. Registration of information is based on difference in optical properties of irradiated and non-irradiated parts in these films. There are two main signs of changes in optical properties: shifts of the absorption edge (photodarkening or photobleaching) and growth (or reduction) of the refraction index. A level of photoinduced changes in optical parameters of films considerably depends on their chemical composition, conditions of preparation, thermal processing and irradiation in all these cases. Therefore, it is of great interest to investigate the photoinduced effects in films of another system.

In this work, we have adduced the results of studying the influence of irradiation and annealing on transmission spectra of the films based on the system As_2S_3–Sb_2S_3 with the antimony content up to 10 at.%.

2. Experimental

$As_{40-x}Sb_xS_{60}$ (x = 0-10) glasses were prepared using the vacuum melting method (0.01 Pa) of the corresponding mixture of As_2S_3 and Sb_2S_3 components synthesized before from high purity elementary substances. As_2S_3 and Sb_2S_3 melts were homogenized for 48 h at the temperatures 780 and 870 K, respectively. $(As_2S_3)_{100-x}(Sb_2S_3)_x$ melts were processed in the same manner for 36 h at 780-830 K. The melts were periodically stirred. The quenching rate of the melts was approximately 10 K/s.

Thin films (thickness ~1–2 μm) were deposited by vacuum thermal evaporation on cool silica substrates. A uniform thickness of layers was provided by planetary rotation of substrates. Light exposure of films was made using defocused radiation of a semiconductor laser (λ = 530 nm, E = 95 mW/cm^2). Annealing of the films was performed in inert atmosphere (argon) for 1 h at the temperature 423 K.

Optical transmission of the films was measured at room temperature within the range 400 to 800 nm by using the method [8] with a monochromator МДР-3. The spectral resolution was no worse than 10^{-3} eV.

3. Results and discussion

Figs 1 and 2 (curves 1) show transmission spectra for the as-prepared films $As_{36}Sb_4S_{60}$ and $As_{30}Sb_{10}S_{60}$. It is obvious that, when passing from arsenic trisulphide to antimony trisulphide, the absorption edge is red-shifted, which is indicative of narrowing pseudogap E_g for these films. This reduction of the optical gap is caused by structural transformations, when passing from As_2S_3 to Sb_2S_3. In this case, the edge slope is practically unchanged. It means that the type of structural matrix is essentially unchanged when the composition of

$As_{40-x}Sb_xS_{60}$ films is varied. Here, the main structural units are trigonal pyramids $AsS_{3/2}$, $SbS_{3/2}$, $As(Sb)S_{3/2}$. However, the film matrix also contains a considerable number of molecular fragments with homopolar bonds [9-11].

The E_g value can be determined from the Tauc relation [12]

$$\alpha(h\nu)\cdot h\nu = B(h\nu - E_g)^2, \quad (1)$$

which is valid within the range of high energies when the absorption coefficient has values $\alpha(h\nu) \geq 10^4$ cm^{-1}. In (1), $h\nu$ is the photon energy, B is the constant that depends on film material (e.g., for as-prepared As_2S_3 film $B = 876$ cm$^{-1/2}$eV$^{-1/2}$ [12], while for GeS_2 – $B = 549$ cm$^{-1/2}$eV$^{-1/2}$ [13]) and characterizes the slope of the Tauc absorption edge.

The E_g values for $As_{40-x}Sb_xS_{60}$ films were determined by extrapolation of the dependences $[\alpha(h\nu)\cdot h\nu]^{1/2} \sim f(h\nu)$ down to $\alpha(h\nu) = 0$ (Fig. 3) and are within limits 2.114 – 2.385 eV. With the growing Sb content in film composition, the pseudogap width is reduced (see Table). The E_g value for As_2S_3 film (2.385 eV) obtained by us is in good accordance with that adduced in [12] (2.38 eV).

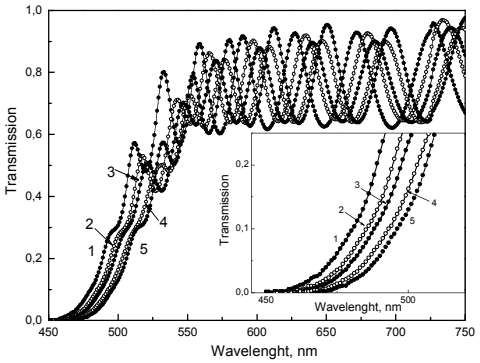


Fig. 1. Dependences of transmission spectra inherent to $As_{36}Sb_4S_{60}$ films on the exposure time: *1* – 0; *2* – 5; *3* – 10; *4* – 20; *5* – 40 min.

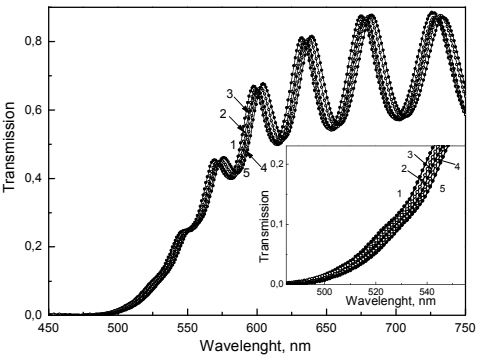
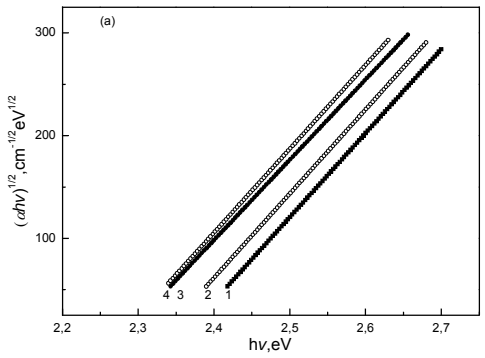


Fig. 2. Dependences of transmission spectra inherent to $As_{30}Sb_{10}S_{60}$ films on the exposure time: *1* – 0; 2 – 5; *3* – 10; *4* – 20; *5* – 40 min.



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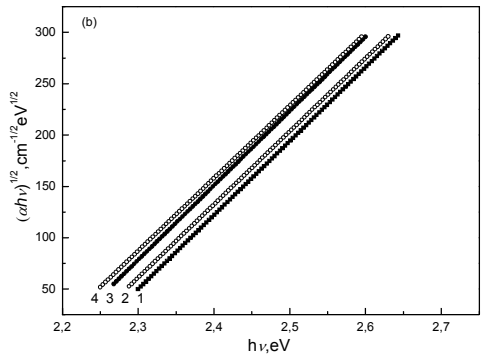

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Fig. 3. Dependence of the absorption edge position on the photon energy for the films $As_{36}Sb_4S_{60}$ (*a*) and $As_{30}Sb_{10}S_{60}$ (*b*) non-exposed (*1*) and exposed (*2 – 4*) for 5 (*2*), 20 (*3*) and 40 min (4).

Table. Values of the pseudogap width E_g (eV) for $As_{40-x}Sb_xS_{60}$ films versus the exposure time.

x, at. %	Exposure time, min					
	0	5	10	20	30	40
0	2.385	2.385	2.365	2.347	2.335	2.329
4	2.355	2.325	2.309	2.274	2.279	2.271
6	2.308	2.262	2.256	2.223	2.215	2.191
8	2.256	2.254	2.231	2.221	2.215	2.213
10	2.114	2.095	2.093	2.090	2.089	2.082

Light exposure of $As_{40-x}Sb_xS_{60}$ films results in a shift of absorption spectra to the longwave range (Figs 1 and 2, curves 2 to 5). It means one observes photodarkening of the films. In this case, the maximum shift (ΔE) of the absorption edge takes place in the films with antimony contents 4, 6 and 8 at.% (Fig. 4) under the same exposure conditions. With further growth of Sb concentration, the ΔE value is decreased. Also decreased is the E_g value calculated from the dependences $[\alpha(h\nu)\cdot h\nu]^{1/2} \sim f(h\nu)$ for these films (see Table). It is noteworthy that the speed of photoinduced changes in optical parameters is reduced with increasing the irradiation time for all the investigated films.

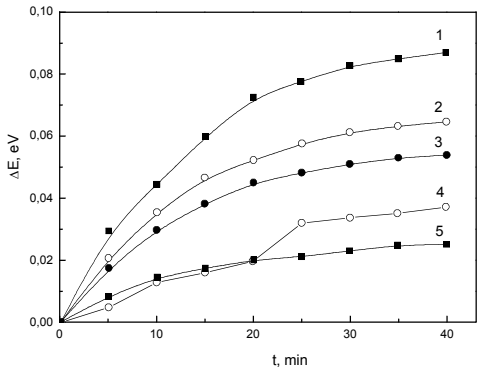
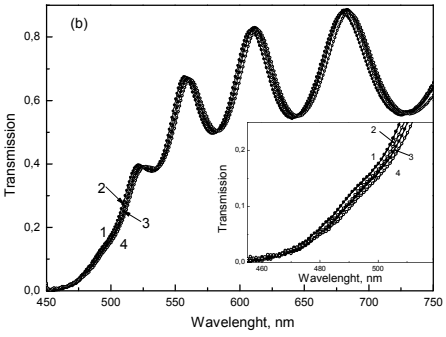


Fig. 4. Shift of the absorption edge at the transmission level 0.2 versus the exposure time for the films $As_{40-x}Sb_xS_{60}$. *x* is equal: *1* – 4; *2* – 6; *3* – 8; *4* – 0; *5* – 10 at.%.

Changes in the absorption edge position (i.e., E_g values) are caused by structural transformations that take place under laser irradiation. As mentioned above, the films are in nanoheterogeneous state. Their matrix is mainly constructed of structural groups with heteropolar bonds ($AsS_{3/2}$, $SbS_{3/2}$, $As(Sb)S_{3/2}$), but contains molecular fragments with homopolar bonds As-As and S-S. It seems that availability of structural units with homopolar bonds Sb-Sb is less probable in the film matrix. As compared with $As_{40}S_{60}$, the higher sensitivity of $As_{40-x}Sb_xS_{60}$ films containing 4, 6 and 8 ат.% of Sb can be indicative of higher disorder in their matrix due to increased content of structural fragments with homopolar bonds As-As. Irradiation of films results in breaking and re-switching the As-As and S-S bonds in the structural fragments of As_4S_4 type and sulphur chains with creation of structural units AsS_3. In its turn, this causes polymerization of molecular groups spatially located in the most optimum way into the network of trigonal pyramids $As(Sb)S_{3/2}$ with small changes in angles between S-As(Sb)-S bonds [6, 9, 11]. It has been shown in [6, 9, 14] that destruction of some chemical bonds and creation of another ones can be accompanied by generation of over- and sub-coordinated atoms of arsenic and sulphur. For instance, in As_2S_3 these defects are As_2^-, As_4^+, S_3^+ and S_1^-. In what follows, these defect states are transformed into the structure of pyramidal AsS_3 units. Besides, defectless photopolymerization of molecular fragments (As_4S_4 and S_2) into the structural network $AsS_{3/2}$ takes place [6, 9, 15].

With the aim to ascertain the influence of temperature on photoinduced changes in optical parameters, we studied transmission spectra of the films $As_{36}Sb_4S_{60}$, $As_{32}Sb_8S_{60}$, $As_{30}Sb_{10}S_{60}$ annealed for 1 h at the temperature $T_{ann} = 423$ K. It should be noted that this temperature is much lower than the vitrification one T_g for these films. Our investigations have shown that annealing results in a shift of transmission spectra to the longwave side, which is indicative of narrowing the pseudogap. When the Sb content in the films increases, the shift value is decreased. These changes of film optical characteristics are caused by structural transformations. Like to the irradiation case, in the course of annealing homopolar bonds in structural groups As_4S_4 and sulphur chains are broken, while structural units with heteropolar bonds are formed. In this case, thermoenhanced transformation of molecular fragments with homopolar bonds into the structural network of $AsS_{3/2}$ type can be realized both via the defectless mechanism and with creation of structural defects, namely, over- and sub-coordinated arsenic and sulphur atoms.

Our investigations of transmission spectra for $As_{40-x}Sb_xS_{60}$ films irradiated after annealing (Fig. 5) have shown that the shift of absorption edge under light action is less in them than that in the as-prepared ones. For example, after irradiation of the annealed $As_{36}Sb_4S_{60}$ film for 10 min the ΔE value is close to 0.015 eV. While the value of this parameter for the as-prepared film is 0.044 eV. Like to the case of as-prepared films, for the same exposure the ΔE value of annealed films is decreased with growth of *x*. So, the value ΔE for the film $As_{32}Sb_8S_{60}$ annealed for 10 min is 0.010 eV. The lower level of changes in optical parameters in the annealed films is conditioned by a rather less number of structural groups with homopolar bonds in their matrix after annealing, which are able to polymerize under irradiation.



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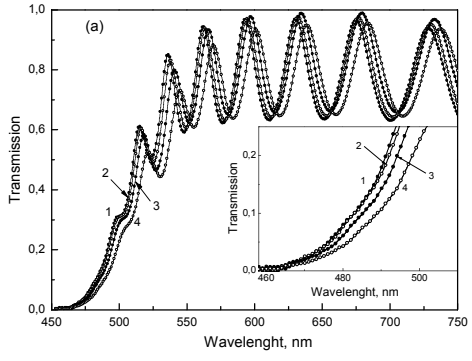

b

Fig. 5. Transmission spectra of $As_{36}Sb_4S_{60}$ (*a*) and $As_{32}Sb_8S_{60}$ (*b*) films annealed for 1 h at the temperature 423 K versus the exposure time: *1* – 0; *2* – 5; *3* – 10; *4* – 20 min.

4. Conclusions

Growth of the Sb content in the composition of amorphous films $As_{40-x}Sb_xS_{60}$ (x = 0-10), irradiation and annealing of them result in the shift of their transmission spectra to the longwave range, which testifies narrowing the pseudogap width. These changes of optical characteristics are caused by photo- and thermostructural transformations that are related with the decreasing content of structural fragments possessing homopolar bonds in their matrix. The level of photoinduced changes in optical parameters of annealed films is much lower than that in the as-prepared ones.

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