

## OPTICAL PHOTOINDUCED PHENOMENA AND HOLOGRAPHIC RECORDING IN AMORPHOUS As-Se THIN FILMS

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The effect of light-induced photodarkening in amorphous  $As_{100-x}Se_x$  ( $x=40-98$ ) thin films for different thickness and film composition was investigated. It was established a strong dependence of the red shift of the absorption edge and refractive index under light irradiation on the film composition and thermal treatment. It was established that the more sensitive films to photodarkening and holographic recording correspond to non-stoichiometric compositions of  $As_{55}Se_{45}$  and  $As_{60}Se_{40}$  glasses. The experimental results are interpreted in terms of structural optical polymerization process, which includes the transformation of  $As_4Se_4$  and  $Se_2$  structural units in homogenius  $AsSe_{3/2}$  network.

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### 1. Introduction

The effect of light-induced photodarkening is characteristic of amorphous chalcogenide films and presents scientific as well as practical interests [1-5]. The considerable changes of the optical absorption and of the refractive index of amorphous material associated with photostructural transformations under the light exposure have been stimulated the application of arsenic chalcogenides as optical and holographic recording media, inorganic photoresists, as passive elements of integrated optics, and imaging devices [6-10]. The arsenic selenide amorphous films usually became darkened under action of light from the region of fundamental optical absorption  $h\nu \geq E_g$  and so-called photodarkening effect takes place. The increasing of the absorption is caused by the shift of the absorption edge to lower photon energies, and is believed to be due to broadening of the valence band, the top of which is formed mainly by states of lone-pair electrons of the chalcogen atom. Because the composition of chalcogenide glass determines the structural units and the mean coordination number of the amorphous solids [11], the effect of the composition in the glassy system  $As_{100-x}Se_x$  ( $x=40-98$ ) on the degree of photostructural transformations has been studied. In the last years many investigations has been done on photodarkening process in amorphous chalcogenides, but still now does not exist a unique model for its explanation. Recently some results on photodarkening in amorphous  $As_{40}Se_{60}$  were interpreted in frame of the "slip motion" model [12], and were obtained some experimental results concerning the thickness dependence of photodarkening in  $\alpha$ - $As_{40}Se_{60}$  [13] and  $\alpha$ - $As_{40}Se_{60}$  doped with Pr and Dy [14].

The more detailed investigations of the composition dependence and the thickness dependence can provide some new information in order to understand the mechanism of photodarkening effect in amorphous chalcogenides. In this paper, we investigate the thickness

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dependence of the transmission spectra before and after light exposure in  $\alpha$ -As<sub>40</sub>Se<sub>60</sub> thin films, the kinetics of photodarkening and the dynamics of optical registration process of micro-holograms in  $\alpha$ -As<sub>100-x</sub>Se<sub>x</sub> thin films. A special attention is done to the composition dependence of photodarkening characteristics in the films of the glassy system As<sub>100-x</sub>Se<sub>x</sub> ( $x=40\div 98$ ). It was established, that the higher sensitivity on photodarkening as result of light exposure is characteristic for the non-stoichiometry As<sub>60</sub>Se<sub>40</sub> amorphous films, and decrease with increasing of Se content in the As<sub>100-x</sub>Se<sub>x</sub> glass. The experimental results are interpreted in terms of structural optical polymerization process, which includes the transformation of As<sub>4</sub>Se<sub>4</sub> and Se<sub>2</sub> structural units in homogeneous AsSe<sub>3/2</sub> network [15,16].

## 2. Experimental

The glasses As<sub>100-x</sub>Se<sub>x</sub> ( $x=40\div 98$ ) were synthesized from the elements of 6N (As, Se) purity by conventional melting technique. The As<sub>100-x</sub>Se<sub>x</sub> thin films of different thickness 0.27 to 4.5  $\mu\text{m}$  were prepared by "flash" thermal evaporation in vacuum onto glass substrates held at  $T_{\text{subs}}=100$  °C. For optical transmission an UV/VIS Specord (in the 0.3-0.8  $\mu\text{m}$  spectrum range) CARLZEISS Jena production was used.

To initiate photostructural transformations in thin film samples a He-Ne laser ( $\lambda=0.63$   $\mu\text{m}$ ,  $W=10$  mW) was used as a source of light exposure. The splitter was used for divide the laser beam: one Si-photodetector was used for measuring the film transmittance, and another Si-photodetector was used for measuring the time stability of the laser intensity. The total transmittance of the film was currently measured during the exposure time with the aid of a registration module. The experimental set-up included a laser, a digital build-in PC-card for data acquisition PCI-1713A connected with the Si-photodetector (Fig.1). Special software was elaborated for automatic measurements.

The relaxation curves were examined by computing fitting procedure using the stretched exponential presentation of the data:  $T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{(1-\alpha)}$ , where  $t$  is the exposure time,  $\tau$  is the apparent time constant,  $A$  characterizes the exponent amplitude,  $t_0$  and  $A_0$  are the initial coordinates, and  $\alpha$  is the dispersion parameter ( $0 < \alpha < 1$ ). The thermal treating effect was examined by annealing of a part of the films in vacuum at  $T_{\text{ann}}=120$  °C during 1 hour. After the annealing, the optical transmission relaxation under light exposure was registered in the same manner. The microholograms on the amorphous As-Se films were registered by means of the interference of two He-Ne laser beams ( $\lambda=6328$  nm) with a power of  $W=30$  mW. The kinetics of diffraction efficiency growth was measured by registration of the intensity of the 1-st interference maximum versus time exposure.

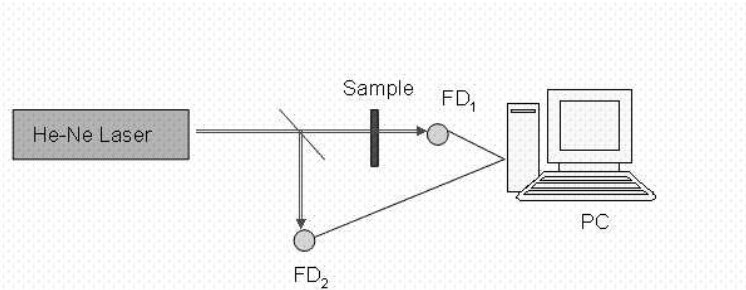


Fig. 1. The experimental set-up for measuring the transmittance during photodarkening.

## 3. Results

### 3.1. Optical transmission

The films based on arsenic chalcogenides usually become darkened due to photo-structural transformations under action of light from the region of fundamental optical absorption (so called photodarkening). Fig. 2a shows the transmission spectra of amorphous As<sub>60</sub>Se<sub>40</sub> thin films, before (curve 1) and after exposure (curve 2) during 1 hour.

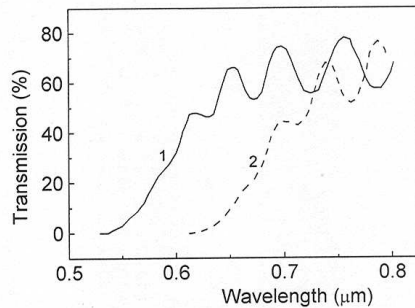


Fig. 2a. The transmission spectra of amorphous  $\text{As}_{60}\text{Se}_{40}$  thin films  $L=1.3 \mu\text{m}$ , before (1) and after exposure (2).

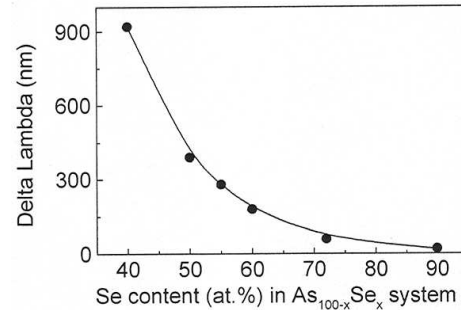


Fig. 2b. The dependence of the photoinduced shifts of the absorption edge ( $\Delta\lambda$ ) versus Se content (at. %) in  $\text{As}_{100-x}\text{Se}_x$  glass system.

The enhancement of the absorption is caused by the shift of the absorption edge to lower photon energies. The photoinduced shift of the absorption edge ( $\Delta\lambda$ ) after exposure decrease the transmission at a fixed wavelength and increase the refractive index  $n$  of the amorphous material. The photoinduced shift of the absorption edge ( $\Delta\lambda$ ) as well as the changes in the refractive index ( $\Delta n$ ) depends at the fixed temperature depends on the exposure intensity, exposure time, film thickness, and on the composition of the amorphous thin film.

The maximum shift of the absorption edge  $\Delta\lambda$  at the level of transmittance  $T=20\%$  consists  $\Delta\lambda=920 \text{ nm}$ , for  $\text{As}_{60}\text{Se}_{40}$  films, while for  $\text{As}_{10}\text{Se}_{90}$  and  $\text{As}_5\text{Se}_{95}$  films this value is only  $\Delta\lambda=2\div 5 \text{ nm}$  (Fig.2b). In the same matter, the relative change of the refractive index  $\Delta n/n$  is bigger for  $\text{As}_{60}\text{Se}_{40}$  films ( $\Delta n/n=0.394$ ) and decrease with increasing the concentration of Se in  $\text{As}_{100-x}\text{Se}_x$  glassz system. Our experimental data correlate with the experimental data for As-Se films obtained in [17].

### 3.2. Photodarkening kinetics

Photocondarkening relaxation was measured during illumination for amorphous  $\text{As}_{100-x}\text{Se}_x$  ( $x=40\div 98$ ), for as-deposited and annealed films at  $T_{\text{ann}}=120^\circ\text{C}$  during 1 hour. The relaxation of the relative optical transmission  $T(t)/T(0)$  of the amorphous  $\text{As}_{60}\text{Se}_{40}$  films of different thickness is shown in Fig. 3a. The experimental data show that for the thicker films the photodarkening is stronger, and almost is absent for the films with thickness about  $0.2\text{-}0.3 \mu\text{m}$ . Our data are in good agreement with the experimental results obtained on The influence of the thickness on the photodarkening effect was investigated for the amorphous  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{Se}_3$  films [17-20], and for  $\text{As}_2\text{Se}_3$  pure and doped with Dy and Pr films [14].

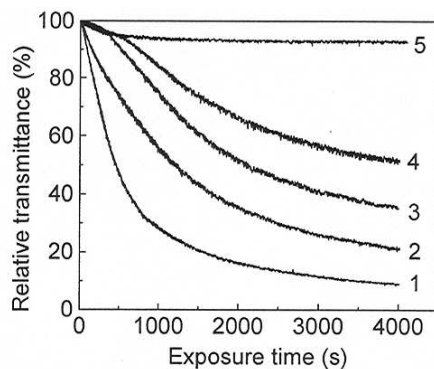


Fig. 3a. The dependence of transmission versus exposure time for amorphous  $\text{As}_{60}\text{Se}_{40}$  films of different thickness  $L, \mu\text{m}$  1-4.07; 2-2.04; 3-0.76; 4-0.54; 5-0.27.

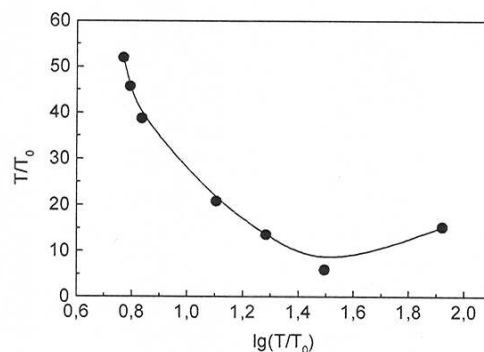


Fig. 3b. The thickness dependence of the photodarkening in amorphous  $\text{As}_{60}\text{Se}_{40}$  films.

For the stoichiometric films irradiated by band gap illumination at room temperature was found that the photodarkening disappears when the films are thinner than 50 nm [19]. The authors explain this anomaly by the fact that the structure of the film is dependent on the film thickness either that the photodarkening exhibits a surface behaviour, which is different from bulk behaviour. On the other hand, a small photodarkening was observed in  $\alpha$ -As<sub>2</sub>Se<sub>3</sub> films of 30 nm in thickness [20].

According to [20] the thickness dependence of the photodarkening is based on the thickness dependence of the initial optical absorption edge before irradiation with band gap light. The authors explain the absence of photodarkening in thinner films by the strain induced by the lattice mismatch between the film and the substrate.

According to transmission spectra measurements and to the results obtained in [14], we suggest that the thickness dependence of photodarkening is caused by different light amount absorbed in the film for different thickness, and which regulate the number of absorbed photons generating the photodarkening effect. The thickness dependence of photodarkening, presented in the coordinates  $T/T_0$  vs.  $\lg(T/T_0)$  according [17] represent a curve with minimum (Fig. 3b). For amorphous As<sub>60</sub>Se<sub>40</sub> composition the maximum sensitivity is obtain for the films with the thickness of  $L=4.0 \mu\text{m}$ .

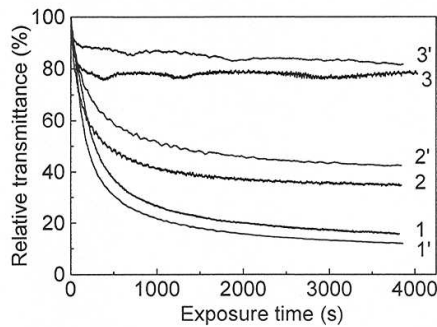


Fig. 4a. Photodarkening kinetics of amorphous As<sub>50</sub>Se<sub>50</sub> (1,1'), As<sub>40</sub>Se<sub>60</sub> (2,2'), and As<sub>28</sub>Se<sub>72</sub> (3,3') thin films. 1,2,3 – as deposited; 1',2',3' – annealed at  $T=120^\circ\text{C}$  during 1 hour.

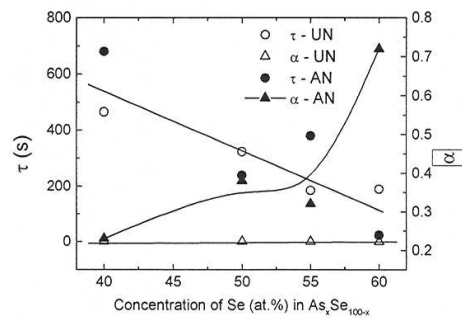


Fig.4b. The dependence of the parameters  $\tau$  and  $\alpha$  of the stretched exponential for the as-deposited (UN) and annealed (AN) amorphous As<sub>100-x</sub>Se<sub>x</sub> thin films.

Fig. 4a shows the relaxation of the optical transmittance during illumination of as-deposited and annealed As<sub>100-x</sub>Se<sub>x</sub> thin films. Increasing of Se content in As<sub>100-x</sub>Se<sub>x</sub> thin films decrease the photodarkening, and this process is very small in the films with high content of Se. The relaxation of photodarkening can be described by the stretched exponential function  $T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{1-\alpha}$ , ( $0 < \alpha < 1$ ). The dependence of the relaxation time  $\tau$  and of the dispersion parameter  $\alpha$  for as-deposited and annealed films is shown in Fig. 4b. It was shown, that the parameter  $\alpha$ , which describe the dispersion of the photodarkening process, after annealing decrease and is almost constant for all film compositions.

### 3.3. Holographic recording process

Fig. 5a shows the kinetics of growth of the diffraction efficiency for amorphous As<sub>50</sub>Se<sub>50</sub> and As<sub>60</sub>Se<sub>40</sub> thin films during exposure as result of interference of two He-Ne laser beams ( $\lambda=6328 \text{ nm}$ ) with a power of  $W=30 \text{ mW}$ . The intensity of the first interference maximum was recorded in the transmittance mode. The maximum of the diffraction efficiency is reached at 10-15 min of the exposure and after that for the compositions richer in Se the saturation take place (Fig. 5b). For the compositions richer in As the kinetics of the diffraction efficiency represents a curve with maximum or a sinusoidal. The deletion process of the optical information due to the time exposure may cause the fall down of the diffraction efficiency after the maximum.

The holographic sensitivity of the amorphous films and the diffraction efficiency of the hologram has, decreases with increasing of the selenium content in As<sub>100-x</sub>Se<sub>x</sub> glassy system (Fig. 6b) in according to the variation of the refractive index under illumination (Fig. 6b). These dependences are in a good agreement with earlier obtained experimental data [17].

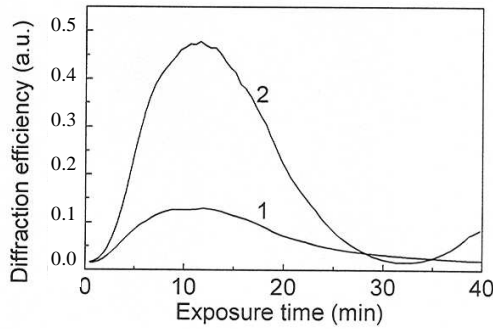


Fig. 5a. The kinetics of growth of the diffraction efficiency versus exposure time for amorphous  $\text{As}_{50}\text{Se}_{50}$  (curve 1,  $L=1.3 \mu\text{m}$ ) and  $\text{As}_{60}\text{Se}_{40}$  (curve 2,  $L=1.3 \mu\text{m}$ ) thin films.

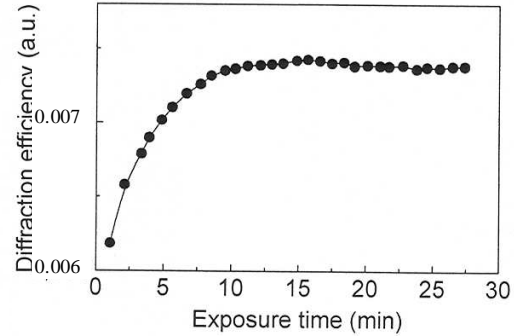


Fig. 5b. The kinetics of growth of the diffraction efficiency versus exposure time for amorphous  $\text{As}_{28}\text{Se}_{72}$  (curve 2,  $L=1.3 \mu\text{m}$ ) thin films.

#### 4. Discussion

The transmission spectra show that the enhancement of the absorption is caused by the shift of the absorption edge to the lower photon energies, and increase with decreasing of Se in the  $\text{As}_{100-x}\text{Se}_x$  glassy system up to 980 nm for  $\text{As}_{60}\text{Se}_{40}$  thin films. The photodarkening exhibits a thickness dependence (Fig. 3a and 3b) and is explained by different authors elsewhere [14, 17-20].

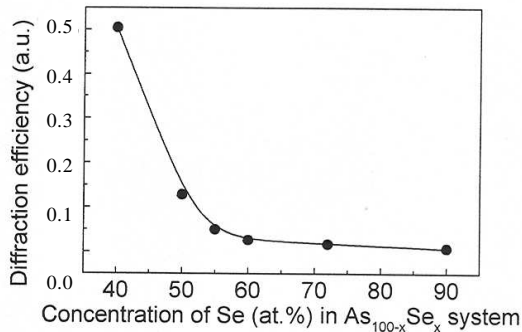


Fig. 5a. The dependence of the diffraction efficiency Versus Se concentration in the  $\text{As}_{100-x}\text{Se}_x$  glassy system.

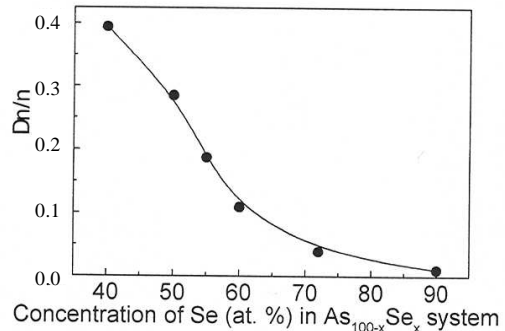


Fig. 5b. The dependence of the variation of the refractive index  $\Delta n/n$  on Se concentration in the glassy system  $\text{As}_{100-x}\text{Se}_x$  under the illumination.

Table 1. Parameters of the stretched exponential obtained by fitting of the experimental points and calculated curves for  $\text{As}_{100-x}\text{Se}_x$  thin films.

As-deposited amorphous films				
Composition	$A_0$ , %	$A$ , %	$\tau$ , s	$\alpha$
$\text{As}_{60}\text{Se}_{40}$	22.06	379.70	465.53	0.34
$\text{As}_{50}\text{Se}_{50}$	16.43	77.25	323.50	0.34
$\text{As}_{45}\text{Se}_{55}$	27.15	72.33	195.27	0.39
$\text{As}_{40}\text{Se}_{60}$	34.41	72.94	189.61	0.49
$\text{As}_{28}\text{Se}_{72}$	71.35	20.02	599.91	0.88
Annealed films at $T_{ann}=120^\circ\text{C}$ during 1 hour				
Composition	$A_0$ , %	$A$ , %	$\tau$ , s	$\alpha$
$\text{As}_{60}\text{Se}_{40}$	26.17	72.17	680.67	0.23
$\text{As}_{55}\text{Se}_{45}$	13.56	77.74	238.96	0.38
$\text{As}_{50}\text{Se}_{50}$	32.13	65.2	380.25	0.32
$\text{As}_{40}\text{Se}_{60}$	38.72	231.69	23.61	0.72
$\text{As}_{28}\text{Se}_{72}$	45.31	103.01	3244.76	0.95

As was mentioned above, the observed relaxation of photodarkening is described by the stretched exponential function  $T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{(1-\alpha)}$ , where  $t$  is the exposure time,  $\tau$  is the apparent time constant,  $A$  characterizes the exponent amplitude,  $t_0$  and  $A_0$  are the initial coordinates, and  $\alpha$  is the dispersion parameter ( $0 < \alpha < 1$ ). The above parameters were calculated for all investigated amorphous films before and after annealing using a computer fitting, and are presented in Table 1.

The fact that the photodarkening kinetics may be described by a stretched exponential we may consider as indication of dispersion in kinetic mechanism, i.e. the time dependence of the process rate [21]. The data allow concluding that formation of photoinduced absorption is limited by a dispersive process with the exponent  $\alpha \approx 0.5$ . In our case it is the dispersive character of hole transport that may cause the dispersive character of the relaxation after photogeneration. The transport of photoexcited holes is included in the "slip motion" model for photodarkening in the stage when the layer clusters are charged due to capture of charge carriers [22]. This model was used by us to explain the experimental results for amorphous  $\text{As}_2\text{Se}_3$  films doped rare-earth ions [23], and tin [24]. Charge transport in chalcogenide glasses is known as highly dispersive due to wide distribution of capture times in multiple-trapping process [25,26]. For glasses like a- $\text{As}_2\text{Se}_3$  the dispersive parameter  $\alpha$  of hole transport is close to 0.5, in accordance with the value found from the stretched exponential presentation of photodarkening kinetics. The fact that  $\alpha$  is increasing in the Se-rich compositions indicates to the increasing of the ordering in the structure of amorphous films. The composition dependence of photodarkening may be caused by the different ratio of homopolar chemical bonds (As-As, Se-Se) and heteropolar (As-Se) in investigated amorphous films, and which are responsible for the photodarkening [15,16].

## 5. Summary

The composition dependence of the transmission spectra, photodarkening characteristics, and kinetics of recording process of holographic information in the films of the glassy system  $\text{As}_{100-x}\text{Se}_x$  ( $x = 40 \div 98$ ) was investigated. It was established, that the higher sensitivity to light exposure exhibit the non-stoichiometric  $\text{As}_{50}\text{Se}_{50}$ ,  $\text{As}_{55}\text{Se}_{45}$ , and  $\text{As}_{60}\text{Se}_{40}$  amorphous films, and decrease with increasing of Se content in the  $\text{As}_{100-x}\text{Se}_x$  glass. The experimental results are interpreted in terms of structural optical polymerization process, which includes the transformation of  $\text{As}_4\text{Se}_4$  and  $\text{Se}_2$  structural units in homogeneous  $\text{AsSe}_{3/2}$  network [15,16].

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