

Optical properties and photoinduced absorption in As-Se and As₂Se₃:Sn thin films

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Photostructural transformations in amorphous films of chalcogenide glasses (ChG) under light irradiation present scientific and practical interests. From scientific point of view, because the composition of ChG determine the kind of structural units and the mean coordination number, in the present work the amorphous films of the chalcogenide systems As_{100-x}Se_x (x=40÷98) and As₄₀Se₆₀:Sn_y (y=0÷10.0 at.% Sn) were studied. The experimental investigation of the transmission spectra, photodarkening relaxation and holographic characteristics of the amorphous films under study, including the thickness dependence are presented. The dependences of the refractive index under light irradiation and heat treatment were revealed. It was established that the more sensitive to light irradiation are the amorphous films of As₆₀Se₄₀ and As₅₀Se₅₀, which exhibit big modifications of the refractive index ($\Delta n/n$) = 0.394). The correlation between the photostructural transformations and holographic characteristics was established.

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1. Introduction

Optical properties and photoinduced phenomena in chalcogenide glasses are very attractive for many applications in photonics and optoelectronics (inorganic photoresists, registration media for optical and holographic information, passive and active elements for integrated optics, all-optical switching, imaging devices, vapor sensors, etc.) [1-7]. 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 red shift of the absorption edge, due to broadening of the valence band, is accompanied of the respective increasing of the refractive index [8-10].

Because the composition of chalcogenide glass determines the structural units and the mean coordination number of the amorphous solids [11,12], the effect of the composition in the glassy system As_{100-x}Se_x (x=40÷98) and As₄₀Se₆₀:Sn_y (y=0÷10.0 at.% Sn) on the optical properties and on the degree of photostructural transformations has been studied. By P. Boolchand [11,12] was shown, that in the glassy system As_{100-x}Se_x glassy system, in dependence of composition can exist three well-marked regions: *floppy*, *intermediate* and *stressed rigid*. The new topological theory permit us correlate the physical properties with the glass structure. Some suggestions regarding the structure of amorphous As₄₀Se₆₀:Sn films, also are based on the experimental data on Temperature Modulated Differential Scanning Calorimetry (TMDSC) [13].

In the last years many investigations has been done on photodarkening process in amorphous chalcogenides, but still now does for its explanation are used different models

[14-19]. Recently some results on photodarkening in amorphous semiconductors were interpreted in frame of the "slip motion" model [17] and using the model which take into account the photoinduced atom displacement (PAD) [18]. Some experimental results on α -As₄₀Se₆₀ and As₅₀Se₅₀ doped with Sn and rare-earth ions successful were interpreted in frame of the "slip motion" model [19-21].

In this paper, the experimental results of the influence of the light exposure and heat treatment on the transmission spectra of the amorphous As_{100-x}Se_x and As₄₀Se₆₀:Sn thin films are presented. The kinetics of photodarkening and the dynamics of optical registration process of micro-holograms in α -As_{100-x}Se_x thin films also were investigated. On the base of the observed changes of the refractive index in both As_{100-x}Se_x and As₄₀Se₆₀:Sn glassy systems was established the higher sensitive to light exposure compounds. It was shown that the more sensitive to photostructural transformations under light exposure a the non-stoichiometric As₅₀Se₅₀ and As₆₀Se₄₀ amorphous films, and decrease with increasing of Se content in the As_{100-x}Se_x glass.

2. Experimental

The glasses As_{100-x}Se_x (x=40÷98) and As₄₀Se₆₀:Sn_y (y=0÷10.0 at.% Sn) were synthesized from the elements of 6N (As, Se, Sn) purity by conventional melting technique. The amorphous As_{100-x}Se_x and As₄₀Se₆₀:Sn_y thin films of different thickness (L=0.2÷5.0 μ m) were prepared by "flash" thermal evaporation in vacuum onto the glass substrates kept at T_{subs} =100 °C. For optical transmission a

UV/VIS (300–800 nm) and 61 NIR (800–3500 nm) Specord's CARLZEISS Jena production were used.

To initiate photostructural transformations in thin film samples a continuous He-Ne lasers ($\lambda=630$ nm, $P=0.6$ mW and $\lambda=540$ nm, $P=0.75$ mW) were 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 intensity of the laser beam during the recording time. 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. Special software was elaborated for automatic measurements. The micro-holograms on the amorphous As-Se films were registered by means of the interference of two He-Ne laser beams ($\lambda=6320.8$ nm) with a power of $P=30$ mW. The kinetics of diffraction efficiency growth was measured by registration of the intensity of the 1-st interference maximum versus time exposure.

3. Experimental results and discussion

3.1 Optical transmission

The optical transmission spectra for amorphous As_xSe_{100-x} ($L\sim 1.3$ μm) was investigate at room temperature (as-deposited, heat treated in vacuum at $T_{\text{treat}}=120$ °C during 1 hour and exposed with light $E=50000$ Lx during 1 hour). Fig.1a represents the transmission spectra for thin films of different compounds in the As_xSe_{100-x} glassy system. Increasing of the As content As_xSe_{100-x} system shift the absorption edge in the red region of the spectra. The band gap value for amorphous As₆₀Se₄₀ thin films, determined from the absorption spectra is $E_g=1.82$ eV. This is in good agreement with the experimental data presented in [22], according which the optical band-gap values decrease from $E_g=1.95$ eV for As₈Se₉₂ up to $E_g=1.83$ eV for As₃₆Se₆₄. The influence of the light exposure and heat treatment on the transmission spectra of amorphous As₄₀Se₆₀ is presented on the Fig.1b.

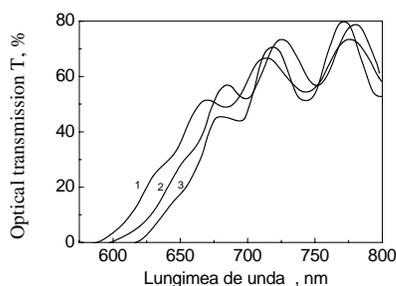


Fig. 1a. The transmission spectra for amorphous As₅Se₉₅ (curve 1, $L=0.87$ μm), As₂₈Se₇₂ (curve 2, $L=1.32$ μm), and As₄₀Se₆₀ (curve 3, $L=1.22$ μm) thin films.

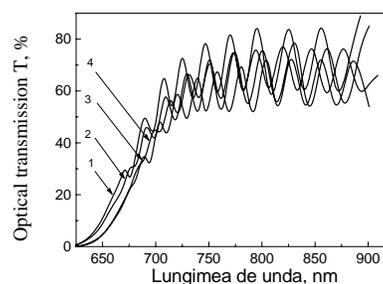


Fig. 1b. The transmission spectra for amorphous As₄₀Se₆₀ ($L=3.08$ μm) as-deposited (curve 1), as-deposited exposed (curve 2), heat treated (curve 3), and heat treated exposed (curve 4) thin films.

The displacement of the absorption edge under light exposure and heat treatment take place for all amorphous films in the As_{100-x}Se_x under study, and is accompanied by the respective modifications of the refractive index. The degree of the displacement of the absorption edge in the red region depends on the composition of the amorphous film, intensity and time of exposure, and heat treatment. Influence of the light exposure at the level of transmission $T=20$ % is manifested by the shift of $\Delta\lambda=920$ nm which correspond to the amorphous As₆₀Se₄₀, and decrease with increasing of Se content up to $\Delta\lambda=2\div 5$ nm for As₅Se₉₅ and As₁₀Se₉₀.

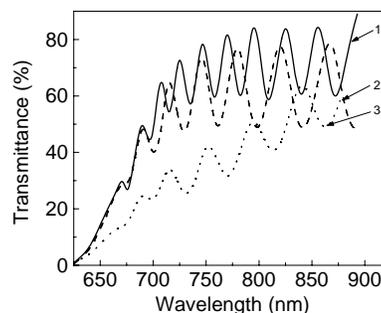


Fig.2a. The transmission spectra for as-deposited amorphous As₄₀Se₆₀ (1), As₄₀Se₆₀:Sn₀₅ (2) and As₄₀Se₆₀:Sn_{2.0} (3) thin films.

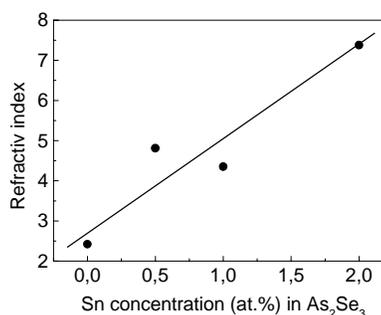


Fig. 2.b. The dependence of the refractive index vs. Sn concentration of amorphous As₄₀Se₆₀:Sn films ($\lambda=720$ nm).

The heat treatment in vacuum at $T=120\text{ }^{\circ}\text{C}$ during 1 hour also shift the absorption edge in the red region of the spectrum, and this shift is greater than under light exposure. That means that the structural transformations of amorphous films under temperature action in our case are more essential.

The increasing of Sn concentration in amorphous $\text{As}_{40}\text{Se}_{60}$ thin films shifts the absorption edge in the red region of the spectra (Fig. 2a). The decreasing of the optical gap with increasing of Sn concentration was observed also in the similar glasses of $\text{As}_{50}\text{Se}_{50}\text{:Sn}$ [23]. From the Fig. 2b it is seen that even small concentration of Sn in amorphous $\text{As}_{40}\text{Se}_{60}$ increase the refractive index n , and for 2.0 at. % of Sn the refractive index $n=7.5$. A such higher value of the refractive index also was observed for amorphous $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ thin films [24].

The optical transmission T in thin semiconductor film is determined by the expression:

$$T = \frac{(1-R)^2 \exp(-kd)}{1-R^2 \exp(-2kd)}, \quad (1)$$

where R - is the optical reflection, k - the absorption coefficient, and d - the thickness of the amorphous film. In the visible region the reflection is constant and for calculations of the absorption coefficient was taken the value $R = 20\%$. In the consideration that the member $R^2 e^{-2kd} \ll 1$ from eqn. (1) we can obtain the expression for calculation of the absorption coefficient

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (2)$$

From the dependence $(\alpha \cdot h\nu)^{1/2} \sim h\nu$ were calculated the values of the optical gap E_g for different compositions, and which are in good agreement with the data obtained by other authors [22,23,25]. Tin impurities in $\text{As}_{40}\text{Se}_{60}$ decrease the optical band gap like in $\text{As}_{50}\text{Se}_{50}$ amorphous films [23].

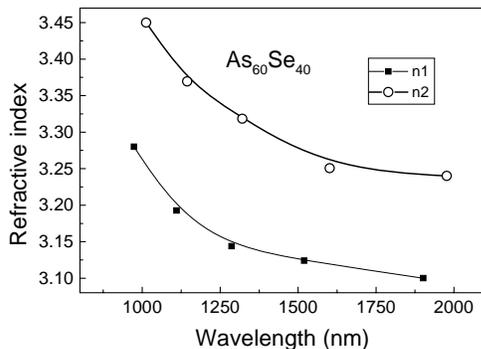


Fig. 3a. The dependence of the refractive index n vs. wavelength for amorphous $\text{As}_{40}\text{Se}_{60}$ films before (n_1) and after (n_2) light exposure.

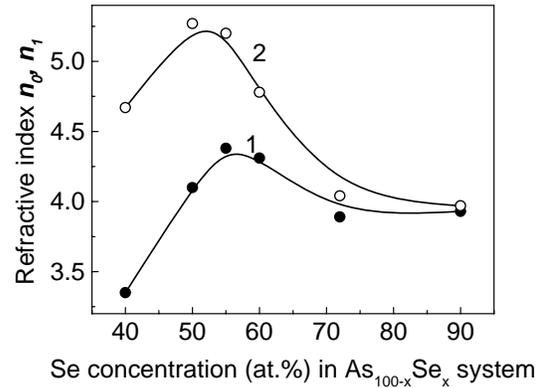


Fig.3b. The dependence of the refractive index n_0 (for as-deposited, curve 1) and n_1 (for light exposed, curve 2) of thin films versus Se concentration (at. %) in $\text{As}_{100-x}\text{Se}_x$ glass system ($\lambda=720\text{ nm}$).

The refractive index n was calculated from the transmission spectra according to the formula $n = \frac{M}{2L(\nu_1 - \nu_2)}$, where M - is the number of the

interference maxima, L - is the thickness of the film, and ν - is the frequencies of the respective interference maxima. The similar dependencies were obtained for all investigated compositions. The dispersive curve of the refractive index n for amorphous $\text{As}_{60}\text{Se}_{40}$ films is presented on the Fig. 3a. According to the experimental data the more sensitive under light irradiation ($\Delta n/n = 0.394$) are the $\text{As}_{60}\text{Se}_{40}$ amorphous films. The maximum value of the refractive index in the $\text{As}_{100-x}\text{Se}_x$ system was obtained for the $\text{As}_{45}\text{Se}_{55}$ composition (Fig. 3b). The results presented in Fig.3a are in good agreement with those published in [26] for the amorphous $\text{As}_{100-x}\text{Se}_x$ thin films, where a maximum of modification of the refractive index was obtained for the composition $\text{As}_{60}\text{Se}_{40}$ ($\Delta n \approx 0.75$).

Photodarkening relaxation was measured during illumination for as-deposited amorphous $\text{As}_{100-x}\text{Se}_x$ ($x=40\div 98$). The relaxation of the relative optical transmission $T(t)/T(0)$ of the amorphous $\text{As}_{100-x}\text{Se}_x$ films is shown in Fig.4a. Increasing of Se in the $\text{As}_{100-x}\text{Se}_x$ system suppressed the photodarkening effect and $x=72\div 98$ is absent or is very small. The experimental data are in good agreement with the experimental results obtained earlier [8]. The specific of the present results is that our results is that it were obtained by using the lower power of the excited light, and in a such way the exposure time is also very long (up to 6000 s).

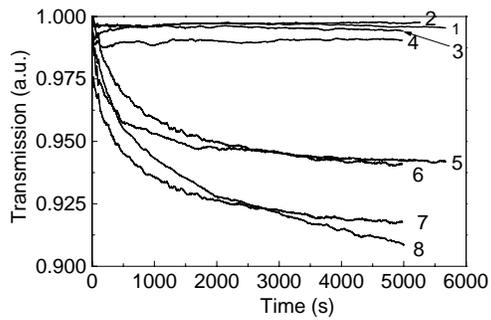


Fig. 4a. Photodarkening kinetics of as-deposited amorphous As_2Se_{98} (1), $As_{55}Se_{95}$ (2), $As_{10}Se_{90}$ (3), $As_{28}Se_{72}$ (4), $As_{40}Se_{60}$ (5), $As_{45}Se_{55}$ (6), $As_{50}Se_{50}$ (7), and $As_{60}Se_{40}$ (8) films with exposure time. Excitation wavelength $\lambda_{exc}=0.63 \mu m+0.54 \mu m$. Sordage wavelength $\lambda_{sord}=0.63 \mu m$.

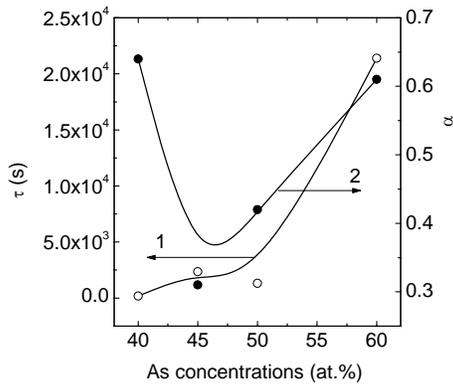


Fig. 4b. The dependence of the parameters τ (left scale) and α (right scale) of the stretched exponential for the as-deposited amorphous $As_{100-x}Se_x$ thin films.

The relaxation of photodarkening is described by the stretched exponential function $T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{1-\alpha}$. Here t is the exposure time, τ is the apparent time constant, A characterizes the exponent amplitude, t_0 and A_0 are the initial co-ordinates, and α is the dispersion parameter ($0 < \alpha < 1$). The dependence of the relaxation time τ and of the dispersion parameter α for as-deposited and annealed films is shown in Fig. 4b. The dispersion parameter α is close to 0.5 for almost all $As_{100-x}Se_x$ ($x=40 \div 60$), and non-monotonously is changed with composition. In our experimental conditions, the lower value of the dispersion parameter $\alpha \approx 0.3$ is for the $As_{45}Se_{55}$ composition and increase up to $\alpha \approx 0.6 \div 0.65$ for the $As_{40}Se_{60}$ and $As_{60}Se_{40}$. Such behaviour of the dispersion parameter α with composition may be associated with the structure of the investigated glasses. According to [27], for the glassy system $As_{100-x}Se_x$ the composition $x=0.45$ took the maximum value of the glass transition temperature T_g .

Fig. 5a shows the kinetics of growth of the diffraction efficiency for amorphous $As_{50}Se_{50}$ and $As_{60}Se_{40}$ thin films

during exposure as result of interference of two He-Ne laser beams ($\lambda=0.63 \mu m$) with a power of $W=30$ mW. Some results on optical recording in amorphous $As_{100-x}Se_x$ films were reported in [8]. 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. For the compositions richer in As the kinetics of the diffraction efficiency represents a curve with maximum or a sinusoidal, like obtained in [26] for amorphous As_2S_3 and As-S-Se thin films. The deletion process of the optical information due to the time exposure may cause the fall dawn of the diffraction efficiency after the maximum. At the same time we show that doping of amorphous As_2Se_3 with tin allow to rich saturation on the curve of growth of the diffraction efficiency in dependence with the exposure dose [28]. This effect we have explained by the specific of structure of the tin doped films.

The holographic sensitivity of the amorphous films and the diffraction efficiency of the hologram have decreases with increasing of the selenium content in $As_{100-x}Se_x$ glassy system (Fig. 5b). These dependences are in a good agreement with earlier obtained experimental data obtained in [6,26].

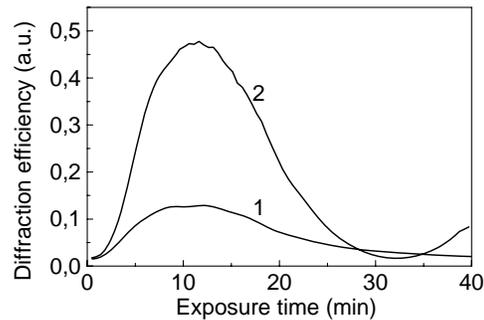


Fig. 5a. The kinetics of growth of the diffraction efficiency versus exposure time for amorphous $As_{50}Se_{50}$ (curve 1, $L=1.3 \mu m$) and $As_{60}Se_{40}$ (curve 2, $L=1.3 \mu m$) thin films.

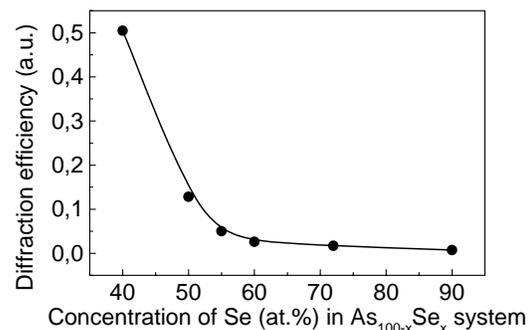


Fig. 5b. The dependence of the diffraction efficiency versus Se concentration in the $As_{100-x}Se_x$ glassy system.

The thickness dependence of the diffraction efficiency for amorphous $As_{60}Se_{40}$ films also was investigated. Increasing of thickness from $L=0.27\ \mu\text{m}$ up to $L=4.07\ \mu\text{m}$ also lead to rising of diffraction efficiency with decreasing of the recording time. The same dependence was obtained for amorphous As_2S_3 films for different grating period [26].

4. Summary

Photostructural transformations in amorphous $As_{100-x}Se_x$ ($x=40\div 98$) and $As_2Se_3:Sn_y$ ($y=0\div 5.0$ at.% Sn) films were investigated. The changes of the refractive index under light irradiation and heat treatment calculated from the transmission spectra exhibits composition dependence due to the difference of the existing structural units. The more sensitive to light irradiation are the amorphous films of $As_{60}Se_{40}$ and $As_{50}Se_{50}$, which exhibit big modifications of the refractive index ($(\Delta n/n) = 0.394$) and high holographic parameters. Metal impurities effectively reduce the photodarkening, and the degree of reduction becomes stronger as the impurity concentration is increased.

Changes in the optical transmission of the investigated amorphous films under illumination may be described by a stretched exponential with the dispersive parameter $0.4 \leq \alpha \leq 1.0$. The strong effect of metal additives on the photodarkening kinetics is in agreement with the "slip-motion" model. In particular, with its tetrahedral type of co-ordination, tin should reduce the flexibility of the layer network, hence retarding the photodarkening phenomenon. Doping of amorphous chalcogenide films by metals assists in stabilising the glassy matrix with respect to light exposure and thermal treatment.

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