Optical Properties of Amorphous As-Se Thin Films

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***Abstract* – 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 $As_{40}Se_{60}$: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 $As_{60}Se_{40}$ and $As_{50}Se_{50}$, which exhibit big modifications of the refractive index (** $(\Delta n/n) = 0.394$ **)**

Keywords –: **Amorphous chalcogenide films, optical absorbtion, refractive index, photoinduced phenomena**

I. 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.) [1-3]. 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. Increasing of the optical absorption is accompanied by the red shift of the absorption edge and increasing of the refractive index. In this paper the effect of the composition in the glassy systems $As_{100-x}Se_x$ (x=40÷98) and $As_{40}Se_{60}$:Sn_y (y=0÷10.0 at.% Sn) on the optical properties and on the degree of photostructural transformations 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 $As_{40}Se_{60}$: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 are the non-stoichiometric $As_{50}Se_{50}$ and $As_{60}Se_{40}$ amorphous films, and decrease with increasing of Se content in the $As_{100-x}Se_x$ glasses.

II. EXPERIMENTAL

The glasses $As_{100-x}Se_x$ (x=40÷98) and $As_{40}Se_{60}$: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 $As_{40}Se_{60}$:Sn_y thin films of different thickness (L=0.2÷5.0 μm) were prepared by "flash" thermal evaporation in vacuum onto the glass substrates kept at T_{subs}=100 °C.

To initiate photostructural transformations in thin film samples a continuous He-Ne lasers (λ=630 nm, P=0.6 mW and λ=*540* nm, P=0.75 mW) were used as a source of light exposure. The experimental set-up included a laser, a digital build-in *PC*-card *PCI-1713A* for data acquisition connected with the *Si*-photodetector. Special software was elaborated for automatic measurements.

III. RESULTS AND DISCUSSION

The optical transmission spectra for amorphous As_xSe_{100-x} (L~1,3 μm) was investigated at room temperature (as-deposited, heat treated in vacuum at T_{treat}=120 °C during 1 hour and exposed with light E=50000 Lx during 1 hour). Increasing of the As content $As_{100-x}Se_x$ system shift the absorption edge in the red region of the spectra. The band gap value for amorphous $As_{40}Se_{60}$ thin films, determined from the absorption spectra is E_g=1.82 eV. This is in good agreement with the experimental data presented in [4], according which the optical band-gap values decrease from E_g=1,95 eV for As_8Se_{92} up to E_g=1,83 eV for $As_{36}Se_{64}$.

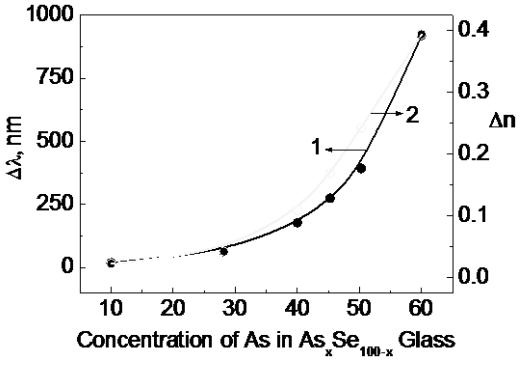

Fig.1. The shift of the absorption edge ($\Delta\lambda$, curve 1) and the degree of modification of the refractive index (Δn, curve 2) under the light irradiation for different film composition of the glassy system $As_{100-x}Se_x$.

The displacement of the absorption edge under light exposure and heat treatment for all amorphous $As_{100-x}Se_x$ films is accompanied by the respective modifications of the refractive index n. For calculation of the optical constants

the Programme ***PARAV-V1.0*** was used [5]. 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 the absorption edge $\Delta\lambda$=920 nm which correspond to the amorphous $As_{60}Se_{40}$, and decrease with increasing of Se content up to $\Delta\lambda$=2÷5 nm for As_5Se_{95} and $As_{10}Se_{90}$ (Fig.1).

Increasing of Sn concentration in amorphous $As_{40}Se_{60}$ thin films shifts the absorption edge in the red region of the spectra. Concentration of Sn in amorphous $As_{40}Se_{60}$ thin films increases the refractive index n (Fig.2).

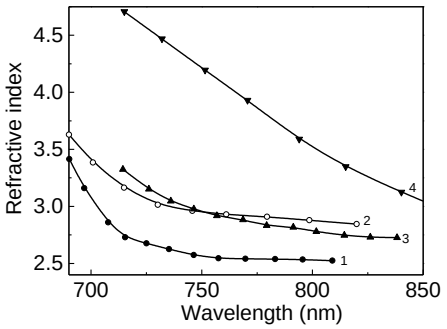

Fig.2. Dispersive curves of the refractive index n for amorphous $As_{40}Se_{60}$ (1), $As_{40}Se_{60}$:$Sn_{0.5}$ (2), $As_{40}Se_{60}$:$Sn_{1.0}$ (3), and $As_{40}Se_{60}$:$Sn_{2.0}$ (4) thin films.

For x=2.0 at. % of Sn the refractive index n=3.5 at λ=800 nm. Fig.3 represents the influence the light exposure and heat treatment on the degree of modification of the refractive index n for amorphous $As_{40}Se_{60}$:$Sn_{1.0}$ thin films. In these cases, the light exposure as well as the heat treatment increases the refractive index n.

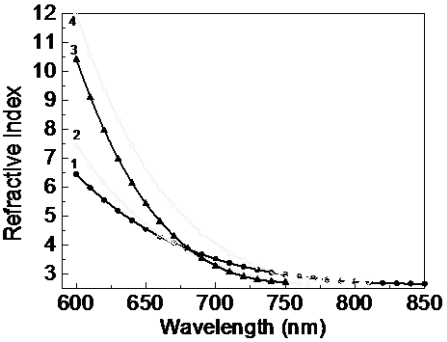

Fig.3. Dispersive curves of the refractive index n for amorphous $As_{40}Se_{60}$:$Sn_{1.0}$ thin films: 1 – as-deposited, 2 – as-deposited and light exposed, 3 – heat treated, 4 – heat treated and exposed.

Fig.4 shows the dependence of the refractive index n on Sn concentration in as-deposited amorphous $As_{40}Se_{60}$:Sn_x thin films calculated at different wavelengths λ.

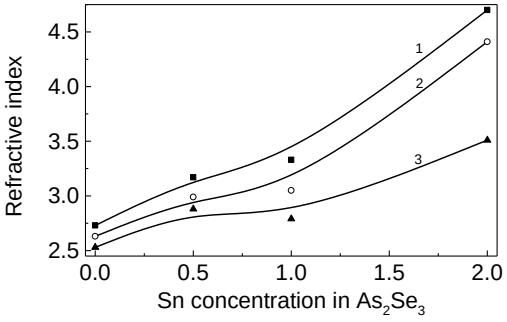

Fig.4. Dependence of the refractive index n vs. Sn concentration in as-deposited amorphous $As_{40}Se_{60}$:Sn_y thin films calculated at different wavelengths λ, nm:

1 – 715, 2 – 735, 3 – 800.

Photodarkening relaxation was measured during illumination for as-deposited amorphous $As_{100-x}Se_x$ (x=40÷98). The relaxation of the relative optical transmission $T(t)/T(0)$ of the amorphous $As_{100-x}Se_x$ films is shown in Fig.5. Increasing of Se in the $As_{100-x}Se_x$ system suppressed the photodarkening effect and x=72÷98 is absent or is very small. The relaxation of photodarckening is described by the stretched exponential function $T(t)/T(0)=A_0+Aexp[-(t-t_0)/\tau]^{(1-\alpha)}$. 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 (UN) and annealed (AN) films is shown in Fig.6. The dispersion parameter α is close to α =0.3 for almost all UN $As_{100-x}Se_x$ (x=40÷60), and non-monotonously is changed with composition.

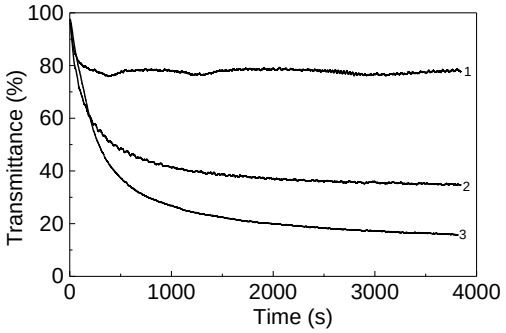

Fig.5. Photodarkening kinetics (T/T_0) of as-deposited amorphous $As_{28}Se_{72}$ (1), $As_{40}Se_{60}$ (2), and $As_{50}Se_{50}$ (3) films vs. exposure time t. Excitation wavelength λ_{exc}=0.63 μm.

In our experimental conditions, for the AN films the lower value of the dispersion parameter $\alpha\approx0.3$ is for the $As_{45}Se_{55}$ composition and increase up to $\alpha\approx0.6\div0.65$ 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 [6], 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.

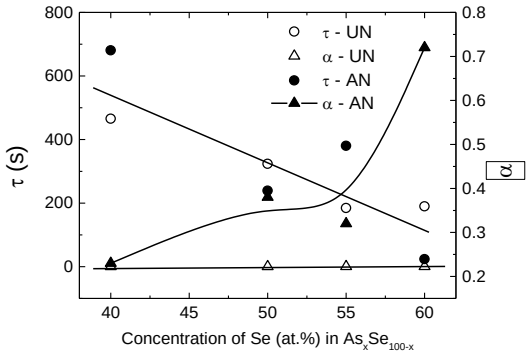

Fig.6. The dependence of the parameters τ and α of the stretched exponential for the as-deposited (UN) and annealed (AN) amorphous $As_{100-x}Se_x$ thin films.

The relaxation of the relative optical transmission *T(t)/T(0)* of the amorphous $As_{60}Se_{40}$ films of different thickness is shown in Fig.7. The experimental data show that for the thicker films the photodarkening is stronger, and almost is absent for the films with thickness about $L \leq 0.2$-0.3 μm. The influence of the thickness on the photodarkening effect also was demonstrated for the amorphous As_2S_3 and As_2Se_3 films [7], and for As_2Se_3 pure and doped with Dy and Pr films [8]. Fig.9 shows the kinetics of growth of the diffraction efficiency for amorphous $As_{100-x}Se_x$ thin films during exposure as result of interference of two He-Ne laser beams (λ=0.63 μm) with a power of W=30 mW. The intensity of the first interference maximum was recorded in the transmittance mode.

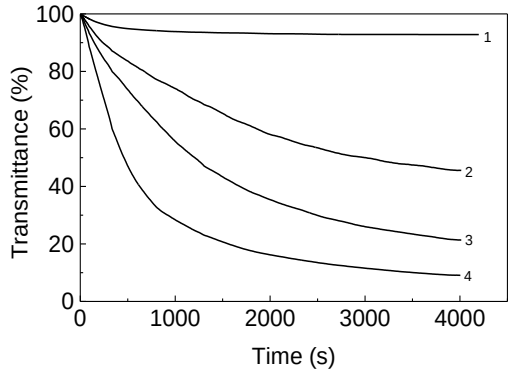

Fig.8. The dependence of transmission versus exposure time for amorphous $As_{60}Se_{40}$ films of different thickness L, μm 1-0.27; 2-0.69, 3-2.04, 4-4.07.

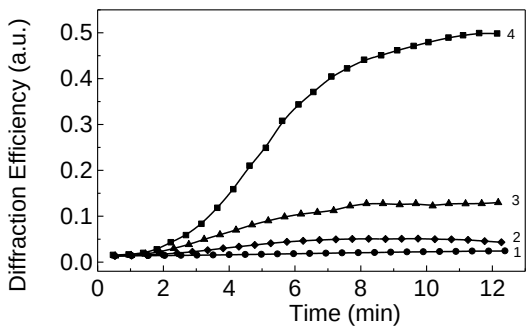

Fig.9. The kinetics of growth of the diffraction efficiency vs. exposure time for amorphous $As_{40}Se_{60}$ (curve 1), $As_{45}Se_{55}$ (curve 2), $As_{50}Se_{50}$ (curve 3), and $As_{60}Se_{40}$ (curve 4) thin films.

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 atoms the kinetics of the diffraction efficiency represents a curve with maximum or a sinusoidal (not shown in the Fig.9).

Prolonged time exposure decreases the diffraction efficiency after the maximum. At the same time we have demonstrated that doping of amorphous $As_{40}Se_{60}$ doped with Sn allow to rich saturation on the curve of growth of the diffraction efficiency in dependence with the exposure dose [9]. 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.10, curve 1).

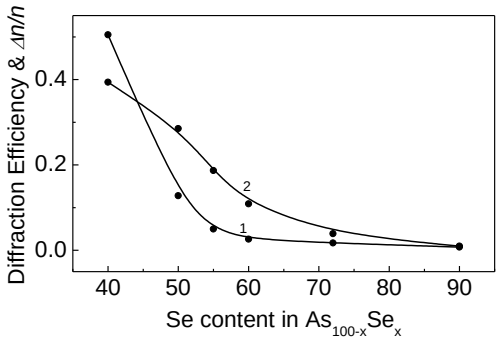

Fig.10. The dependence of the diffraction efficiency (curve 1) and the degree of modification of the refractive index $\Delta n/n$ (curve 2) vs. Se concentration in the $As_{100-x}Se_x$ glassy system.

The measured value of the diffraction efficiency for different amorphous films of the $As_{100-x}Se_x$ glassy system are in good correlation with the degree of modifications of the refractive index $\Delta n/n$ under the light exposure (Fig.10, curve 2).

The thickness dependence of the diffraction efficiency for amorphous $As_{60}Se_{40}$ films also was investigated. Increasing of thickness from L=0.27 μm up to L=4.07 μm also lead to rising of diffraction efficiency with decreasing of the recording time.

IV. CONCLUSION

Photostructural transformations in amorphous $As_{100-x}Se_x$ (x=40÷98) and $As_{40}Se_{60}$:Sn_y (y=0÷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 composition dependence of the transmission spectra, photodarkening characteristics, and kinetics of recording

process of holographic information in the films of the glassy system $As_{100-x}Se_x$ (x=40÷98) was investigated. It was established, that the higher sensitivity to light exposure exhibit the non-stoichiometric $As_{50}Se_{50,}$ $As_{55}Se_{45}$, and $As_{60}Se_{40}$ amorphous films, and decrease with increasing of Se content in the $As_{100-x}Se_x$ glass. 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.

The photodarkening phenomenon in chalcogenide glass films under illumination has no plain explanation up to now in spite of detailed investigation and a series of models advanced for interpretation of it. The red shift of the absorption edge indicating the narrowing of the optical gap of the film at photodarkening, is believed to be due to broadening of the valence band, the top of which is formed mainly by states of lone-pare electrons of the chalcogen atom. According to the model for photodarkening in a-$As_2Se(S)_3$ [10], the photoexcited charge carriers in extended states are considered as responsible for photodarkening. Unlike to the previous conceptions this takes into account the layered cluster structure of a chalcogenide glass. During exposure the layer is negatively charged due to capture of photoexcited electrons, and repulsive forces are built between the layers. These forces cause enlargement of the interlayer distance (leading to photoexpansion) and slip motion along the layers. This latter process alters interaction of lone-pair electrons between the layers leading to photodarkening effect.

AKNOWLEDGEMENTS

For calculation of the optical constants the Programme ***PARAV-V1.0*** was used (www.chalcogenide.eu.org).

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