OPTICAL PROPERTIES OF SOME $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ CHALCOGENIDE GLASSES

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Abstract

The transmission spectra of bulk and thin films of $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ in the visible and near infrared (IR) regions were investigated. The doping of $As_2(S, Se)_3$ chalcogenide glass with tin impurities essentially reduces the absorption bands of S-H (Se-H) and H_2O located at $\nu = 5190$ cm^{-1} and $\nu = 3617$ cm^{-1}, respectively. The amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films exhibit photoinduced effects under the light irradiation with photon energy above the optical band gap ($h\nu \geq Eg$), which makes them promising materials for registration of optical and holographic information. The modification of optical parameters (optical band gap Eg, absorption coefficient α, refractive index n) under light irradiation and heat treatment of amorphous thin films with different amounts of Sn was studied. The relaxation of photodarkening effect in amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films, which is described by the stretch exponential function $T(t)/T(0) = A_0+Aexp[-(t-t_0)/\tau]^{(1-\alpha)}$, was also investigated.

1. Introduction

Chalcogenide glasses of the As-S-Se system exhibit photostructural transformations, and are promising materials for registration media, for fabrication of diffractive elements, and other optoelectronic applications [1-3]. It is well known that the optical properties (absorption coefficient α, refractive index n, optical band gap Eg) depend on the glass composition. In the last years, a special attention has been devoted to the influence on the photostructural transformation in amorphous thin films doped with metal impurity [4-6]. It was shown that the Sn impurity introduced in the As_2Se_3, AsSe, and Sb_2S_3 glass network reduces the photodarkening effect [4, 5, 7]. According to Mössbauer spectroscopy of ^{119}Sn in the As_2Se_3:Sn glassy system, new tetrahedral $Sn(Se_{1/2})_4$ and quasi-octahedral SnSe structural units, which influence the photostructural transformations, can be formed [5]. The advantages of application of amorphous (As_2S_3):(As_2Se_3) and (As_2S_3):(As_2Se_3):Sn as gas sensors and for registration of optical information were shown in [8-10]. Some optical properties of $(As_2S_{1.5}Se_{1.5})_{0.99}:Sn_{0.01}$ were reported in [11]. In the present paper, we report the optical transmission spectra and the modification of optical parameters (optical band gap Eg, absorption coefficient α, refractive index n) under light irradiation and heat treatment of amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films with different amounts of Sn. The relaxation of photodarkening effect under light exposure was also investigated.

2. Experimental

The bulk chalcogenide glasses $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ ($0 \le x \le 0.1$) were prepared from the elements of 6N (As, Se, Sn) purity by a conventional melt quenching method. The thin-film samples with a thickness of d = 0.5÷3 μm were prepared by flash thermal vacuum evaporation of the synthesized initial glasses onto glass substrates held at T_{subs} = 100°C. For optical transmission spectra measurements, a UV/VIS (λ = 300÷800 nm), the 61 NIR (λ = 800÷3500 nm) Specord's CARLZEISS Jena production and Spectrum 100 FTIR Spectrometer (PerkinElmer) (λ = 1280÷25000 nm) were used. For calculation of the optical constants from the transmission spectra, we used the method proposed by Swanepoel and Tauc [12, 13] and the computer program PARAV-V1.0 (www.chalcogenide.eu.org) [14]. To initiate photostructural transformations in thin-film samples, continuous He-Ne lasers (λ = 633 nm, P = 0.6 mW and λ = 540 nm, P = 0.75 mW) were used as a source of light exposure.

3. Results and discussion

The mid-IR transmission spectra of As_2S_3 and some $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ bulk glasses are shown in Fig.1 and, as in the case of vitreous As_3S_3 doped with metals [15], are characterized by several well-resolved absorption bands. For vitreous As_2S_3, these bands are located at frequencies of ν = 5190 cm^{-1} (S-H), ν = 3617-3522 cm^{-1} (H_2O), ν = 2482 cm^{-1} (S-H), ν = 1857 cm^{-1} (As-H), ν = 1597 cm^{-1} (H_2O), and ν = 1003 cm^{-1} (As_2O_3), and are summarized in Table 1. The characteristic absorption bands for pure As_2S_3 at ν = 5190, 3617, 3522, 1857, and 1597 cm^{-1} are significantly reduced upon doping with Sn. At the same time, for the $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{0.98}:Sn_{0.02}$ glass, additional absorption bands appear at ν = 5190 cm^{-1} 3194, 2026, and 1493 1500 cm^{-1}. The observed changes upon doping in the mid infrared region are most likely related to interactions of a portion of the introduced metal ion impurities with the inherent impurities of the host glass, such as hydrogen and oxygen atoms. These interactions result in the reduction of the relative intensity of bands associated with O-H, S-H, As-O, and As-H bonds in the parent glass.

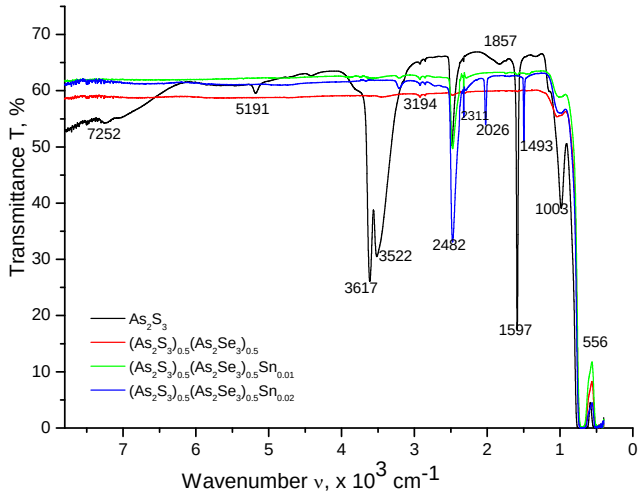

Fig.1. Transmission spectra of bulk samples of $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ glasses.

Fig. 2 shows the typical transmission spectra for some compositions of amorphous glass $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films. From the transmission spectra T = f(λ), using the expressions:

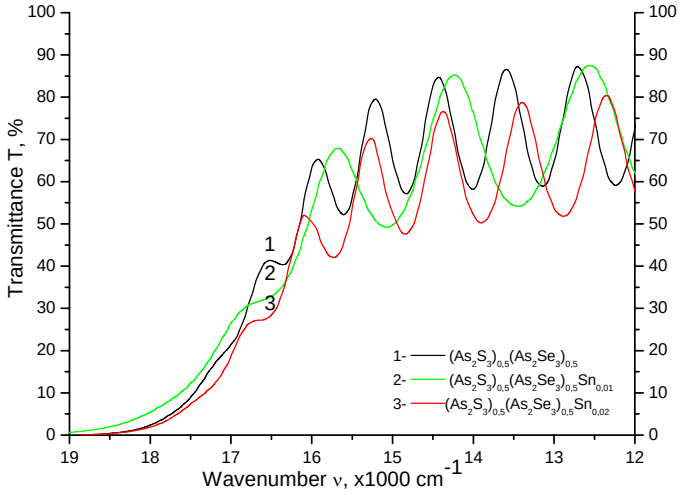

Fig.2. Transmission spectra of some amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films.

$\alpha = \frac{1}{d}\ln\frac{(1-R)^2}{T}, n = \left[M + (M^2 - n_s^2)^{1/2}\right]^{1/2}$, where $M = \frac{2n_s}{T_m} - \frac{n_s^2+1}{2}$ and the dependence $(\alpha h\nu)^{1/2} = A(h\nu - Eg)$, we calculated the absorption coefficient α, the refractive index n, and the value of the optical band gap *Eg*, respectively. Here *d* is the thickness of the sample (measured with a Linnik interferometer), *R* is the reflection, n_s is the refractive index of glass substrate, T_m is the experimental values of transmission minimum points of particular fringes of transmission spectra, and *A* is a constant.

In chalcogenide glasses, the absorption edge is broader than in crystalline analogues, and this is caused by a broad energy distribution of electronic states in the band gap due to disorder and defects. The absorption edge in the high absorption region ($\alpha > 10^4$ cm^{-1}) is described by the quadratic function

$$\alpha \propto \frac{1}{h\nu}(h\nu - E_g)^2 , \quad (1)$$

and when plotted in the Tauc co-ordinates (α·hν)1/2 vs. (hν) [16] gives the value of the optical band gap *Eg* determined as the energy difference between the onsets of exponential tails of the allowed conduction bands [17].

Figure 3 represents the absorption spectra in the Tauc co-ordinates $(\alpha h\nu)^{1/2} = A(h\nu - Eg)$. The Sn impurities in the $(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}$ increase the absorption coefficient α and decrease the optical band gap Eg, as was observed in the case of the amorphous AsSe:Sn films [18]. These peculiarities indicate that the tin impurities in chalcogenide glasses induce a broadening of the electronic tail states in the conduction bands and shift the Urbach edge in the red region of the spectrum. This broadening of the electronic tail states can be attributed to the formation of new

tetrahedral structural units containing Sn [5], which leads to an additional structural disorder to that existing in the matrix of chalcogenide glass.

Table 1. Assignments of characteristic vibration bands for vitreous As_2S_3 and $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ bulk glasses

Bond	Position (cm^{-1})	As_2S_3	x = 0	x = 0.01	x = 0.02
Unidentified	7252	7252	–	–	–
S-H (Se-H)	5190	5190	–	–	–
H_2O	3617	3617	–	–	–
H_2O	3522	3522	–	–	–
-S-H-	3194	–	–	–	3194
-S-H-(Se-H-)	2482	2482	–	2482	2482
CO_2	2311	–	–	2311	2311
-C-O-S-	2026	–	–	–	2026
-As-H-	1857	1857	–	–	–
H_2O	1597	1597	–	–	–
CS_2	1493	–	–	–	1493
AsO (As_2O_3)	1003	1003	1003	1003	1003

Figure 4 represents the dispersion curves of the refractive index $n = f(\lambda)$. It is evident that an increase in the tin content in amorphous glass $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films increases the refractive index *n*. The values of the refractive index n at the wavelength λ = 633 nm are presented in Table 2. Figure 4 and Table 2 show that a sharp increase in the refractive index *n* takes place upon the introduction of 10 at % (or x=0.1) Sn in the $(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}$ host glass.

Table 2. Optical parameters α, Eg^{opt}, and *n* for some amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films

Nr.	Film composition	$\alpha \cdot 104$, cm^{-1} ($h\nu$ = 2.3 eV)	Eg^{opt}, eV, ±0.01	n (λ = 633 nm), ±0.02
1	$(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}$	2.44	1.96	2.52
2	$[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{0.99}:Sn_{0.01}$	3.17	1.90	2.70
3	$[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{0.98}:Sn_{0.02}$	3.07	1.94	2.74

The relaxation of the relative optical transmission $T/T_0 = f(t)$ under light exposure (λ = 633 nm) for amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films is shown in Fig. 5. At a constant light intensity, the presented dependences characterize the decay of the film optical transmittance with the increase in the dose of absorbed photons. To obtain a unified basis for comparison of the transmission relaxation T(t)/T(0) curves, we used the so-called stretched exponential presentation for the relaxation curves in the form

$$T(t)/T(0) = A_0 + A\exp[-(t-t_0)/\tau]^{(1-\beta)}, \quad (2)$$

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 coordinates, and α is the dispersion parameter ($0<\beta<1$).

For the obtained relaxation curves, a rather wide scatter of parameters is observed for samples of the different composition. For doped samples, this dispersion can be caused by the fact that the concentration and distribution uniformity of the impurity is not adequately preserved along the film at deposition. But the relaxation curves are significantly different in the case of nondoped $(As_2S_3)_{0.5}$:$(As_2Se_3)_{0.5}$ as well. The main cause is the difference in thickness. For these samples, the effect of interference of light reflected at the front and rear film boundaries significantly changes the amount of absorbed light leading to a strong dependence of photodarkening at a fixed laser wavelength on film thickness [5].

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, which indicates the narrowing of the optical gap of the film at photodarkening, is believed to be due to the broadening of the valence band, the top of which is formed mainly by states of lone-pare electrons of the chalcogen atom. Several models have been put forward to substantiate this broadening with a particular individual atom regarded as an initial object of photoexcitation [19, 20]. Recently, a novel model for photodarkening in a-$As_2Se(S)_3$ has been proposed [21, 22], in which photoexcited charge carriers in extended states are considered to be responsible for photodarkening.

A comparison of the parameters of the relaxation curves for the samples deposited at different incident angles has shown that, in the considered limits of distance from the center over the evaporator, the greatest effect of photodarkening is observed for the central samples, in contrast to the results reported in the literature for obliquely deposited films [20]. The slight decrease in the photodarkening amplitude with the distance from the center is due to the decrease in the film thickness.

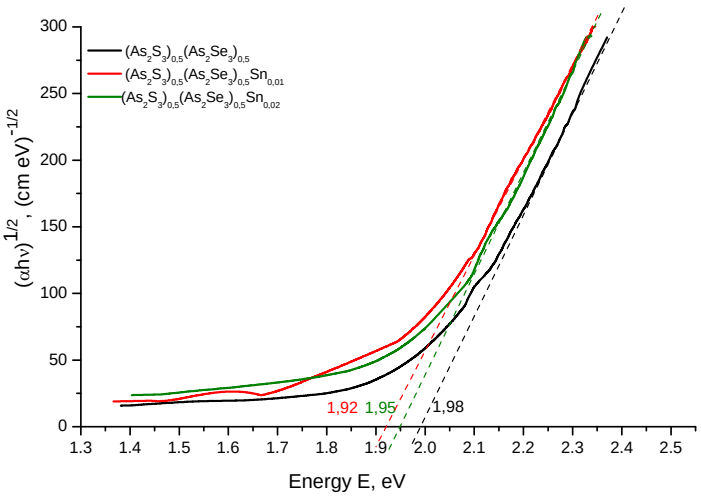

Fig. 3. Absorption spectra in the Tauc coordinates $(\alpha\ h\nu)^{1/2} = A(h\nu - Eg)$.

Unlike the previous conceptions, the new model takes into account the layered cluster structure of a chalcogenide glass. During exposure, the layer is negatively charged due to the capture of photoexcited electrons, and repulsive forces are built between the layers. These forces cause an enlargement in the interlayer distance (leading to photoexpansion) and slip motion along

the layers. The last mentioned process alters the interaction of lone-pair electrons between the layers leading to a photodarkening effect. Earlier, in his structural model proposed for explanation of photodarkening phenomena, M. Popescu [23] has pointed out that distortion in the second and third coordination spheres should be taken into account as important factors.

The model of Shimakawa et al. [21, 22] offers a good basis for consideration of the effect on photodarkening of impurity atoms with coordination different from that of the host glass atoms, as in the case of tin. The foreign metal atoms provide bridging between the layers and hence reduce the slip motion, thus hindering the photodarkening. We suggest that this consideration is applicable in the case of tin impurity in amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films.

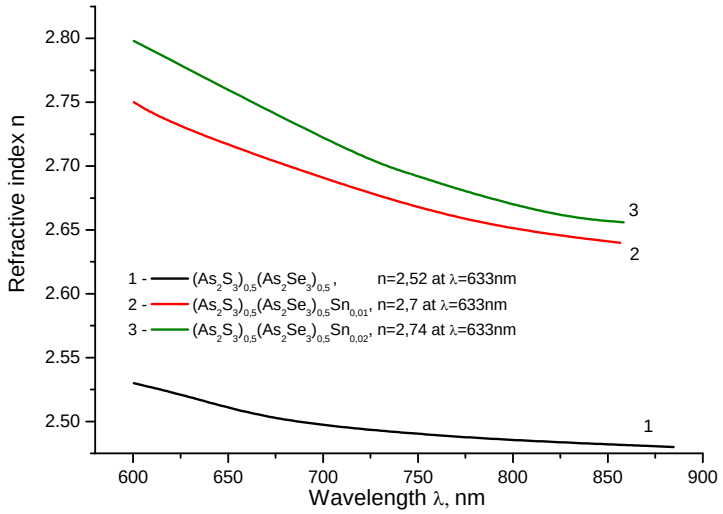

Fig. 4. Dispersion curves n = f(λ) for amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films.

In the absence of tin, the arsenic chalcogenide glass is formed of corrugated and disordered layer domains with some correlation between them. This correlation leads to a rather compact packing with low inter-configurational distance. Upon the introduction of Sn, due to the tetrahedral disposal of the sp3 bonds with the chalcogens, the dopant atom inserted in the network increases the thickness of the layered configuration as revealed by the significant shift of the FSDP towards lower angles. This insertion corresponds, in fact, to the introduction of the structural units of the type $SnSe_2$ in the network. The effect is greater for higher dopant content but only up to a certain concentration, because further the separation of the reciprocally ordered configurations is interrupted by increasing interconnection between layers followed by the transition to three-dimensionally (3D) connected network. The transition is preceded by the appearance of structural units of the SnSe type. Then, the direct consequence of this transition will be shown in the intensity of the FSDP, which gradually disappears. The interruption of the two-dimensional structure and transition is probably due to a more ionic nature of the Sn-Se bonds.

The ionic component gives a higher structural mobility in the network and therefore a higher instability of the glass. Thus, we can expect that the tin impurity strongly affects the

network of the host glass inducing changes in both short-range and medium-range order; in particular, they have a significant effect on the structural layers and the pattern of their relative motion. This fact clearly indicates a strong retardation of the slip motion of the structure layers due to the presence of impurity. Since tin tends to form directional bonds when introduced in the host glass, and especially during the annealing process, some bridging bonds should appear between the layers. The structure of the glasses that contains a tin impurity requires, therefore, some excess slip forces, i.e., leads to greater exposition doses and time constants. Furthermore, the formation of clusters, such as of the $SnSe_2$ type, can decrease the density of lone-pair defects typical for AsSe and AsS (i.e., D-centers) thus lowering the charge state of the layers and, finally, the photodarkening.

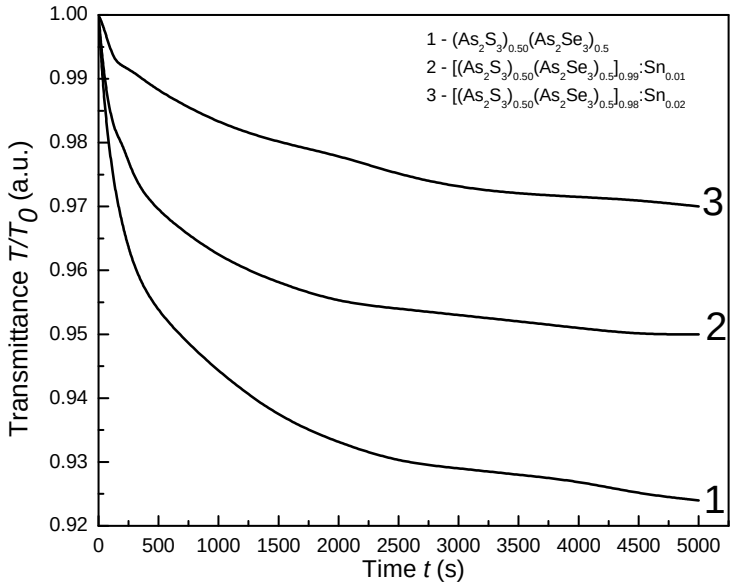

Fig. 5. Relaxation curves of photodarkening $T/T_0 = f(t)$ for amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films.

The fact that the photodarkening kinetics can be described by a stretched exponential can be regarded as an indication of dispersion in the kinetic mechanism, i.e., the time dependence of the process rate [24]. The data suggest that the formation of photoinduced absorption is limited by a dispersive process with the exponent $\alpha \cong 0.5$. In our case, it is the dispersive nature of hole transport that can cause the dispersive nature of relaxation after photogeneration. In fact, the transport of photoexcited holes is included in the model at the stage at which the layer clusters are charged due to the capture of charge carriers. Charge transport in chalcogenide glasses is known as highly dispersive due to a wide distribution of capture times in multiple-trapping process [25]. For a-As_2Se_3-like glasses, the dispersive parameter α of hole transport is close to 0.5 in accordance with the value found from the stretched exponential presentation of photodarkening kinetics [5]. The fact that α is increasing with the addition of metal impurities indicates that the dispersion of the transport is decreased. In general, this is agreement with both the stabilization of structure and the expected alteration of defect center density.

4. Conclusion

The doping of $As_2(S, Se)_3$ chalcogenide glass with tin impurities essentially reduces the absorption bands of S-H (Se-H) and H2O located at ν = 5190 cm^{-1} and ν = 3617 cm^{-1}, respectively. The reduction in the optical gap of As_2Se_3 glass upon alloying Sn, most likely, results from a broadening of the valence band. The top of the valence band in these glasses has a contribution from chalcogen S(Se) lone-pair electrons. The modification of optical parameters (optical band gap Eg, absorption coefficient α, refractive index n) under light irradiation of amorphous thin films with different amount of Sn was investigated. The relaxation of photodarkening effect in amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films is described by the stretch exponential function $T(t)/T(0) = A_0+Aexp[-(t-t_0)/\tau^{](1-\beta)}$. The main feature of the photodarkening effect in the samples under study is that the tin impurities suppressed the photodarkening.

Acknowledgments

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