NEW OPTICAL MATERIALS OF Ge-As-S AND As-S-Se GLASSY SYSTEMS

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Abstract

Nowadays chalcogenide glasses are well known as multifunctional materials with specific electrical and optical properties, for their potential applications in microelectronics and optoelectronics as ovonic devices, passive and active optical elements, components of the photonic structures and recording media of high density. Chalcogenide glasses (As-Se, As-S-Se, As-Sb-S, Ge-As-Se) are characterized by the wide region of glass formation, high glass transition temperatures (T_g=300÷400 ^{0}C) and thermal stability. These glasses are of considerable interest also due to high values of refractive index (n=2.4÷2.65), high nonlinearities (n_2=2.5·10^{-17} cm^2/W) for g-$As_{15}Ge_{35}Se_{50}$, and optical transmission at 1.55 μm, that makes them suitable for photonic applications. Chalcogenide glasses are sensitive to the external illumination and exhibit reversible and irreversible photoinduced effects. These effects are used for the fabrication of different registration media, diffractive structures, waveguides, photonic structures, and optical amplifiers. Arsenic chalcogenide films usually become darkened under light irradiation in the region of the fundamental absorption edge. The changes in the optical constants (absorption coefficient α, optical band gap E_g, and refractive index n) of the investigated materials under ionization irradiation and heat treatment were evaluated.

1. Introduction

Chalcogenide glasses of As-S-Se and Ge-As-Se systems are characterized by the widest region of glass formation in comparison to other ternary chalcogenide compounds, high glass transition temperatures (T_g=300÷400^{0}C), and thermal stability. These glasses are of considerable interest also due to high values of refractive index (n=2.4÷2.65) [1], nonlinearities (n_2=2.5·10^{-17} cm^2/W for g-$As_{15}Ge_{35}Se_{50}$ [2]), and optical transmission at 1.55 μm, that makes them suitable for photonic applications. Chalcogenide glasses are sensitive to the external illumination and exhibit reversible and irreversible photoinduced effects. These effects are used for the fabrication of different registration media, diffractive structures, waveguides, photonic structures, and optical amplifiers [3-6]. The $Ge_xAs_xSe_{2-x}$ glasses are widely investigated, especially their thermally properties [7, 8]. It is well known that the optical properties (absorption coefficient α, refractive index n, optical band gap E_g) depend on glass composition and mean coordination number <r>. In this paper, we report the experimental results on some optical properties of amorphous $Ge_xAs_xSe_{1-2x}$ thin films (0.05≤x≤0.30) and $As_{45}S_{15}Se_{40}$. The absorption coefficient α, refractive index n, and the optical band gap E_g were calculated from the transmission spectra. It was shown that some features in the dependences of the optical constants (α, n, E_g) versus mean coordination number <r> for $Ge_xAs_xSe_{1-2x}$ glasses take place in the reversibility window. The variety of light-induced structural transformations in amorphous chalcogenide films is rather wide and attracts scientific as well as technical interest [9, 10]. As the composition of glass determines both the structural units and the mean coordination number of the amorphous solid, the effect of the composition in Ge-As-Se and As-S-Se glassy systems on the degree of photostructural transformations has been studied. Furthermore, the fact that the composition induced changes in photodarkening kinetics presents special interest as regards the recent photodarkening model [11]. This model takes into account the layered cluster structure of a chalcogenide glass as well as the photoexcited charge carriers in extended states, which are responsible for photodarkening.

It was shown that, after the irradiation of the as-deposited amorphous films, the IR spectrum becomes similar to that of a thermally annealed sample, similar to that of a bulk material. In order to explain the role of S/Se ratio in As-S-Se glasses, it was investigated different glasses using Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and extended x-ray absorption fine structure spectroscopy (EXAFS) and compared with the stochiometric compositions $As_{40}S_{60}$ and $As_{40}Se_{60}$ [12]. It was demonstrated that the molecular structure of the mixed glasses is similar to the binary glasses and consists of a network of chalcogen chain fragments cross-linked by pyramidal $AsCh_3$ units. At the same time, the presence of the substantial amount of S-S, S-Se, Se-Se, As-As, and S_8 rings is possible. For amorphous $As_{40}Se_{60-x}Se_x$ thin films, it was established that an increase in the Se concentration leads to an increase in the refractive index [13]. The exposure and annealing lead to the polymerization of the As_4S_4 and As_4Se_4 molecular groups and the S_n and Se_n chains in the film matrix, with the subsequent formation of structural units characterized with heteropolar As-S and As-Se bonds. The latter is accompanied by the shift of the absorption edge towards the long wavelength region and the increasing of the refractive index. In this work, we present the experimental investigations of the influence of the light irradiation and thermal annealing on the optical parameters of one of highest sensitive chalcogenide glass $[(As_{40}S_{60})_{0.5}:(As_{40}S_{60})_{0.5}]_{0.5}:(As_{50}Se_{50})_{1.0}$ (the short formula is $As_{45}S_{15}Se_{40}$), and $Ge_xAs_xSe_{1-2x}$. It is expected that the adding of As_5Se_5 to the glass composition $(As_2S_3)_{0.5}:(As_2S_3)_{0.5}$ (or $As_{40}S_{30}Se_{30}$) will provide the shift of the absorption edge in the longer wavelength, an increase in the refractive index *n*, and the photoinduced changes in the refractive index Δn. The optical constants (absorption coefficient α, optical bad gap E_g, and the refractive index *n*) were calculated from the experimentally measured transmission spectra $T(\lambda)$. The kinetics of photodarkening in amorphous $Ge_xAs_xSe_{1-2x}$ and $As_{45}S_{15}Se_{40}$ thin films also was investigated and interpreted in the framework of the existing models for photodarkening in amorphous semiconductors.

2. Experimental

The glassy samples of the $As_{45}S_{15}Se_{40}$ and $Ge_xAs_xSe_{1-2x}$ ($0.05 \le x \le 0.30$) (Table 1) were prepared by a conventional melt quenching method. A mixture of high-purity precursors was melted in sealed evacuated quartz ampoules ($p = 5 \cdot 10^{-6}$ Torr) placed in a rocking furnace. The total weight of the synthesized sample was 50 g. The temperature of the quartz ampoule was slowly increased to 550°C at a rate of 50°C/h and kept at this temperature during 24 h for homogenization. Then, the temperature was increased up to 980°C at a rate of 50°C/h and homogenized at this temperature during 72 h, and then quenched in the regime of the disconnected furnace.

Thin film samples of thickness $d = 0.5 \div 4$ μm were prepared by the flash thermal vacuum evaporation of the synthesized initial glasses onto glass substrates held at T_{subs}=100^{o}C. For optical transmission spectra measurements, a UV/VIS (λ=300÷800 nm) and 61 NIR (λ=800÷3500 nm) Specord's CARLZEISS Jena production were used. For the calculation of the optical constants from the transmission spectra, the computer program *PARAV-V1.0* (*www.chalcogenide.eu.org*) was used [14]. To initiate photostructural transformations in the 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 and a digital built-in *PC*-card *PCI-1713A* for data acquisition connected with a *Si*-photodetector.

3. Results and discussion

Figures 1a and 1b represent the typical transmission spectra for two amorphous $Ge_xAs_xSe_{1-2x}$ thin film samples (x=0.07 and x=0.25) and $As_{45}S_{15}Se_{40}$, respectively. The transmission spectra of amorphous $As_{45}S_{15}Se_{40}$ thin film are situated in the intermediate region of wavelengths characteristic of amorphous As_2S_3 and As_2Se_3 films. An increase in the content of Ge and As in the $Ge_xAs_xSe_{1-2x}$ glassy system shifts the Urbach tail in the red region of the spectrum. In some cases, for some glass compositions, depending on mean coordination number <r>, the shift of the absorption edge can take place in the short wave region.

Table 1. Synthesized chalcogenide $Ge_xAs_xSe_{1-2x}$ glasses, mean coordination number $\langle r\rangle$, thickness d of amorphous deposited films, and the parameters of the stretched exponential function $T(t)/T(0) = A_0+A\exp[-(t-t_0)/\tau]^{(1-\beta)}$

No.	Composition, $Ge_xAs_xSe_{1-2x}$	$\langle r\rangle$	d (μm)	A_0	A_1	τ (s)	β
1	$Ge_{0.05}As_{0.05}Se_{0.90}$	2.15	0.511	0.990	0.010	156.267	0.740
2	$Ge_{0.07}As_{0.07}Se_{0.86}$	2.21	1.160	0.978	0.022	96.597	0.457
3	$Ge_{0.09}As_{0.09}Se_{0.82}$	2.27	2.550	0.979	0.021	91.260	0.540
4	$Ge_{0.11}As_{0.11}Se_{0.78}$	2.33	1.290	0.976	0.024	62.585	0.452
5	$Ge_{0.14}As_{0.14}Se_{0.72}$	2.42	1.150	0.982	0.018	93.528	0.361
7	$Ge_{0.18}As_{0.18}Se_{0.64}$	2.54	1.940	0.989	0.011	78.425	0.226
8	$Ge_{0.20}As_{0.20}Se_{0.60}$	2.60	1.980	0.978	0.022	182.263	0.202
9	$Ge_{0.25}As_{0.25}Se_{0.50}$	2.75	4.010	0.971	0.038	222.876	0.703
10	$Ge_{0.30}As_{0.30}Se_{0.40}$	2.90	0.910	0.970	0.034	232.712	0.688

From the transmission spectra $T=f(\lambda)$, using the expressions $\alpha = \frac{1}{d}\ln\frac{(1-R)^2}{T}$, $n = \frac{\lambda_m\lambda_{m-1}}{2d(\lambda_{m-1}-\lambda_m)}$ and the dependence $(\alpha\, h\nu)^{1/2} = A(h\nu - E_g)$, we calculated the absorption coefficient α, the refractive index n, and the value of the optical band gap E_g, respectively. Here d is the thickness of the sample, R is the reflection, λ_m, λ_{m-1} are the minimum and maximum of the interference in the transmission spectra, and A is a constant.

For the amorphous $Ge_xAs_xSe_{1-2x}$ thin films, the light exposure with the integrated light shifts the absorption edge in the high energy region, and leads to an increase in the optical band gap E_g (Fig. 2a) and a decrease in the refractive index n. As result of light exposure, the optical band gap is changed by the value of ΔE_g=0.01 eV, and the refractive index by the value of Δn=0.141 (λ = 700 nm), respectively. The same effect was observed also for the $Ge_{33}S_{67}$ thin films, where, owing to light exposure, the optical band gap was increased from E_g = 2.68 eV up to E_g = 3.06 eV, and the refractive index decreased from n = 2.16 up to 2.08, respectively [15]. This is the so-called "photobleching" effect in chalcogenide glasses. In contrast, for the amorphous $As_{45}S_{15}Se_{40}$ thin films, the light exposure decreases the optical band gap E_g and increases the refractive index n ("photodarkening" effect) (Fig.2b).

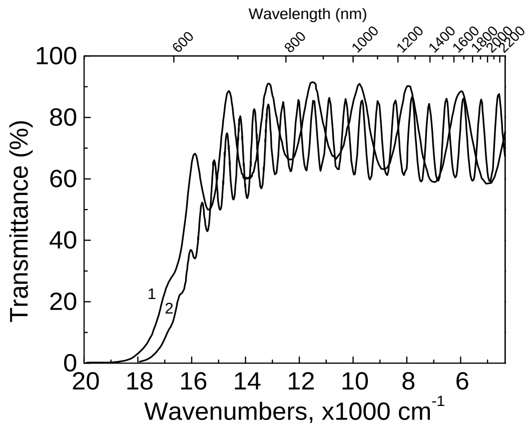

Fig. 1a. Transmission spectra for two amorphous $Ge_xAs_xSe_{1-2x}$ thin film samples x=0.07 (1) and x=0.25 (2).

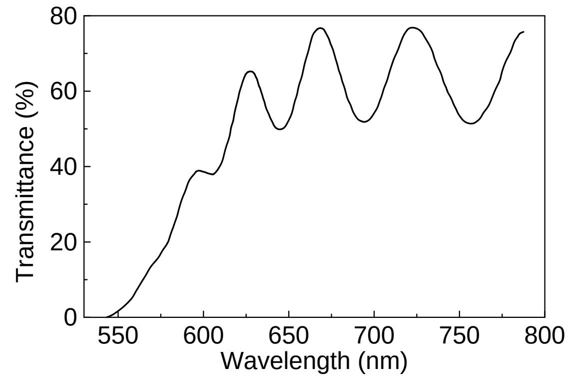

Fig. 1b. Transmission spectra of amorphous $As_{45}S_{15}Se_{40}$ thin film (d=2.4 μm).

The experimental results regarding the dispersion curves $n=f(\lambda)$ for all thin films of the investigated compositions of the glassy $Ge_xAs_xSe_{1-2x}$ system were examined in [16]. In the present work, the main attention is paid to the investigation of modifications of optical constants of the amorphous $Ge_xAs_xSe_{1-2x}$ and $As_{45}S_{15}Se_{40}$ thin films in dependence on annealing temperature (T_{an}=15÷140°C).

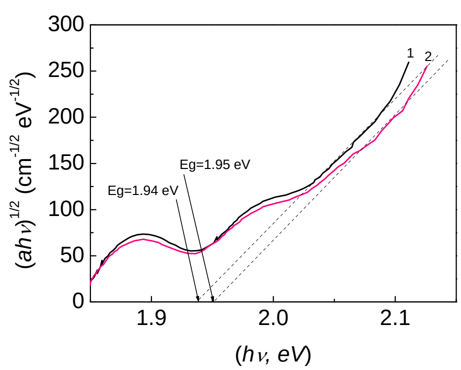

Fig. 2a. Dependence $(\alpha\ h\nu)^{1/2}$ vs. $(h\nu)$ for amorphous $Ge_{0.05}As_{0.04}Se_{0.90}$ thin films: (*1*) as-deposited and (*2*) exposed for 2 h. The dashed line is a computing fitting giving the value of E_g.

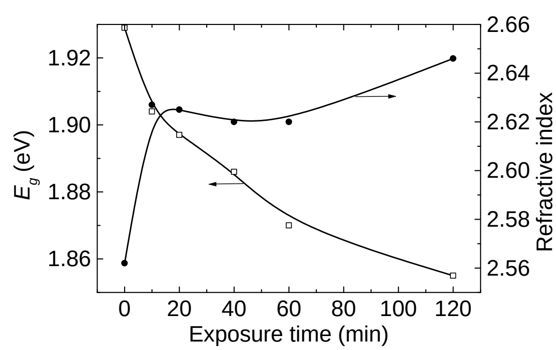

Fig. 2b. Dependence of the optical band gap E_g and refractive index n versus the exposure time t_{exp} for amorphous $As_{45}S_{15}Se_{40}$ thin films.

Figure 3a represents the dependence of the absorption coefficient α versus annealing temperature T_{an} for some amorphous $Ge_xAs_xSe_{1-2x}$ thin films. With increasing annealing temperature T_{an}, the absorption coefficient α decreases. Figure 3b represents the dispersion curves of the refractive index $n=f(\lambda)$ for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ thin films annealed at different temperatures T_{an}. An increase in the annealing temperature T_{an} decreases the refractive index n.

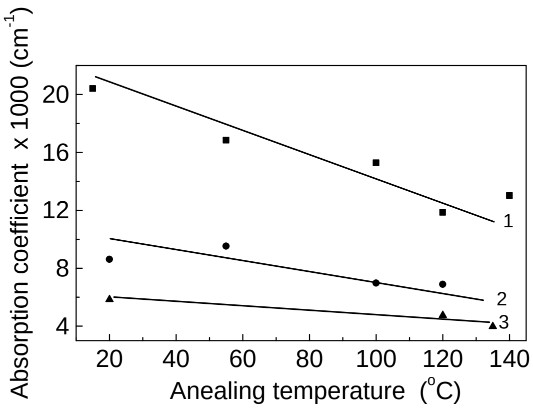

Fig. 3a. Dependence of the absorption coefficient α versus annealing temperature T_{an} for amorphous (*1*) $Ge_{0.09}As_{0.09}Se_{0.82}$, (*2*) $Ge_{0.18}As_{0.18}Se_{0.64}$, and (*3*) $Ge_{0.25}As_{0.25}Se_{0.50}$ thin films.

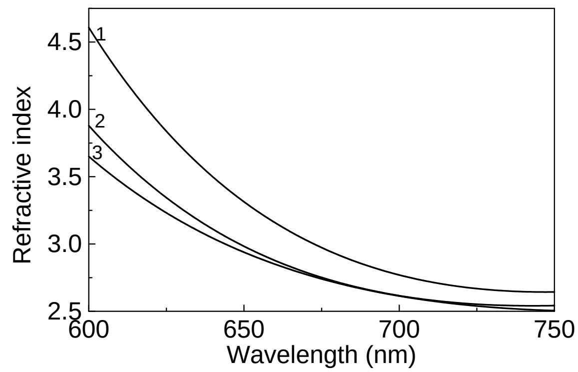

Fig. 3b. Dispersion curves of the refractive index n for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ thin films annealed at different temperatures T_{an}, ^oC: (*1*) 20, (*2*) 120, and (*3*) 135.

For amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ and $Ge_{0.18}As_{0.18}Se_{0.64}$ films, the dependence of the refractive index n versus annealing temperature T_{an} is very weak, in contrast with the same dependence for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ films, for which $\Delta n/\Delta T_{an}=4.8\cdot10^{-3}$ $1/^oC$. In the region of the annealing temperatures T_{an}=20-100°C, the optical band gap Eg increases with annealing temperature (Fig. 4a) with the value $\Delta E_g/\Delta T_{an}=(1.15\div1.27)\cdot10^{-4}$ eV/°C and slightly decreases with increasing Ge concentration in the $Ge_xAs_xSe_{1-2x}$ glassy system. For $As_{45}S_{15}Se_{40}$, the annealing at high temperatures T_{an} decreases the optical band gap ($\Delta E_g/\Delta T_{an}=-5.8\cdot10^{-4}$ eV/°C); it firstly decreases the refractive index ($\Delta n/\Delta T_{an}=-9.2\cdot10^{-4}$ 1/°C) and then increases it (Fig. 4b).

The relaxation of the relative optical transmission T/T_0 for amorphous exposure for amorphous $Ge_{0.07}As_{0.07}Se_{0.86}$ thin films in the co-ordinates $T(t)/T(0)$ versus t is shown in Fig. 5a, when excited with He-Ne laser (λ=630 nm). The kinetics of photodarkening in amorphous $As_{45}S_{15}Se_{40}$ (curve *1*), As_2Se_3 (curve *2*), and As_2S_3 (curve *3*) thin films are presented in Fig. 5b. These dependences describe the excess absorbance induced by light absorption during the exposure. At a constant light intensity, the presented dependences characterize the decay of the film optical transmittance with increasing dose of absorbed photons. To obtain a unified basis for the comparison of the transmission relaxation $T(t)$ curves, we used the so-called stretched exponential presentation for the relaxation curves in the form:

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

Here t is the exposure time, τ is the apparent time constant, $A=1-A_0$ characterizes the "steady-state" optical losses due to photodarkening, t_0 and A_0 are the initial coordinates, and β is the dispersion parameter ($0<\beta<1$).

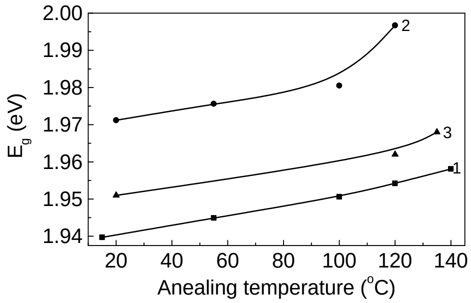

Fig. 4a. Dependence of the optical band gap E_g versus the annealing temperature T_{an} for amorphous (*1*) $Ge_{0.09}As_{0.09}Se_{0.82}$, (*2*) $Ge_{0.18}As_{0.18}Se_{0.64}$, and (*3*) $Ge_{0.25}As_{0.25}Se_{0.50}$ thin films.

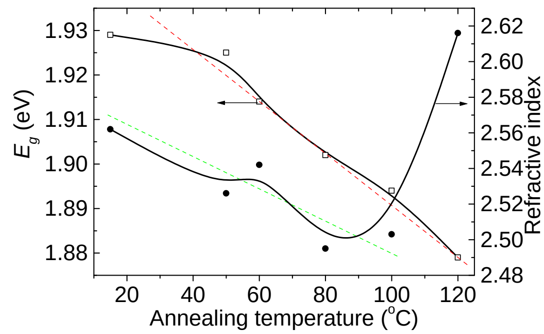

Fig. 4b. Dependence of the optical band gap E_g and refractive index *n* versus the annealing temperature T_{ann} for amorphous $As_{45}S_{15}Se_{40}$ thin films.

The parameters of the stretched exponential for all $Ge_xAs_xSe_{1-2x}$ samples were calculated by the computing fitting of the experimental points (Table 1). In the novel model proposed for explanation of photodarkening in a-$As_2Se(S)_3$, the photoexcited charge carriers in extended states are considered as responsible for photodarkening [11]. Unlike to the previous conceptions the new model takes into account the layered cluster structure of chalcogenide glass. According to this model, 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. This process alters the interaction of lone-pair electrons between the layers leading to a photodarkening effect. This model was successfully used for the explanation of the photodarkening phenomena in amorphous As-Se films doped with metals [17-19]. 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 under photodarkening is believed to be due to the broadening of the valence band, the top of which is formed mainly by the states of lone-pare electrons of the chalcogen atom.

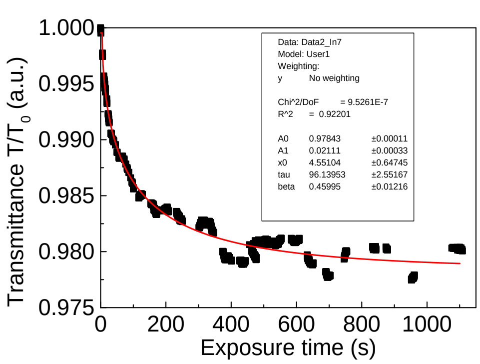

Fig. 5a. The kinetics of photodarkening during the light exposure for amorphous $Ge_{0.07}As_{0.07}Se_{0.86}$ thin films.

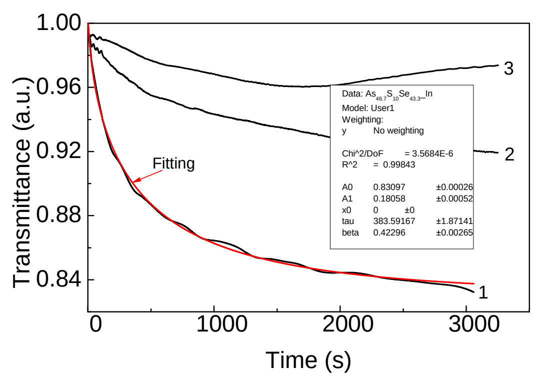

Fig. 5b. The kinetics of photodarkening in amorphous $As_{45}S_{15}Se_{40}$ (curve *1*), As_2Se_3 (curve *2*), and As_2S_3 (curve *3*) thin films.

The nonmonotonic dependence of the parameters of the stretched exponential for the $Ge_xAs_xSe_{1-2x}$ samples is connected with the transition from 2D to 3D network with increasing concentration of Ge. In our previous works [17-19], it was shown that the tin impurity in As_2Se_3 strongly affects the network of the host glass inducing changes in both short-range and medium-range order; in particular, they exert a significant influence on the structural layers and the character of their relative motion. The formation of clusters, such as $SnSe_2$ type , decreases the density of the lone-pair defects typical for AsSe (D-centers), the charge state of the layers also is lowering, and the photodarkening phenomena are quenched. It is probable that four-coordinated Ge in $Ge_xAs_xSe_{1-2x}$ glasses plays an analogue role and influences the photodarkening parameters.

4. Conclusions

The optical transmission spectra of amorphous $Ge_xAs_xSe_{2-x}$ (x=0.05÷0.30) thin films were measured. From the transmission spectra, the optical constants (absorption coefficient α, refractive index n, and the optical band gap E_g) for the amorphous $Ge_xAs_xSe_{1-2x}$ thin films were evaluated. A nonmonotonic dependence of optical parameters versus mean coordination number Z was found. The experimental results show that the optical band gap E_g decreases, while the refractive index n increases with increasing concentration of Ge and As in the $Ge_xAs_xSe_{2-x}$ glassy system. The light exposure and the annealing at high temperatures increase the optical band gap E_g and decrease the absorption coefficient α and the refractive index n of the investigated amorphous films. The relaxation of the relative optical transmission $T(t)/T(0)$ of the amorphous $Ge_xAs_xSe_{1/2x}$ thin films in dependence on exposure time t was also investigated. It was shown that, under the light exposure with He-Ne laser (λ=630 nm), all investigated amorphous $Ge_xAs_xSe_{1-2x}$ films exhibit a photodarkening effect. An increase in the content of Ge and As in the glassy $Ge_xAs_xSe_{1-2x}$ system increases the photodarkening. The kinetics of photodarkening process in the amorphous $Ge_xAs_xSe_{1-2x}$ thin films is described by the stretched exponential function $T(t)/T(0) = A_0+A\exp[-(t-t_0)/\tau]^{(1-\beta)}$.

The experimental investigations of the influence of the light irradiation and heat treatment on the optical parameters of one of highest sensitive chalcogenide glass $As_{45}S_{15}Se_{40}$ were carried out. It was found that, for the amorphous $As_{45}S_{15}Se_{40}$ thin films, the value of the refractive index n, which was n=2.921 at λ=650 nm, increases with exposure time and decreases for the annealed samples. The optical band gap E_g determined from the Tauc plot E_g=1.929 eV decreases in both cases under the light exposure and heat treatment $\Delta E_g/\Delta T_{ann}$=-5.8·10^{-4} eV/^{o}C. The kinetics of photodarkening in amorphous $As_{45}S_{15}Se_{40}$ thin films is described by a stretch exponential function and the effect under illumination with a laser beam λ=540 nm is more pronounced than in amorphous As_2S_3 and As_2Se_3 films.

Acknowledgments

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