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On the compositional dependence of refractive index in amorphous $Ge_xAs_xSe_{1-2x}$ films

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Some optical properties of amorphous $Ge_xAs_xSe_{2-x}$ thin films prepared by thermal "flash" evaporation on the glass substrates at T_{substr}=100 °C are presented. From transmission spectra $T(\lambda)$, have been calculated the absorption coefficient $\alpha(h\nu)$, the values of optical band gap E_g and dispersion curves of refractive index $n(\lambda)$. It was established that annealing of thin films at high temperatures decreased the absorption coefficient α and refractive index n. The values of optical band gap E_g, determined from the Tauc plot $(\alpha \cdot h\nu)^{1/2}$ vs. $(h\nu)$, increased with annealing temperature T_{an}. Thus, for $As_{0.09}Ge_{0.09}Se_{0.82}$ composition, the variation of optical band gap versus annealing temperature is $\Delta E_g/\Delta T_{an}=1.275\cdot 10^{-4}$ eV/°C. These features may be used in developing of new functional media based on $Ge_xAs_xSe_{1-2x}$ films for modern optoelectronics.

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Keywords: Chalcogenide glass, Amorphous films, Optical absorption, Refractive index, Photodarkening effect

1. Introduction

Chalcogenide glasses of Ge-As-Se system are characterized by the widest region of glass formation in comparison to other ternary chalcogenide compounds, high glass transition temperatures (T_g=300÷400 °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 ($n_2=2.5\cdot 10^{-17}$ cm²/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 fabrication of different registration media, diffractive structures, waveguides, photonic structures, and optical amplifiers [3-6]. The glasses $Ge_xAs_xSe_{2-x}$ are widely investigated, especially its thermally properties [7,8]. Using the scattering, T-modulated Differential Scanning Calorimetric (MDSC), and ^{119}Sn Mossbauer spectroscopy techniques established existence in these glasses three distinguished phases: mechanically floppy (free from mechanical stress at $x<x_c(1)=0.09$), intermediate - at $x_c(1)<x<x_c(2)=0.16$, and stressed-rigid - at $x>x_c(2)$ phases. The synthesized $Ge_xAs_xSe_{2-x}$ is from different above-mentioned phases, and then we expect de dependence of the optical properties on glass composition. It is well known that the optical properties (absorption coefficient α, refractive index n, optical band gap E_g) depend on the glass composition and on the 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). From the transmission spectra was calculated the absorption coefficient α, refractive index n, and the optical band gap E_g. It was shown that some peculiarities 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]. The arsenic chalcogenide films usually become darkened under light irradiation in the region of the fundamental absorption edge. As the composition of a glass determines both the structural units and the mean coordination number of the amorphous solid, the effect of the composition in glassy systems Ge-As-Se 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. From this point of view, investigation of optical properties and photodarkening effect in amorphous $Ge_xAs_xSe_{1-2x}$ thin films present interests, because in the composition dependences increasing of the Ge concentration induce changes in the intermediate ordering, which can restrict or accelerate the slip motion of the structure clasters.

2. Experimental

The glassy samples of the $Ge_xAs_xSe_{1-2x}$ glasses (0.05≤x≤0.30) were prepared by conventional melt quenching method. Elemental Arsenic (99.999 % purity), elemental Germanium (99.999 % purity), and elemental Selenium (99.999 % purity) were used as the starting materials. The mixture of high-purity precursors was melted in sealed evacuated quartz ampoules ($p=5\cdot10^{-6}$ Torr) placed in a rocking furnace. The total weight of the synthesized sample was 35 grams. The temperature of the quartz ampoule was slowly increased to 550 °C at the rate of 50 °C/hour and kept at this temperature during 24 hours for homogenization. Than the temperature was increased up to 980 °C at the rate 50 °C/hour and homogenized at this temperature during 72 hours, and then quenched in the regime of the disconnected furnace. Thin film samples of thickness d=0.5÷3 μm were prepared by flash thermal evaporation in vacuum of the synthesized initial $Ge_xAs_xSe_{1-2x}$ chalcogenide glasses onto glass substrates held at $T_{subs}=100$ °C. Table 1 reflects the synthesized compositions of chalcogenide glasses $Ge_xAs_xSe_{1-2x}$, the mean coordination number <r>, and the thickness d of amorphous deposited films. 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 calculation of the optical constants from the transmission spectra, the computer program PARAV-V1.0 (www.chalcogenide.eu.org) was used [12]. To initiate photostructural transformations in thin film samples, as a source of light exposure, a continuous He-Ne lasers (λ=630 nm, P=0.6 mW and λ=540 nm, P=0.75 mW) were used. The experimental set-up included a laser, a digital build-in PC-card PCI-1713A for data acquisition connected with the Si-photodetector.

Table 1. The synthesized chalcogenide glasses $Ge_xAs_xSe_{1-2x}$, the mean coordination number <r>, and the thickness d of amorphous deposited films.

No.	**Composition, $Ge_xAs_xSe_{1-2x}$**	<r>	**d (μm)**
1	$Ge_{0.05}As_{0.05}Se_{0.90}$	2.15	0.511
2	$Ge_{0.07}As_{0.07}Se_{0.86}$	2.21	1.160
3	$Ge_{0.09}As_{0.09}Se_{0.82}$	2.27	2.550
4	$Ge_{0.11}As_{0.11}Se_{0.78}$	2.33	1.290
5	$Ge_{0.14}As_{0.14}Se_{0.72}$	2.42	1.150
7	$Ge_{0.18}As_{0.18}Se_{0.64}$	2.54	1.940
8	$Ge_{0.20}As_{0.20}Se_{0.60}$	2.60	1.980
9	$Ge_{0.25}As_{0.25}Se_{0.50}$	2.75	4.010
10	$Ge_{0.30}As_{0.30}Se_{0.40}$	2.90	0.910

3. Results and discussion

Fig. 1 represents the typical absorption spectra for two amorphous $Ge_xAs_xSe_{1-2x}$ thin film samples (x=0.07 and x=0.25). Increasing of Ge and As content in the $Ge_xAs_xSe_{1-2x}$ glassy system shift the Urbach tail in the red region of the spectrum. In some cases for some glass compositions, depending of mean coordination number <r>, the shift of the absorption edge can take place in the short wave region.

From the transmission spectra T=f(λ), 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 $(\alpha\, h\nu)^{1/2} = A(h\nu - E_g)$, was 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 – the reflection, λ_m, λ_{m-1} – the minimum and maximum of the interference in the transmission spectra, A - is a constant.

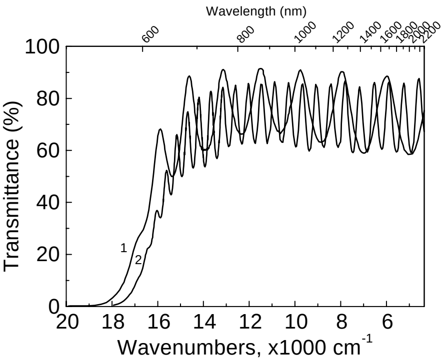

Fig.1. The transmission spectra for two amorphous $Ge_xAs_xSe_{1-2x}$ thin film samples x=0.07 (1) and x=0.25 (2).

Fig.2 represents the absorption coefficient for as-deposited (1) and exposed during 2 hours (2) amorphous $Ge_{0.05}As_{0.05}Se_{0.90}$ thin films. The light exposure with the integrated light shifts the absorption edge in the high energy region, and leads to an increasing of the optical band gap E_g, and decreasing of the refractive index n (Fig.3). As result of light exposure the optical band gap is changed by the value of $\Delta E_g=0.01$ eV, and the refractive index by the value of $\Delta n=0.141$ (λ=700 nm), respectively. The same effect was observed also for the $Ge_{33}S_{67}$ thin films, where as result of light exposure the optical band gap was increased from $E_g=2.68$ eV up to $E_g=3.06$ eV, and to decreasing of the refractive index from n=2.16 up to 2.08, respectively [13]. This is so called photobleching effect in calcogenide glasses.

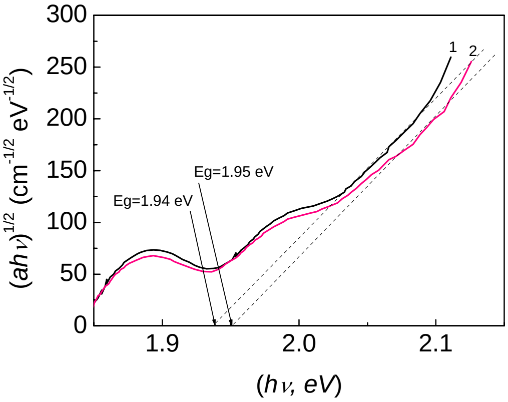

Fig.2. The dependence $(\alpha\, h\nu)^{1/2}$ vs. $(h\nu)$ for amorphous $Ge_{0.05}As_{0.04}Se_{0.90}$ as-deposited (1) and exposed during 2 hours (2) thin films. The dashed line is a computing fitting giving the value of E_g.

The dispersion curves n=f(λ) for all thin films of the investigated compositions of the glassy $Ge_xAs_xSe_{1-2x}$ system are presented in [14]. In the present work the main attention is done to investigation of variation of optical constants of the amorphous $Ge_xAs_xSe_{1-2x}$ thin film in dependence of the annealing temperature (T_{an}=15÷140 °C).

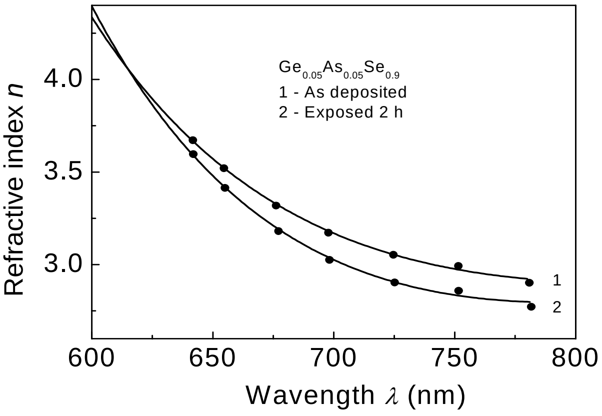

Fig.3. The dispersion curve n=f(λ)amorphous $Ge_{0.05}As_{0.04}Se_{0.90}$ as-deposited (1) and exposed during 2 hours (2) thin films.

Fig.4 represents the dependence of the absorption coefficient α versus annealing temperature T_{an} for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ thin film. With increasing of the annealing temperature T_{an}, the absorption coefficient α decrease. At the same time, increasing of the annealing temperature T_{an} increase the optical band gap E_g (Fig.5).

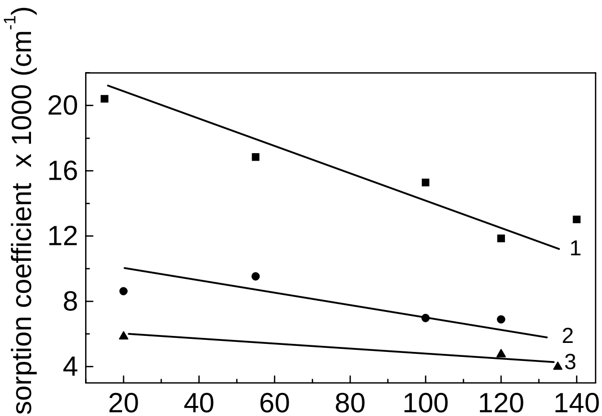

Fig. 4. The dependence of the absorption coefficient α versus annealing temperature T_{an} for amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ (1), $Ge_{0.18}As_{0.18}Se_{0.64}$ (2), and $Ge_{0.25}As_{0.25}Se_{0.50}$ (3), thin films.

Fig.6 represents the dispersion curves of the refractive index n=f(λ) for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ thin films annealed at different temperatures T_{an}. Increasing of the annealing temperature T_{an} decrease the refractive index n. The dependence of the refractive index n versus annealing temperature T_{an} for amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ (1), $Ge_{0.18}As_{0.18}Se_{0.64}$ (2), and $Ge_{0.25}As_{0.25}Se_{0.50}$ (3) thin films is presented on Fig.7. For amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ (curve 1) and $Ge_{0.18}As_{0.18}Se_{0.64}$ (curve 2) films this dependence is very weak, in contrast with the same dependence for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ (curve 3) films, for which $\Delta n/\Delta T_{an}=4.8\cdot10^{-3}$ 1/°C. In the region of the annealing temperatures T_{an}=20-100 °C the optical band gap Eg increase with the annealing temperature and the value $\Delta E_g/\Delta T_{an}=(1.15\div1.27)\cdot10^{-4}$ eV/°C, and slightly decrease with the increasing of Ge concentration in the $Ge_xAs_xSe_{1-2x}$ glassy system.

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.8, when excited with He-Ne laser (λ=630 nm). This dependence describe the excess of absorbance induced by light absorption during the exposure.

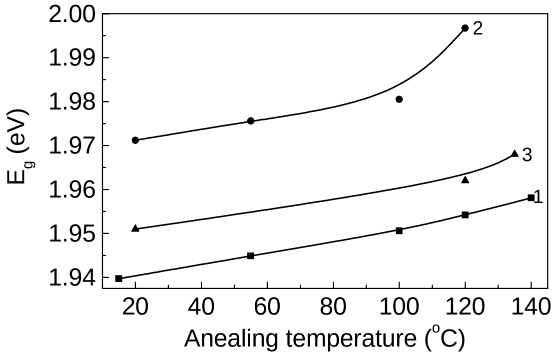

Fig. 5. The dependence of the optical band gap E_g versus the annealing temperature T_{an} for amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ (1), $Ge_{0.18}As_{0.18}Se_{0.64}$ (2), and $Ge_{0.25}As_{0.25}Se_{0.50}$ (3), thin films.

At a constant light intensity the presented dependences characterize the decay of the film optical transmittance with the increase of the dose of absorbed photons. To obtain a unified basis for comparison of the transmission relaxation T(t) curves we used 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<β<1). The parameters of the stretched exponential for all $Ge_xAs_xSe_{1-2x}$ samples were calculated by computing fitting of the experimental points.

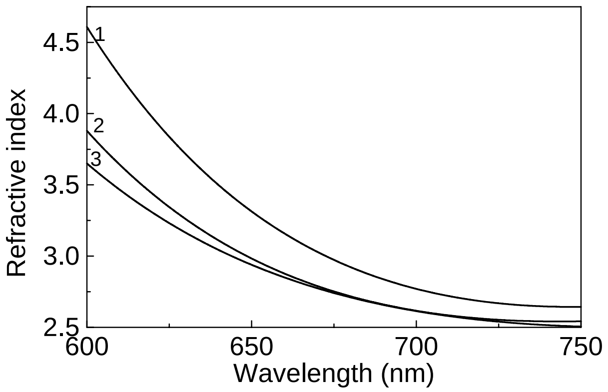

Fig. 6. The dispersion curves of the refractive index n for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ thin films annealed at different temperatures T_{an}, ^oC: 1-20; 2-120; 3-135.

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 a chalcogenide glass. According to this model, during exposure the layer is negatively charged due to capture of photoexcited electrons, and repulsive forces are built between the layers.

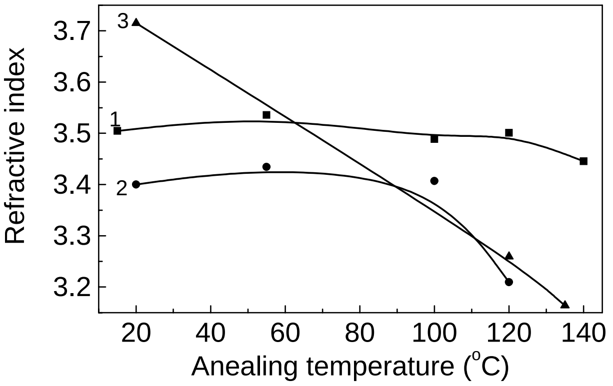

Fig. 7. The dependence of the refractive index n versus annealing temperature T_{an} for amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ (1), $Ge_{0.18}As_{0.18}Se_{0.64}$ (2), and $Ge_{0.25}As_{0.25}Se_{0.50}$ (3), thin films.

These forces cause enlargement of the interlayer distance (leading to photoexpansion) and slip motion along the layers. This process alters interaction of lone-pair electrons between the layers leading to photodarkening effect. This model was successfully used for explanation the photodarkening phenomena in amorphous As-Se films doped with metals [15-17].

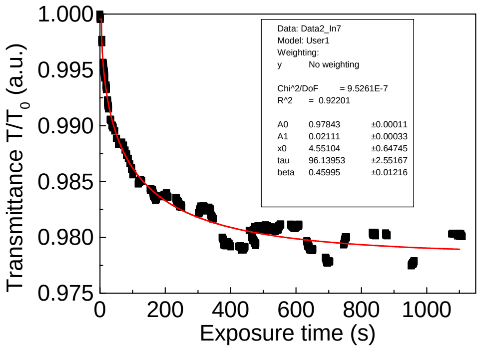

Fig.8. Excess absorbance induced by light absorption during the light exposure for amorphous $Ge_{0.07}As_{0.07}Se_{0.86}$ thin films.

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.

The non-monotony dependence of the parameters of the stretched exponential for $Ge_xAs_xSe_{1-2x}$ samples is connected with the transition towards from 2D to 3D network with increasing the concentration of Ge (Fig.9). In our previous works [14,15] it was shown that the tin impurity in As_2Se_3 strongly affect the network of the host glass inducing changes in both short-range as well as medium-range order, in particular they exert significant influence on the structural layers and the character of their relative motion.

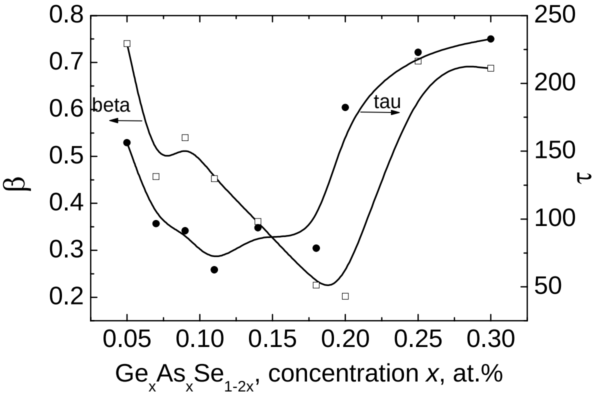

Fig. 9. The dependence of the parameter β and τ of the stretched exponential versus composition of amorphous $Ge_xAs_xSe_{1-2x}$ thin films.

Table 2. Parameters of the stretched exponential obtained by fitting of the experimental points and calculated curves for $Ge_xAs_xSe_{1-2x}$ samples.

Composition, x	A_0	A_1	τ (s)	β
$Ge_{0.05}As_{0.05}Se_{0.90}$	0.990	0.010	156.267	0.740
$Ge_{0.07}As_{0.07}Se_{0.86}$	0.978	0.022	96.597	0.457
$Ge_{0.09}As_{0.09}Se_{0.82}$	0.979	0.021	91.260	0.540
$Ge_{0.11}As_{0.11}Se_{0.78}$	0.976	0.024	62.585	0.452
$Ge_{0.14}As_{0.14}Se_{0.72}$	0.982	0.018	93.528	0.361
$Ge_{0.18}As_{0.18}Se_{0.64}$	0.989	0.011	78.425	0.226
$Ge_{0.20}As_{0.20}Se_{0.60}$	0.978	0.022	182.263	0.202
$Ge_{0.25}As_{0.25}Se_{0.50}$	0.971	0.038	222.876	0.703
$Ge_{0.30}As_{0.30}Se_{0.40}$	0.970	0.034	232.712	0.688

Creation of clusters such as $SnSe_2$ type lowering the density of the typical for AsSe lone-pair defects (D-centers), the charge state of the layers also is lowering, and the photodarkening phenomena is quenched. Probable the four-coordinated Ge in $Ge_xAs_xSe_{1-2x}$ glasses play the analogue role, and influence the photodarkening parameters.

Fig. 10 represents the distribution of the investigated compositions in the three distinguished phases: mechanically floppy (free from mechanical stress at $x<x_c(1)=0.09$), intermediate - at $x_c(1)<x<x_c(2)=0.16$, and stressed-rigid - at $x>x_c(2)>0.18$ phases, determined from the photocapacitance measurements [21].

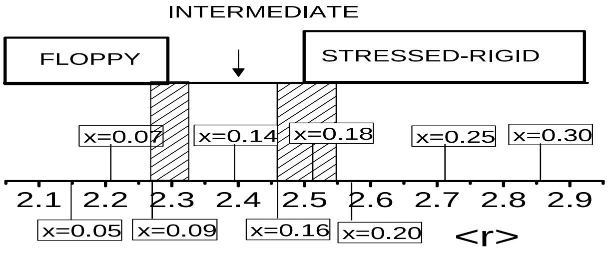

Fig.10. The diagram of the investigated compositions (x) on an axis of average coordination number <r> in glasses $Ge_xAs_xSe_{1-2x}$.

The arrow shows Phillips-Thorpe threshold. The thresholds x(C1) and x(C2), which were reported by some authors [7, 18-20] are shown by dashed regions.

4. Summary

The optical transmission spectra of of amorphous $Ge_xAs_xSe_{2-x}$ ($x=0.05\div0.30$) thin films was measured. From the transmission spectra the optical constants (absorption coefficient α, refractive index n and the optical band gap Eg) for the amorphous $Ge_xAs_xSe_{1-2x}$ thin films were evaluated. It was established a non monotony dependence of the optical parameters vs. mean coordination number Z. The experimental results show, that the optical band gap E_g decreases, while the refractive index n increases with the increasing of the 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.

Relaxation of the relative optical transmission T(t)/T(0) of the amorphous $Ge_xAs_xSe_{1/2x}$ thin films in dependence of the exposure time t also was 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 photodarkening effect. Increasing of Ge and As content in the glassy $Ge_xAs_xSe_{1-2x}$ system increase the photodarkening. The kinetics of photodarkening process in amorphous $Ge_xAs_xSe_{1-2x}$ thin films is described by stretched exponential function $T(t)/T(0) = A_0+A\exp[-(t-t_0)/\tau]^{(1-\beta)}$. The parameters of stretched exponential show a good correlation with the values of the optical band gap E_g of the $Ge_xAs_xSe_{1-2x}$ thin films.

Acknowledgment

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