THE DEPENDENCE OF OPTICAL PARAMETERS ON COMPOSITION IN THE $Ge_xAs_xSe_{1-2x}$ GLASSY SYSTEM

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Abstract

The optical properties of amorphous $Ge_xAs_xSe_{2-x}$ (x = 0.05÷0.30) thin films prepared by thermal evaporation on glass substrates held at T_{substr} = 100 °C are reported. The transmission spectra was used for the calculation of the absorption coefficient α, optical band gap E_g, and the values of the refractive index n. The dependences of α, E_g, and n on the film composition in the $Ge_xAs_xSe_{1-2x}$ glassy system were determined. It was established 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 time dependence of the transmission $T(t)$ during the light exposure for the above band gap illumination *(photodarkening)* is described by a strength exponential behavior $T(t)/T(0) = A_0+A\exp[-(t-t_0)/\tau]^{(1-\beta)}$, where 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 β is the dispersion parameter $(0<\beta<1)$.

1. Introduction

Ge-As-Se chalcogenide glasses have a wide region of glass formation in respect with other ternary compounds, high glass transition temperatures T_g, thermal stability, and high transparency in the IR region. Glasses of the Ge-As-Se system are of interest due to high nonlinearity, high refractive index (2.4-2.6), and suitable optical transmission at λ = 1.55 μm [1]. 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 Z. In this paper, we report the experimental results on some optical properties of amorphous $Ge_xAs_xSe_{1-2x}$ thin films ($0.05 \leq x \leq 0.30$). From the transmission spectra, we 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 vs mean coordination number Z for $Ge_xAs_xSe_{1-2x}$ glasses take place in the reversibility window [2, 3].

The variety of light-induced structural transformations in amorphous chalcogenide films is rather wide and attracts scientific and technical interest [4, 5]. Arsenic chalcogenide films usually become darkened under light irradiation in the region of the fundamental absorption edge. Since 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 glassy systems on the degree of photostructural transformations was studied.

2. Experimental

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_{subst}=100 °C. For optical transmission spectra measurements, a UV/VIS (300÷800 nm) and 61 NIR (800÷3500 nm) Specord's CARLZEISS Jena production were used. For the calculation of the optical constants, the *PARAV-V1.0* computer program (www.chalcogenide.eu.org) was used [6]. To initiate photostructural transformations in thin film samples, as a source of light exposure, 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 and a digital build-in *PC*-card *PCI-1713A* for data acquisition connected with the *Si*-photodetector.

3. Results and discussion

Figure 1a represents the typical absorption spectra for two amorphous $Ge_xAs_xSe_{1-2x}$ thin film samples (*x* = 0.07 and 0.25). The increase in the Ge and As content in the $Ge_xAs_xSe_{1-2x}$ glassy system shifts the Urbach tail in the red region of the spectrum. As we will show below in the dependence of E_g vs mean coordination number *Z*, in some cases, the shift of the absorption edge takes place in the short wave region. 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 (Fig. 1b), the refractive index *n* (Figs. 2a, 2b), and the value of the optical band gap E_g (Fig. 4b).

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.

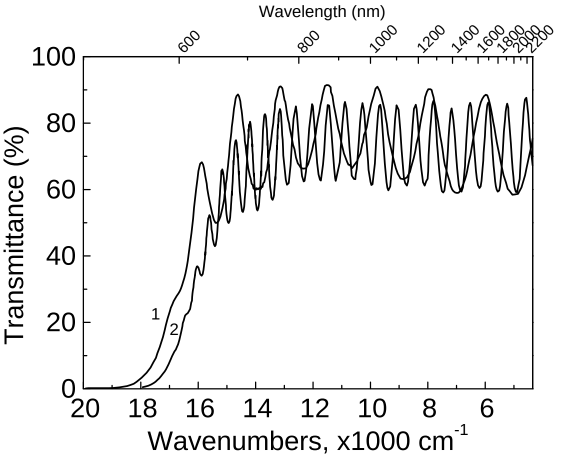

Fig. 1a. Transmission spectra for two amorphous $Ge_xAs_xSe_{1-2x}$ thin film samples *x* = 0.07 (*1*) and *x* = 0.25 (*2*).

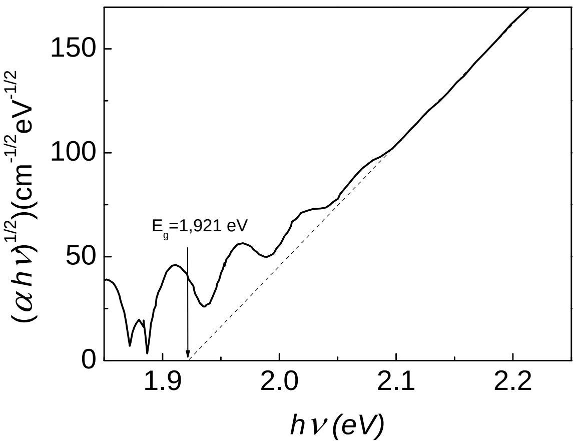

Fig. 1b. Dependence $(\alpha\ h\nu)^{1/2}$ vs. $(h\nu)$ for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ thin film. The dashed line is a computing fitting giving the value of E_g.

The calculated values of the refractive index *n* for amorphous $Ge_xAs_xSe_{1-2x}$ thin films for two wavelengths are shown in Fig. 2a. The plot $(n^2-1)^{-1}$ *vs.* $(h\nu)^2$ (Fig. 2b) makes it possible to

determine the oscillator parameters by fitting a straight line to the experimental points. By extrapolating the fitting line towards $h\nu = 0$, one can obtain the static refractive index n_0.
The relaxation of the relative optical transmission for amorphous $Ge_xAs_xSe_{1-2x}$ thin films in the co-ordinates $1-T(t)/T(0)$ vs t is shown in Fig. 3a. These dependences describe the excess of absorbance induced by light absorption during the exposition.

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 comparison of the transmission relaxation $T(t)$ curves, we used the so-called stretched exponential presentation for the relaxation curves in the form

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

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 ($0 < \beta < 1$). Parameters of the stretched exponential obtained by the fitting of the experimental points and calculated curves for $Ge_xAs_xSe_{1-2x}$ samples are presented in Table 1 and Fig. 3b.

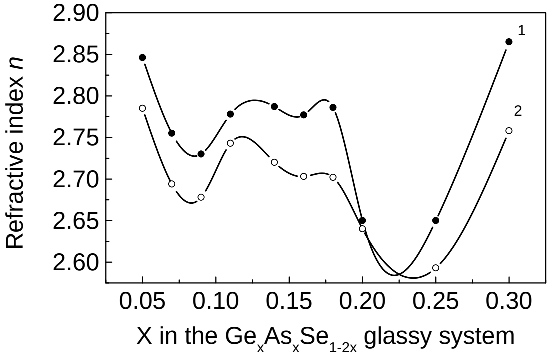

Fig. 2a. Dependence of the refractive index n on the composition for amorphous $Ge_xAs_xSe_{1-2x}$ thin films: λ = 700 nm (1) and 750 nm (2).

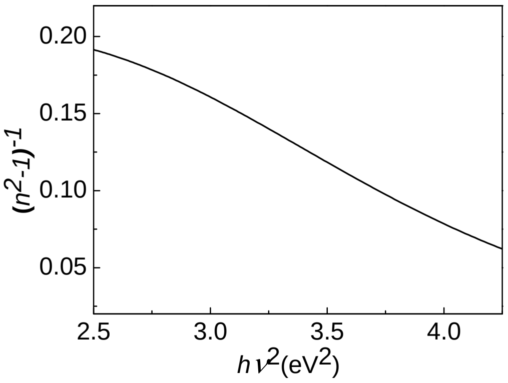

Fig. 2b. Dependence of the refractive index $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ thin film.

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

No	***Composition, x***	***Z***	***L(μ)***	A_0	A_1	t_0 ***(s)***	τ ***(s)***	β
1	$Ge_{0.05}As_{0.05}Se_{0.90}$	2.15	0.511	0.9899	0.0101	0.0001	156.2669	0.7403
2	$Ge_{0.07}As_{0.07}Se_{0.86}$	2.21	1.160	0.9785	0.0215	0.0452	96.5967	0.4569
3	$Ge_{0.09}As_{0.09}Se_{0.82}$	2.27	2.550	0.9793	0.0207	0.5480	91.2604	0.5398
4	$Ge_{0.11}As_{0.11}Se_{0.78}$	2.33	1.290	0.9762	0.0244	-0.0730	62.5848	0.4524
5	$Ge_{0.14}As_{0.14}Se_{0.72}$	2.42	1.150	0.9823	0.0177	16.7063	93.5285	0.3611
7	$Ge_{0.18}As_{0.18}Se_{0.64}$	2.54	1.940	0.9888	0.0112	0.1849	78.4247	0.2257
8	$Ge_{0.20}As_{0.20}Se_{0.60}$	2.60	1.980	0.9781	0.0217	-0.0113	182.2629	0.2017
9	$Ge_{0.25}As_{0.25}Se_{0.50}$	2.75	4.010	0.9709	0.0375	-2.1699	222.8756	0.7030
10	$Ge_{0.30}As_{0.30}Se_{0.40}$	2.90	0.910	0.9697	0.0339	0.0070	232.7119	0.6875

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. Recently, a novel model for photodarkening in a-$As_2Se(S)_3$ has been proposed, in which photoexcited charge carriers in extended states are considered to be responsible for photodarkening [7]. 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 the enlargement of the interlayer distance (leading to photoexpansion) and slip motion along the layers. The nonmonotonic dependence of the parameters of the stretched exponential for the $Ge_xAs_xSe_{1-2x}$ samples is connected with the transition towards the 3D network (Figs. 3b and 4a). This model was successfully used for explaining the photodarkening phenomena in amorphous As-Se films doped with metals [8].

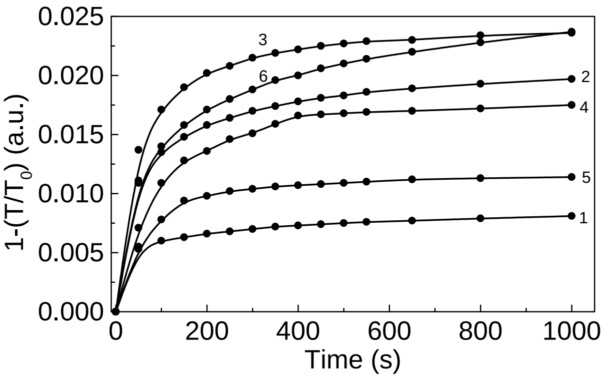

Fig. 3a. Excess absorbance induced by light absorption during the exposition of the $Ge_xAs_xSe_{1-2x}$ samples; x: (*1*) 0.05; (*2*) 0.09; (*3*) 0.11; (*4*) 0.14; (*5*) 0.18; and (*6*) 0.30.

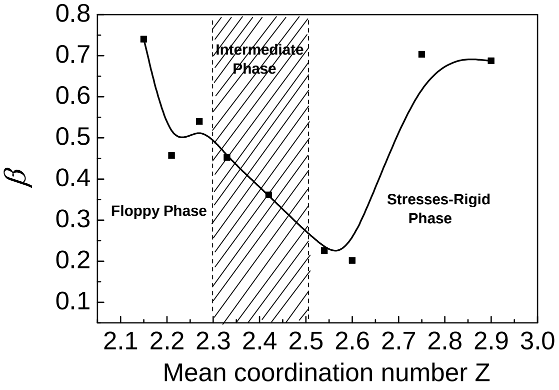

Fig. 3b. Dependence of the parameter β of the stretched exponential vs. mean coordination number *Z*.

Thus, we can expect that the tin impurity strongly affects the network of the host glass inducing changes in both short-range as well as medium-range order; in particular, they exert a significant effect on the structural layers and the character of their relative motion. We can observe a good correlation between the parameters of the stretched exponential *(β, τ)* and the optical band gap E_g for different $Ge_xAs_xSe_{1-2x}$ samples (Figs. 3b, 4a, 4b).

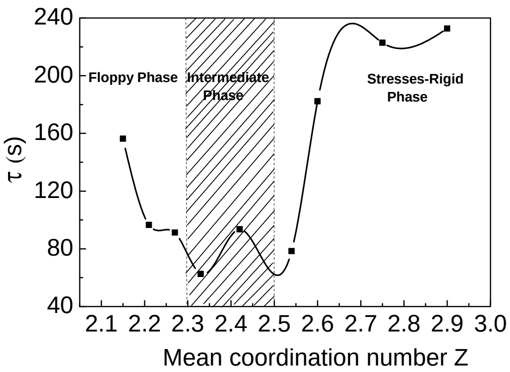

Fig. 4a. Dependence of the parameter τ of the stretched exponential vs. mean coordination number *Z* in the $Ge_xAs_xSe_{1-2x}$ glassy system.

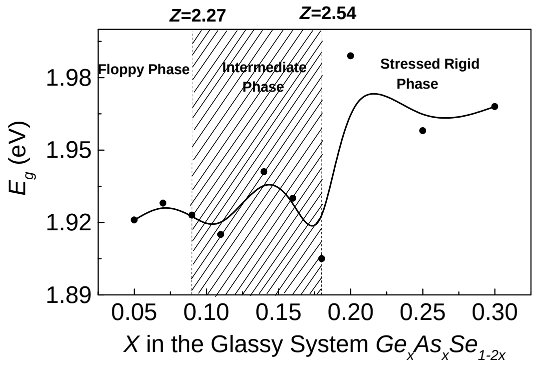

Fig. 4b. Dependence of the optical band gap E_g vs. mean coordination number *Z* in the $Ge_xAs_xSe_{1-2x}$ glassy system.

4. Conclusions

From the transmission spectra the optical constants (α, n and E_g) for the amorphous $Ge_xAs_xSe_{1-2x}$ thin films were evaluated. A nonmonotonic dependence of the optical parameters vs. mean coordination number was found. The kinetics of photodarkening process in 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 parameters of stretched exponential show a good correlation with the values of the optical band gap of the $Ge_xAs_xSe_{1-2x}$ thin films.

Acknowledgments

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