NEW OPTICAL MATERIALS BASED ON CHALCOGENIDE GLASSES

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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 fabrication of different registration media, diffractive structures, waveguides, photonic structures, and optical amplifiers. The arsenic chalcogenide films usually become darkened under light irradiation in the region of the fundamental absorption edge. The changes of the optical constants (absorption coefficient α, optical band gap E_g, and refractive index n) of the investigated materials under the ionization irradiation and heat treatment was evaluated.

Keywords: Chalcogenide glasses, amorphous films, optical absorption, refractive index, holography

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 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]. 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]. 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.

2. Experimental

The glassy samples of the As-S-Se and $Ge_xAs_xSe_{1-2x}$ (0.05≤x≤0.30) were prepared by conventional melt quenching method. Thin film samples of thickness d=0.5÷3 μm were prepared by flash thermal evaporation in vacuum 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 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.

3. Results and discussions

Figure1 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 $T=f(\lambda)$, 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 $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$, 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.

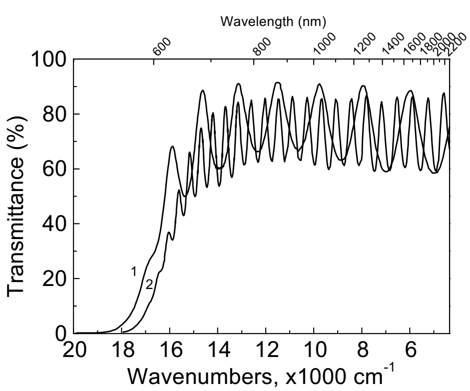

Figure1. The transmission spectra for two amorphous $Ge_xAs_xSe_{1-2x}$ thin film samples x=0.07 (1) and x=0.25 (2).

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. 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 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. In contrast, for the amorphous $As_{45}S_{15}Se_{40}$ thin films the light exposure decrease the optical band gap E_g and increase the refractive index n.

The dispersion curves $n=f(\lambda)$ 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). Figure2 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 (Figure3).

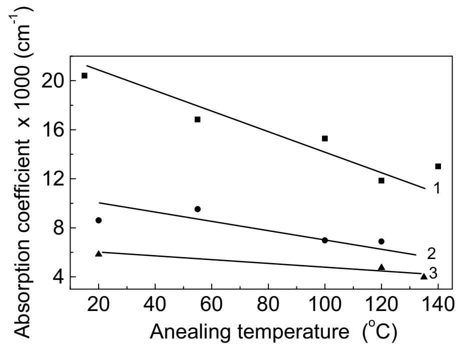

Figure 2. The dependence of the absorption coefficient α versus annealing temperature T_{an} for amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ (1), $Ge_{0.18}As_{0.18}Se_{0.64}$ (2), and $Ge_{0.25}As_{0.25}Se_{0.50}$ (3), thin films.

Figure4 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}. 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 Figure5. 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 $\Delta n/\Delta T_{an}$=4.8·10^{-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÷1.27)·10^{-4} eV/°C, and slightly decrease with the increasing of Ge concentration in the $Ge_xAs_xSe_{1-2x}$ glassy system. For the $As_{45}S_{15}Se_{40}$ the annealing at high temperatures decrease the optical band gap ($\Delta E_g/\Delta T_{an}$=-5.8·10^{-4} eV/°C), and firstly decrease the refractive index ($\Delta n/\Delta T_{an}$=-9.2·10^{-4} 1/°C), and then increase it.

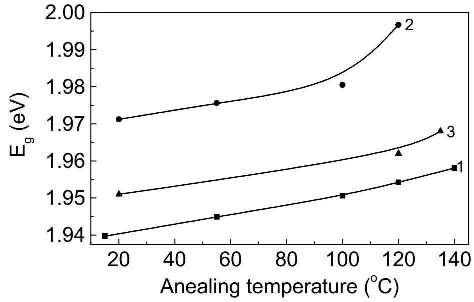

Figure3. The dependence of the optical band gap E_g versus the annealing temperature T_{an} for amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ (1), $Ge_{0.18}As_{0.18}Se_{0.64}$ (2), and $Ge_{0.25}As_{0.25}Se_{0.50}$ (3), thin films.

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 Figure6, when excited with He-Ne laser (λ=630 nm). This dependence describes the excess of 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 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 ($0<\beta<1$). The parameters of the stretched exponential for all $Ge_xAs_xSe_{1-2x}$ samples were calculated by computing fitting of the experimental points.

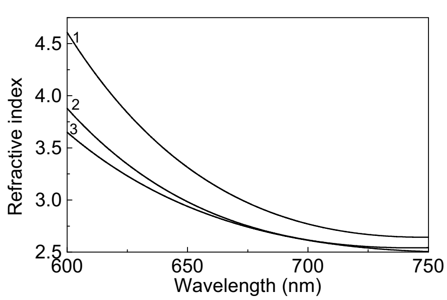

Figure 4. The dispersion curves of the refractive index *n* for amorphous $Ge_{0.25}As_{0.25}Se_{0.50}$ thin films annealed at different temperatures T_{an}, °C: 1-20; 2-120; 3-135.

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.

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].

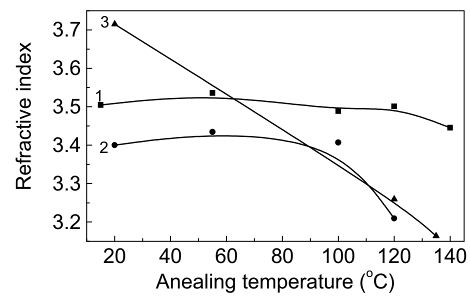

Figure 5. The dependence of the refractive index *n* versus annealing temperature T_{an} for amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ (1), $Ge_{0.18}As_{0.18}Se_{0.64}$ (2), and $Ge_{0.25}As_{0.25}Se_{0.50}$ (3), thin films.

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.

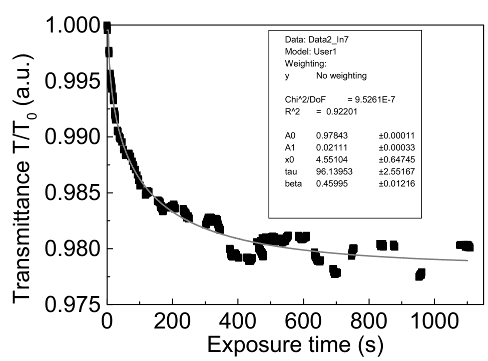

Figure 6. Excess absorbance induced by light absorption during the light exposure for amorphous $Ge_{0.07}As_{0.07}Se_{0.86}$ thin films.

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 (Figure7). 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.

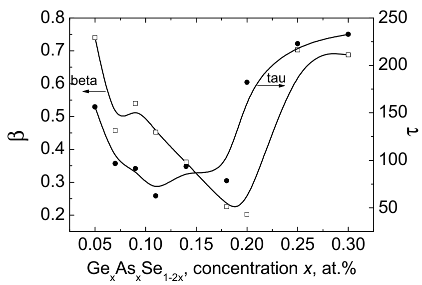

Figure 7. The dependence of the parameter β and τ of the stretched exponential versus composition of amorphous $Ge_xAs_xSe_{1-2x}$ thin films.

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.

4.Summary

The optical transmission spectra of of amorphous $Ge_xAs_xSe_{2-x}$ (x=0.05÷0.30) 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 $T(t)/T(0) = A_0+A\exp[-(t-t_0)/\tau]^{(1-\beta)}$.

Aknowledgment

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