Light and Thermal Induced Modification of the Refractive Index in $As_{45}S_{15}Se_{40}$ Glasses

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***Abstract* - The experimental investigations of the influence of the light irradiation on the optical parameters of amorphous $As_{45}S_{15}Se_{40}$ thin films prepared by „flash" thermal evaporation was investigated. From the experimental transmission spectra $T=f(\lambda)$ the value of the refractive index *n*, and optical band gap E_g was determined. It was established that the light exposure and the heat treatment modify the optical constants of the investigated amorphous films. From the Tauc plot $(\alpha \cdot h\nu)^{1/2}$ vs. $(h\nu)$ the optical band gap E_g for amorphous $As_{45}S_{15}Se_{40}$ thin films is E_g=1.929 eV. For amorphous $As_{45}S_{15}Se_{40}$ thin films the exposure time decrease the optical band gap E_g and the refractive index *n*, but the annealing temperature increase these values. The modifications of the optical constants under the light exposure and heat treatment allow using these materials as effective media for registration of the optical and holographic information.**

Keywords: Amorphous films, optical absorption, refractive index, dielectric constant

1. Introduction

Amorphous As_2S_3, As_2Se_3, and As_2S_3-As_2Se_3 have been intensively studied as promising materials for recording media and different methods have been applied to fabricate diffractive optical elements using holographic or electron beam lithography methods [1,2]. The physical principles of these methods are based on the effect of photoinduced phenomena in chalcogenide glasses, e.g. the changes of the optical constants (absorption coefficient α, optical band gap E_g, and refractive index *n*) of the material under the ionization irradiation. It was demonstrated, that in amorphous As_2S_3 thin films can be recorded can be recorded the transmission holographic gratings with the diffraction efficiency up to η=80 % [3]. For the amorphous $As_{100-x}Se_x$ films the maximum photoinduced refractive index (Δn=0.73) [3] and ($\Delta n/n$=0.394) [4] changes was observed for the glass composition $As_{60}Se_{40}$. The surface relief holographic gratings with the period Λ=0.15÷1 μm in amorphous As_2S_3 and $As_{40}S_{15}Se_{45}$ thin films were recorded using the solid immersion holographic method (using prisms from ZnS or GaP with a refractive index of *n*=3 or more) [1,5]. The photoinduced changes in vacuum evaporated amorphous As_2S_3-As_2Se_3 thin films in the infrared absorption spectra are interpreted by rearrangement (polymerization) of bonding configurations (Such molecular units as As_4, As_4S_3, As_4S_4, S_8, As_4Se_4, etc.) [6]. It was shown that after 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, 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 $As_{40}Se_{60}$ [7]. It was demonstrated that the molecular structure of the mixed glasses i s 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 are possible. For the amorphous $As_{40}Se_{60-x}Se_x$ thin films was established that increasing of Se concentration leads to increasing of the refractive index [8]. The exposure and annealing lead to polymerization of the molecular groups As_4S_4 and As_4Se_4 and the chains S_n and Se_n in the film matrix, with further 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. The non-reversible photostructural transformations in amorphous $As_{40}S_{60-x}Se_x$ thin films and the possibility to apply it for fabrication of holographic protective elements were reported in [9]. Using the Raman spectroscopy characterization, it was shown that the photostructural transformations are considered as changes in their network structure including three types of pyramidal units $AsS_{3/2}$, $AsSe_{3/2}$ and $AsS(Se)_{3/2}$, as well as $As_4S(Se)_4$ and $S(Se)_n$ fragments in the initial phase. Thermal annealing or light exposure result in polymerization of the molecular groups and the decreasing number of homopolar bonds.

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In the present work we present the experimental investigations of the influence of the light irradiation and thermal annealing on the optical parameters of amorphous $As_{45}S_{15}Se_{40}$ thin films. The optical constants (absorption coefficient α, optical bad gap E_g, and the refractive index n, the static refractive index $n^2(0)= \varepsilon_s$, the average electronic energy gap E_0, and the dielectric oscillator strength E_d were calculated from the experimental measured transmission spectra.

2. Experimental

The bulk samples of chalcogenide glasses $As_{45}S_{15}Se_{40}$ was prepared by the conventional melting method and 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 chalcogenide glass onto glass substrates held at T_{subs}=100 °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 [10].

3. Results and discussion

Fig.1 represents the typical transmission spectra for as-deposited amorphous $As_{45}S_{15}Se_{40}$ thin film sample and exposed during different time. 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.

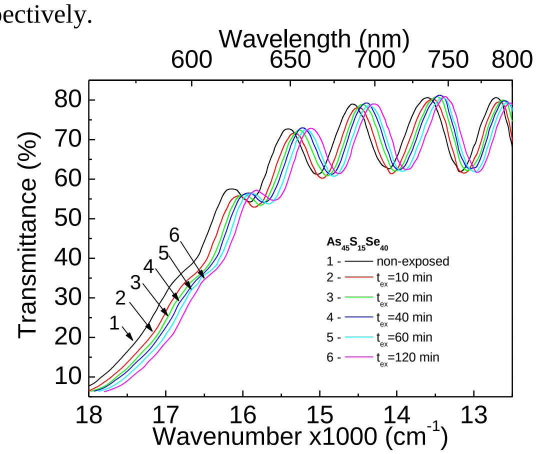

Fig.1. The transmission spectra $T=f(\lambda)$ of as-deposited $As_{45}S_{15}Se_{40}$ thin films (1) and light exposed for different time exposure (2-6).

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. The computing fitting of the dependence $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$ and the extrapolation of the Urbach tail to zero give the value of the optical band gap E_g=1.929 eV. Fig.2 represents the dispersion curves of the refractive index $n=f(\lambda)$ of as-deposited $As_{45}S_{15}Se_{40}$ thin films (1) and light exposed for different time exposure (2-6). The analogical results was obtained for the annealed thin films in the temperature range T_{ann}=15÷120 °C.

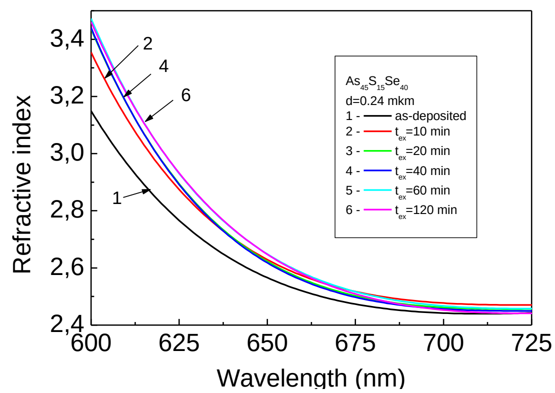

Fig.2. The dispersion curves of the refractive index $n=f(\lambda)$ of as-deposited $As_{45}S_{15}Se_{40}$ thin films (1) and light exposed for different time exposure (2-6).

The dispersion of the refractive index is related to the electronic absorption spectrum through the Wemple equation based on the single electronic oscillator model [11,12]:

$$(n^2 - 1) = \frac{E_d E_0}{E_0} - (h\nu)^2 \qquad (4)$$

where E_0 is the average electronic energy gap, and E_d is the dielectric oscillator strength. Large values of the refractive index n are obtained for smaller E_0 and for large E_d and leads to a large dispersion throughout the chalcogenide glass material. From equation (4) we obtain

$$(n^2 - 1)^{-1} = \frac{E_0}{E_d} - (\frac{1}{E_0 E_d})(h\nu)^2 \qquad (5)$$

Using the expressions (4,5) and the experimental data, the E_0 and E_d were calculated with the values E_0=2.28 eV and E_d=4.40 eV, respectively. The value of E_0 is higher than optical band gap E_g=1.929 eV obtained from the Tauc plot. Fig.3. represents the dependence $(n^2-1)^{-1}$ *vs. exposure time* for amorphous $As_{45}S_{15}Se_{40}$ thin films. We observe a non-linear dependence; the maximum changes of the refractive index take place in the beginning of the illumination process. The same situation is observed for the static values of the refractive index n_0 and dielectric permeability ε_0 (Fig.4).

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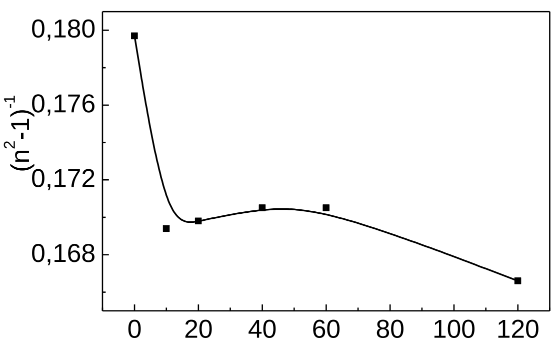

Fig.3. The dependence $(n^2-1)^{-1}$ *vs. exposure time* of amorphous $As_{45}S_{15}Se_{40}$ thin films

Fig.5 represents the 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. Increasing of the exposure time decrease the value of the optical band gap E_g, while the value of the refractive index n increase. Increasing of the refractive index n for exposed and annealed amorphous $As_{40}S_{60-x}Se_x$ films was observed in [8], and was explained by polymerization of the molecular groups As_4S_4 and As_4Se_4 and the chains S_n and Se_n in the film matrix, with further formation of structural units characterized with heteropolar As-S and As-Se bonds. These features of the molecular structure of chalcogenide amorphous films also lead to decreasing of the optical band gap during illumination and annealing.

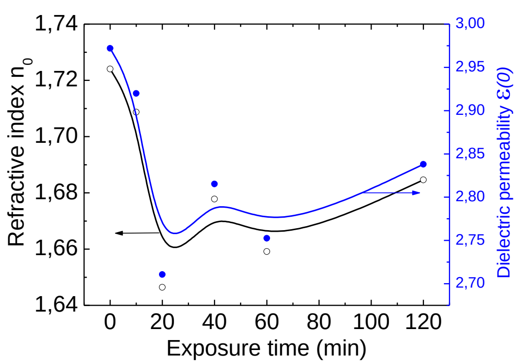

Fig.4. The dependence of the static values of the refractive index n_0 and dielectric permittivity ε_0 versus *exposure time* for amorphous $As_{45}S_{15}Se_{40}$ thin films.

According to [13], the shift of the band gap $\Delta E_g(t)$ versus time of illumination for amorphous $Ge_5As_{41}S_{15}Se_{39}$ films can be describe by the relation $\Delta E_g(t)= \Delta E_{g\infty}(1-\exp[-(kt)^{\beta}])$, where $\Delta E_{g\infty}=E_g(t\rightarrow\infty)-E_g$, k is the formal rate constant of the overall process, t is the time of illumination and β is so called stretching parameter. For different processes (illumination with sub-gap light, with over-band light and with white light) were obtained different dependences. In our case this dependence $\Delta E_g(t)$ also can be approximate with stretch exponential. On the other hand, the dependences of the optical band gap ΔE_g and refractive index n versus annealed temperature T_{ann}, up to T_{ann}=100 °C are almost linearly (Fig.5). For amorphous $As_{45}S_{15}Se_{40}$ thin films these coefficients, approximated from the dashed lines in Fig.5 took the values; $\Delta E_g/\Delta T_{ann}$=-5.8·10^{-4} eV/°C, and $\Delta n/\Delta T_{ann}$=-9.2·10^{-4} 1/°C, respectively.

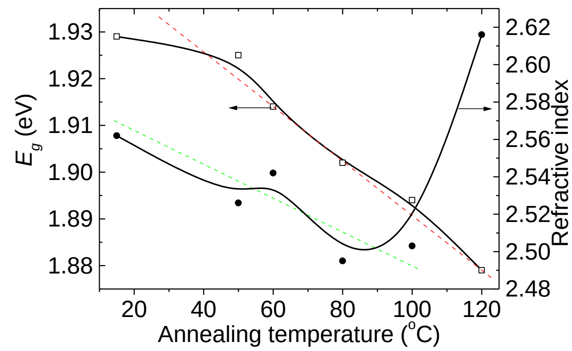

Fig.5. The dependence of the optical band gap E_g and refractive index n versus the annealing temperature T_{ann} for amorphous $As_{45}S_{15}Se_{40}$ thin films.

The relaxation of the relative optical transmission for some amorphous $As_{45}S_{15}Se_{40}$ thin film thin films in the co-ordinates $T(t)/T(0)$ vs t is shown in Fig.6 when excited with He-Ne laser λ=630 nm (1) and with λ=543 nm (2).

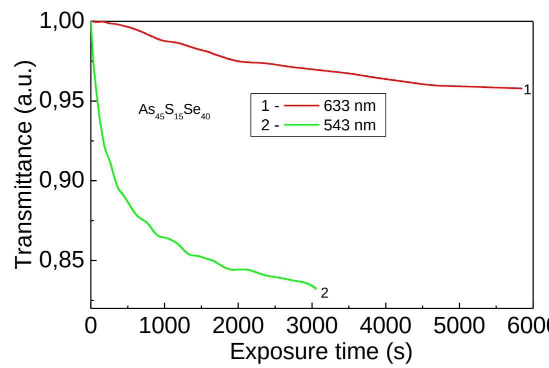

Fig.6. The relaxation of the relative optical transmission for amorphous $As_{45}S_{15}Se_{40}$ thin films in the co-ordinates $T(t)/T(0)$ vs t when excited with He-Ne laser λ=630 nm (1) and with λ=543 nm (2).

These dependences describe the excess of absorbance induced by light absorption during the time 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

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obtain a unified basis for comparison of the transmission relaxation $T(t)/T(0)$ curves we used so called stretched exponential presentation for the relaxation curves in the form:

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

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 fitting of the experimental points. The high photoinduced changes of the refractive index Δn=0.1÷0.5 in amorphous films of chalcogenide glasses make it promising materials for holographic recording media with high density. The microholograms were recorded as result of interference of two He-Ne laser beams (λ=540 nm) with a power of W=0.75 mW. Fig.7 shows the kinetics growth of the diffraction efficiency versus recording time for amorphous $As_{45}S_{15}Se_{40}$ thin films.

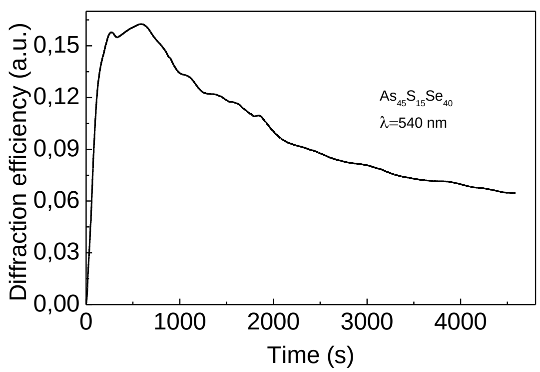

Fig.7. The kinetics growth of the diffraction efficiency versus recording time for amorphous $As_{45}S_{15}Se_{40}$ thin films.

It is observed, that the maximum diffraction efficiency for amorphous $As_{45}S_{15}Se_{40}$ is reached at about 500 s. The intensity of the first interference maximum was recorded in the transmittance mode. The data allow concluding that formation of photoinduced absorption is limited by a dispersive process with the exponent $\beta\cong$ 0.4÷0.5. In our case, for the composition $As_{45}S_{15}Se_{40}$, the value of the dispersion parameter was found β=0.42. Detailed explanations of the photodarkening effect in amorphous chalcogenides is done in [14].

4. Summary

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 investigated. It was found that for the amorphous $As_{45}S_{15}Se_{40}$ thin films the value of the refractive index n was found n=2.921 at λ=650 nm, increase with exposure time and decrease for the annealed samples. The optical band gap E_g determined from the Tauc plot E_g=1.929 eV decrease in both cases under the light exposure and heat treatment $\Delta E_g/\Delta T_{ann}$=-5.8·10^{-4} eV/^{o}C.

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