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PHOTO-INDUCED TRANSFORMATIONS IN METAL-CHALCOGENIDE COMPOSITE LAYERS

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Metal-chalcogenide composites were fabricated in a form of nanolayered structures like Bi/As_2S_3, and Au/As_2S_3, with the purpose to further develop the technology and mechanism of solid-state modification of multicomponent chalcogenide glasses and apply it for optical recording. It was shown, that the efficient changes of optical parameters (transmission, refraction) could be realized in Bi-containing structures due to the interdiffusion activated by the focused He-Ne laser irradiation and formation of multicomponent glass with Bi_2S_3 structural elements up to the phase separation.

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1. Introduction

Light- and thermo-stimulated interdiffusion effects in Se/As_2S_3-type amorphous nanolayered chalcogenide films provide new insight to the mechanism of induced structural transformations at nano-scale dimensions and promise new possibilities for optical recording as well [2]. Diffusion of silver into the chalcogenide glasses is widely investigated for optical recording including the novel experiments in $Ag/As_{30}S_{70}$ multilayers [3,4], but other metals are also interesting regarding the above-mentioned problems. As far Cu, Au-chalcogenide bi-layer structures are not so effective for the stimulated diffusion experiments and optical recording as the Ag-chalcogenide glass structures, we have investigated nanolayered structures like Au/As_2S_3, Bi/As_2S_3 with the aim to further develop the technology of photo-sensitive non-silver materials for optical recording and establish new details of the mechanism of solid-state modification of multicomponent chalcogenide glasses at nano-scale as well.

2. Experimental

Pure As_2S_3 glass and Bi, Au metals were used for the fabrication of nano-layered structures by the method of cyclic thermal vapor deposition of selected pairs (As_2S_3 and Bi, for example) from separate sources onto the Corning 7059 glass or Si wafer substrata. The evaporation temperatures for As_2S_3 were near 750 K i.e. close to the minimal necessary for obtaining separate layers with negative sensitivity (photo-darkening instead of photo-bleaching, which occurs at high-temperature evaporation [5]). The period Λ of compositionally-modulated structure was ≈15 nm with a ratio of sub-layer thickness $d_{Me}/d_{As2S3} \approx 1/12$ or 1/6 (samples type I or II) and with total thickness d of the multilayer (ML) up to 1-2 μm. ML structures were mounted on a sample-holder with regulated temperature, in a normal atmosphere, which allowed illumination of the sample by the He-Ne laser

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beam (λ=0,63 μm, *P*=20 mW focused into 0.2 mm wide spot and weakened by neutral filters) and *in situ* measurement of the optical transmission change at this wavelength. The spectra of optical transmission were measured with SF-18-type spectrophotometer. Since the low-angle X-ray diffraction measurements showed only weak first-order diffraction peak it was supposed, that the metal sub-layer and the interfaces in as-deposited ML were rather rough, and the whole structure of ML, especially at small thickness ratio of sub-layers, may be considered as clustered metal layers between As_2S_3 barriers. This peak disappears after the heat treatments, annealing that point to the interdiffusion process in ML structure. Sensitivity to the illumination was determined as the exposition (energy per square centimeter) necessary for the certain change of optical transmission at 0.63 μm and the deviations from this energy showed the possible non-linearity of the optical recording.

3. Results and discussion

Photo-bleaching effect was observed in all investigated ML structures but it was possible to measure the transmission change in a real time-scale of experiments only at rather high, $P \geq 1$ W/cm^2 intensities of illumination. The annealing of the multilayers resulted similar bleaching and optical transmission spectra showed blue-shift of the absorption edge in annealed samples, which was more efficient in the ML with thicker Bi sub-layers (see Fig. 1.a,b). Since *n.d* value grows up in a bleached region, phase recording also is possible in such ML structures.

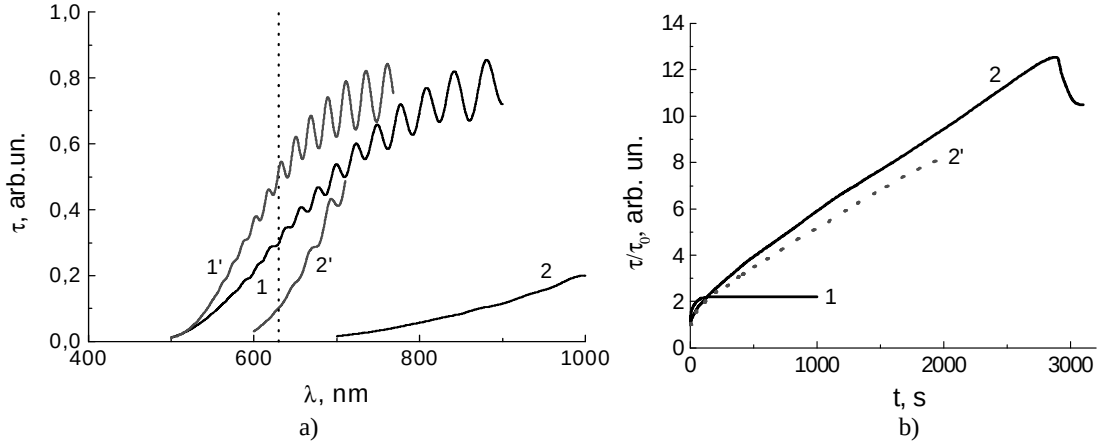

Fig. 1. a) Optical transmission of Bi/As_2S_3 multilayers. 1-before and 1' –after the annealing during 10 min at T=140 °C (samples type I, Bi to As_2S_3 thickness ratio 1:12); 2, 2'- the same for samples type II with Bi to As_2S_3 thickness ratio 1:6. b) Optical transmission change relative to the initial one induced by focused laser illumination (P= 18 W/cm^2) of sample I (curve 1) and sample II (curve 2) and the optical transmission change of the sample II at 140 °C as measured by the low-intensity, P=0.1 W/cm^2 beam at λ= 0.63 μm (curve 2').

So the efficiency of the bleaching effect correlates with initial and final transmission spectra of ML and depends on the selected wavelength for the measurement, as well as on the thickness of the metal sub-layers, which can influence the light absorption and scattering in as-deposited structures. Basically the amorphous semiconductor-type of absorption spectra is determined by the As_2S_3 matrix or later by the Bi-As_2S_3 solid solutions, which are created due to the interdiffusion of adjacent sub-layers and can reach the super-saturated state if the amount of metal is sufficient. Really, the curve of photo-bleaching in II-type samples (see curve 2 in Fig. 1a) shows a drop at long expositions, which indicates the possible phase separation due to the Bi_2S_3 phase formation, since the maximun solubility of Bi in As_2S_3 do not exceeds ~4 % like some other metal-chalcogenide glass systems [6].

As far as both initial (dark) and bleached states of the multilayers are stable (the ML do not changes optical parameters at 290 K and normal day-light illumination), archival optical recording can be performed both on Bi and Au- containing ML, but the amplitude of transmission changes as well as the change of the refractive index were less in Au/As_2S_3 samples as in Bi-containing ones. Since the technology of Bi/As_2S_3 ML was better and easier as of Au-containing ML, further experiments were performed mostly with these samples. It was established, that measurable photo-bleaching in the real-time scale of experiments occurs only at intensities $\sim P > 1$ W/cm^2 depending on the initial absorption at the recording wavelength. The rate of the transmission change grows up with intensity of illumination (see. Fig. 2a) but at the same time the deviations from the linear dependence of the exposition on the intensity for the same optical density (transmission at the given wavelength) occur (see. Fig. 2b).

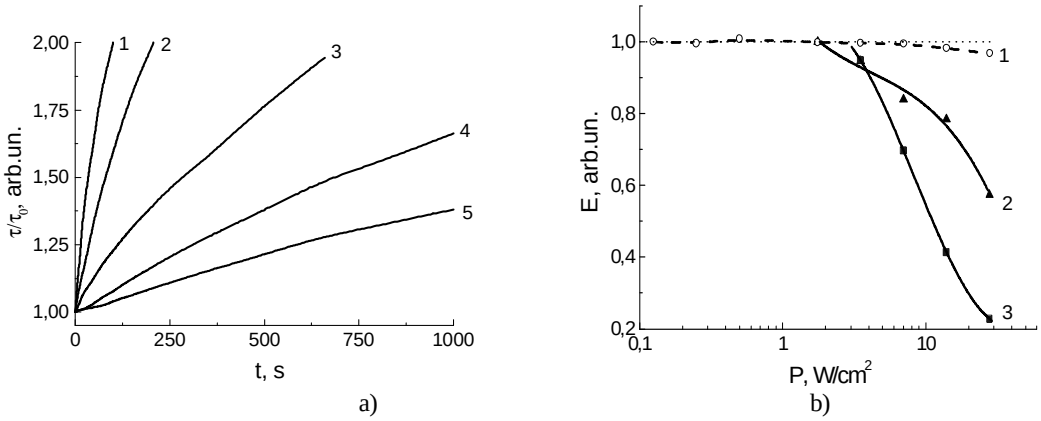

Fig. 2. a) The change of optical transmission in type-II ML at different illumination intensities *P*: 1- 28 W/cm^2, 2- 14 W/cm^2, 3- 7 W/cm^2, 4 -3.5 W/cm^2, 5- 1.75 W/cm^2. b) The dependence of exposition on the recording intensity for different ML: 1 – a - Se/As_2S_3, 2 – Bi/As_2S_3, 3–Au/As_2S_3.

Comparing the similar data for a-Se/As_2S_3 multilayer (curve 1 in Fig. 2b) with these obtained for Bi- or Au-containing ML, one can see, that there is no threshold for photo-bleaching in Se-containing ML and only a small non-linearity appears at high intensities of illumination. The difference consists in the mechanism of diffusion stimulation: pure light-stimulated change of the diffusion conditions occurs in a-Se/As_2S_3 ML [1] while thermal effects, heating of the sample by the focused laser beam occur in the Me-containing ones, like it was established also for SeTe/AsSe-type ML [7]. This conclusion was supported by the thermally stimulated interdiffusion measurements, i.e from the time dependences of transmission at the given temperatures (curves like 3 in Fig. 1b) the *D(T)* dependence was analyzed. Taking into account the temperature dependence of the diffusion coefficient *D* and the correlation between *D* and the time *t* of intermixing of two adjacent nanometer-thick layers (in our case *t* is the time necessary for 50% change of transmission at λ=0.63 μm, similarly as it was done in [1]), the E_a activation energy of interdiffusion can be determined from the dependence $t \sim exp\ (E_a / kT)$ (see Fig. 3).

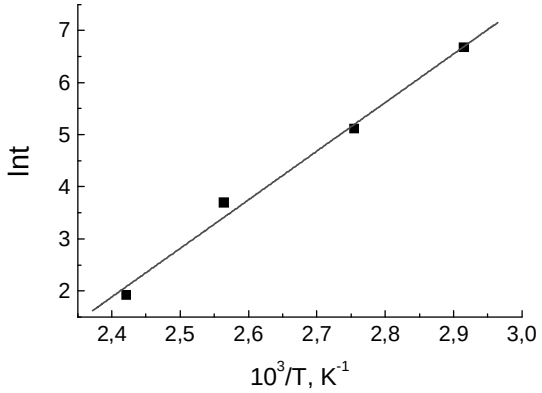

Fig. 3. Temperature dependence of the intermixing time in Bi/As_2S_3 ML. The line is guide for eyes.

The estimated value of E_a was 0.8 eV for Bi diffusion into As_2S_3 and similar data was obtained for Au/As_2S_3 system. So, rather large range of amplitude contrast and smooth dependence of this contrast on exposition can be realised in investigated metal-chalcogenide composites within the range of metal solubility in the As_2S_3 matrix. This process is limited from one side by the amount of Bi available and by the possible formation of Bi_2S_3 phase in Bi-As_2S_3 system from other side, which can cause darkening due to the light scattering in a heterogeneous system and small band-gap of Bi_2S_3. The details of phase separation process and nano-size cluster formation need further investigations.

4. Conclusions

Metal-chalcogenide glass metastable nanolayered composites like Bi/As_2S_3, and Au/As_2S_3 can be fabricated by the method of cyclic thermal evaporation in vacuum and used for optical recording in a visible spectral range by focused laser beam. Thermally stimulated interdiffusion is the basic effect of this type of recording. The resulting optical relief depends on the type of metal, initial thickness ratio of the metal and chalcogenide (matrix) sub-layers and on the solubility of the metal in this matrix.

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