Giant photoinduced effects in films from the Ge_2S_3-AsS_3 system

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The photo- and thermoinduced changes in the optical band gap (E_g) and thickness (d) of films from the Ge_2S_3-AsS_3 system as well as their dependence on the decrease of the film thickness are studied. It is found that the irreversible photobleaching (PB), which reaches giant values up to ~27% accompanied with photoexpansion ~11% in 600 nm films, do not disappear at the decrease of d down to 95-100 nm. The values of the reversible photodarkening ($\Delta E_g \approx 220$ meV in some compositions) depend on the annealing temperature (T_{ann}). The reversible photodarkening decreases with decreasing T_{ann} and a conversion into reversible PB is observed at low T_{ann}. The appearance only of reversible PB in ~100 nm films from the studied system after annealing up to the highest T_{ann} is discussed. Possibilities for recording of holographic gratings are shown.

1. Introduction

Photoinduced effects in chalcogenide films are still a matter of interest especially their changes in the optical parameters: refractive index, absorption coefficient and optical band gap, as well as in the thickness. Recently, efforts to obtain the maximal magnitude of the photoinduced (PI) effects in amorphous thin films of binary and ternary chalcogenides exist. Giant reversible thickness increase, photo-expansion (PE), about 5% in As_2S_3 [1], as well as giant reversible red absorption edge shift, photodarkening (PD), in some Ge-As-S ($Ge_{16}As_{26}S_{58}$) films [2] have been reached. Our previous studies have shown [3] that high PI changes can be obtained in some of the composition from Ge_2S_3-As_2S_3 system, composed from two components one of which is non-stoichiometric. Lately, new results have been obtained for the Ge_2S_3-AsS_3 system [4,5] where the reversible PD ($\Delta E_g = 220$ meV) is accepted as "giant" in accordance with Ref. 2. However, it is more remarkable that the irreversible PI changes have exceeded the greatest known up to now values, for example: PE ~11% and an increase in the optical band gap, photo-bleaching (PB), about 27%. The results depend not only on the irradiation (wavelength λ, intensity, exposure) but also on the film thickness d (connected with the penetration depth of the irradiation, as well as on structure factors in the very thin films). It was accepted that the PD disappears at decreasing film thicknesses down to 50 nm [6]. As can be seen in Ref. 5 the irreversible PI effects do not decrease down to 600 nm. Because of the extended interest in the nano-sized films for practical uses, in this paper we have studied the thickness dependence of both reversible and irreversible PI effects. The dependence of the PD on the annealing temperature is established, as well as the appearance of reversible PB, well expressed with decreasing the film thickness. In films with $d \approx 100$ nm the irreversible PB does not disappear and the reversible PI effect is only PB. Some possibilities for optical recording are shown.

2. Experimental

Films with thickness 0.1–1.5 μm were prepared by vacuum thermal evaporation with a rate 6-8 nm/sec from the previously synthesized $Ge_{32}As_5S_{63}$ and $Ge_{30.8}As_{5.7}S_{63.5}$ glasses. The thickness was controlled by quartz oscillator MIKI-FFV. The compositions have been chosen because they shown the highest, and nearly the same PI effects [4,5]. The composition of the thick films (>1 μm) was checked by electron microprobe X-ray analysis (Joel JSM 35 CF) and it differs from the respective glass composition within the accuracy of the method (± 1.5 at. %).

The films were exposed with a high pressure Hg lamp (500 W) through an IR cut off filter for 45 min (or up to 180 min in fresh state). The power density was ~160 mW/cm^2. The annealing was performed in Ar atmosphere for 45 min.

The optical transmission of the films was measured in the region 0.3-2.5 μm using spectrophotometers Specord UV-VIS and Specord NIR, with ±0.1 % accuracy. The optical parameters (n, α) and the thickness d of the films with thickness more than 600 nm were determined by the well-known method of Swanepoel. The values of the optical band gap E_g were obtained by the Tauc plot.

Holographic recording of transmission diffraction gratings is performed. The conventional set-up includes an Ar-ion laser, acting at 488 nm, beam-splitter and mirrors, providing interference pattern with pitch of 1 μm. He-Ne

laser is applied simultaneously to monitor the real-time kinetics of the recording.

3. Results

The values of the irreversible photo- and thermobleaching, parallel with the accompanying changes in film thickness of a thick film ($d \approx 1.5$ µm) evaporated from $Ge_{32}As_5S_{63}$ glass are shown in Fig 1. It can be seen that the high PB ~16.5% is accompanied with PE ~7.3%. The further thermo-bleaching (TB) after annealing procedure at 330 °C for 45 min does not induce thermoexpansion; moreover a thermocontraction (TC) is well expressed. The value of reversible PD reaches 8.5%. With decreasing the film thickness to ~900 nm we find that the annealing after illumination of fresh films hardly leads to additional bleaching. In thinner films ($d \approx 600$ nm) a low thermodarkening effect accompanied with TC can be seen, besides the higher PB (~26%) and PE (~7.7%) (Fig. 2). A decrease of the PD was also observed [5]. To clarify the role of the annealing on the magnitude of the reversible PD, experiments with samples with varying thicknesses have been made.

An increase of the magnitude of the reversible PD with increasing the annealing temperature T_{ann} up to 350 – 400°C for samples from both
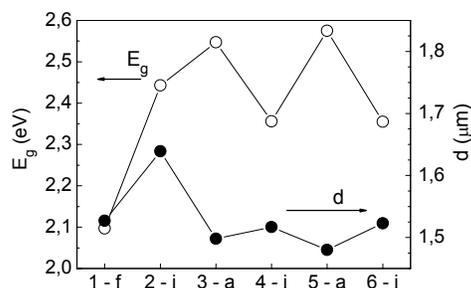
compositions under study is shown in Fig. 3. T_{ann} are more than 20° lower than T_g of the glasses. Here the most interesting result is an appearance of reversible PB after annealing at too low temperature (190°C) for film with $d \approx$ 900 nm (curve 1). The data given for samples with $d \approx 600$ nm show that PB can be seen even after annealing at $T_{ann} = 230°C$. The temperature for the transition from reversible PB to reversible PD as expected is ~260°C. The data for the thinnest films (~100 nm) display the result that in the nanosized films the PD effect is replaced with reversible PB. This result is illustrated with the transmission curves of $Ge_{32}As_5S_{63}$ film ($d \approx 100$ nm) in Fig. 4. After illumination of the fresh films high irreversible PB can be seen (curve 2), but the subsequent annealing (350°C) leads to red shift, TD (curve 3). The expected reversible PD of the well-annealed films is replaced with low reversible PB effect (curve 4).

Fig. 3. The PI edge shift of the transmission curves, $\Delta\lambda = \lambda_i - \lambda_a$ at T = 20%, vs. the annealing temperature for samples with $d \approx 900$ nm (1), $d \approx 600$ nm (2) and $d \approx 100$ nm (3). Some data for $-\Delta E_g$ (right axis) for the samples with $d \approx 900$ nm are also given.

Fig. 1. Optical band gap $\mathbf{E_g}$ and thickness $\mathbf{d}$ of a film from $Ge_{32}As_5S_{63}$ glass in different states: f – fresh (as-evaporated), a – annealed, i – illuminated for 90 min (2-i) or 45 min (4-i ,6-i).

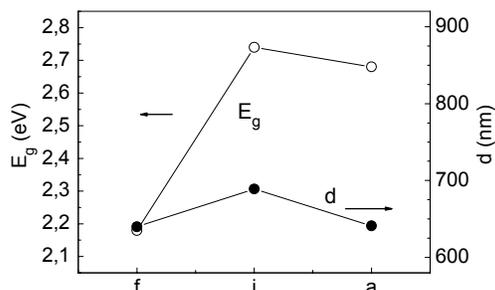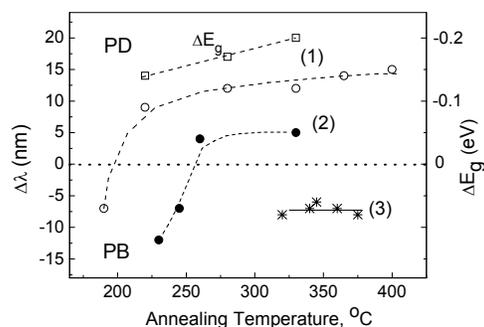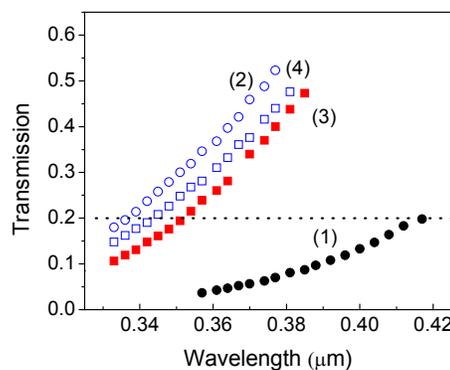*Fig. 4. Transmission curves of the thinnest film from $Ge_{32}As_5S_{63}$ glass in different states: (1) – fresh, (2) – illuminated., (3) – annealed., (4) – illuminated. after annealing.*

Fig. 2. The $\mathbf{E_g}$ and $\mathbf{d}$ values of a film ($d \approx 600$ nm) from $Ge_{30.8}As_{5.7}S_{63.5}$ glass in fresh, illuminated (180 min) and annealed states.

The examined Ge_2S_3-AsS_3 films are tested for holographic recording. In order to determine the proper laser wavelength, where the material possesses higher absorption, the spectral transmission in the region 300-900 nm is measured. The observed interference fringes at λ > 500 nm are caused by the multiple reflections inside the

material in consequence of its high refractive index ($n >$ 2). The transmission spectra of films (~900 nm) show that the Ar-ion laser can be adjusted at 488 nm. The spatial frequency of the interference pattern created by conventional transmission set-up is 1000 lines/mm (corresponding to 1 μm pitch). The laser intensity is 10 mW/cm^2. Diffraction gratings are recorded in layers with thickness 900, 600 and 95 nm. The diffraction efficiency kinetic is shown in fig. 5.
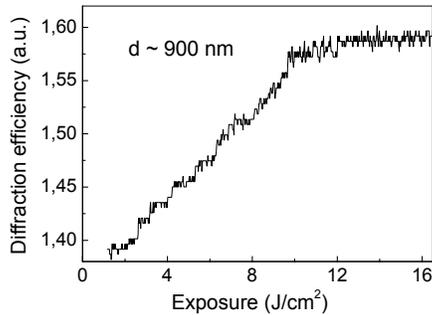

Fig. 5. Diffraction efficiency kinetics of Ge$_{30.8}$As$_{5.7}$S$_{63.5}$ film

The obtained diffraction efficiency value in the 900 nm thick Ge-As-S films is ~1%, which is relatively low. In the samples with thicknesses 600 and 100 nm the diffraction efficiency is lower than that in Fig. 5. It should be taken into account that this is the first step in the holographic investigations of films from Ge$_2$S$_3$-AsS$_3$ systems. At the same time, the realization of recording in thin layers (~95 nm) is a promising result for further investigations.

4. Discussion

The extremely high values of the irreversible PI changes of the optical band gap, the photo-bleaching, and of the film thickness, the photo-expansion, are obviously of great interest not only for practical uses but also for elucidation of their origin.

It is well known that between the *reversible* PD and the accompanying PE in As$_2$S$_3$ there is no one-to-one correspondence, established for example in their time evolution [1,7,8]. This leads to the conclusion that their origin is not the same and is still a matter of interest [8]. At first time we show here that the origin of the *irreversible* PB and the accompanying PE should be also not the same.

In the films from the studied system a correlation between the course of the *reversible* changes of the optical parameter E_g and the volume changes can be seen – the decrease in E_g (PD) is accompanied with increase of d (PE) as can be seen in Fig. 1. However the correlation is disturbed in the *irreversible* case – the giant PE accompanies the giant PB and usually the further increase in E_g at subsequent annealing is not attended with increase in the volume (TB is accompanied by TC). It can be pointed that in some preliminary studies with illumination of the fresh film in vacuum the PB has nearly the same

high value, but it is not accompanied with high PE. Contrary, in some cases d slightly decreases. So, it could be concluded that the origin of the *irreversible* PB and PE differ and the *irreversible* PE is connected with the influence of the oxygen. (Independent on the problems with the nature of the effect, for practical uses the magnitudes of PB and PE in air are more interesting).

We have shown that in illuminated (~600 nm) fresh films the annealing does not increase the bleaching effect (Fig. 2). In films with thicknesses around 900 and 600 nm the reversible PD depends on the annealing temperature, more over PD transforms in PB if the T_{ann} values are too low (Fig. 3). It is remarkable that the nanosized films (~100 nm) show only reversible PB after annealing to the optimally high T_{ann}. This fact is in accordance with our result published in 1985 [9]. After annealing to 190°C reversible bleaching appears in Ge$_x$As$_{40-x}$S$_{60}$ films (x = 25) with d ~90 nm. Here we show that this reversible PB appears not only by insufficient annealing, because we anneal up to very high temperatures close to which damaging of the layers begins.

The reason for the obtained reversible PB is not clear. Our illumination source has rather high photon flux in the blue and UV spectral region. In accordance with Ref. 10 considerable number of photons is absorbed within a small volume and the probability for cooperative two-photon processes, and consequently for structural changes, increases. This could be connected with the fact that the irreversible PB is higher than the TB [5]. But taking into account that the reversible PB is dominant in thin films it can be supposed that the PB is governed by processes mainly on the surfaces, which in the thinnest films suppress the processes in the volume that lead to PD. This will be discussed in a forthcoming paper. Here we will only point that the high irreversible PB as well as the reversible PB in the nanofilms (Fig. 4) are promising and suitable to be test for some optical applications.

5. Conclusion

The comparison of the giant irreversible photobleaching and photoexpansion leads to the conclusion that the origin of the PB and the PE in the as-evaporated films from the Ge$_2$S$_3$-AsS$_3$ system is not the same. The dependence of the reversible PI effect on the annealing temperature shows that the PD not only decreases with decreasing of the annealing temperature, but at low T_{ann} the PD converts into PB effect. With decreasing film thicknesses below ~900 nm the temperature of the conversion increases and in nanosized films (95 – 100 nm) the PD effect is converted in reversible photobleaching also after annealing at sufficient high temperatures. For the first time the irreversible PI effects in Ge-As-S films have been used for recording of holographic gratings. It is promising that films with thickness ~100 nm can be used for optical recording.

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