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Photoinduced changes in sulphur rich Ge-As-S thin films♣

D. ARSOVA*, E. VATEVA, V. PAMUKCHIEVA
Institute of Solid State Physics, Bulgarian Academy of Sciences,
72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria.

The irreversible and reversible photoinduced (PI) changes in thin films of $Ge_{11.2}As_{18}S_{70.8}$ glass (Z = 2.4) have been studied. Glasses with compositions close to that of the Ge_2S_3-AsS_3 system can be regarded as self-organized. The changes in the thickness, as well as in the refractive index and optical band gap energy, have been evaluated for films thicker than 0.5 μm, after photo- and thermal-treatments. A decrease in the magnitude of the irreversible photobleaching and reversible photodarkening has been obtained with decreasing film thickness. For nanosized films (90-100 nm) low-magnitude photobleaching is established, while photodarkening nearly disappears. The peculiarities of the reversible PI effects at these thicknesses are related to the self-organised structure. A comparison with results from our previous studies has revealed that for higher PI effects and conversion to reversible photobleaching in nanosized films, stressed-rigid Ge_2S_3-AsS_3 compositions are favourable.

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1. Introduction

Recently, amorphous chalcogenides from the Ge-As-S system have been intensively studied as materials interesting for various applications, as well as for richness in the network arrangement. For this reason, a series of chemical compositions with various network connectivities, or in a wide range of the mean coordination number *(Z)*, have been examined. Theoretical considerations from 1979 to 2000 [1,2] have identified the existence of three phases of network glasses as a function of Z, namely floppy, intermediate and stressed rigid, as has been pointed out recently [3]. The intermediate phases are centred on Z = 2.4, and consist of rigid unstressed structures. They are thought to be stable and self-organized structures. Three phases have been distinguished experimentally in various binary and ternary systems [3,4], including the Ge-As-S one. The structure of Ge-As-S glasses is formed by bridging tetrahedral and pyramidal units and various entities, some of which could be incorporated in or separated from the backbone.

Nowadays, our interests are concentrated on the photoinduced effects in thin films from Ge_2S_3-AsS_3 glasses with a wide range of network arrangements. For some compositions from this system (with Z=2.6-2.7), we have found a remarkable irreversible photoinduced (PI) increase in the optical band gap energy (photobleaching, PB), accompanied by an increase in thickness (photo-expansion) [5,6]. The values of these so-called "giant" PI changes exceed the greatest values known until now [7]. The reversible photodarkening (PD) is highly evident too. Upon decreasing the film thickness to nanometric sizes new effect has been obtained – conversion of the PD to reversible PB [8].

Because of the lack of detailed studies on sulphur rich compositions with $Z \approx 2.4$ from the Ge_2S_3-AsS_3 system, in the present work the irreversible and reversible photoinduced changes in films of $Ge_{11.2}As_{18}S_{70.8}$ glass (Z = 2.4) have been studied. The $Ge_{11.2}As_{18}S_{70.8}$ glass can be regarded as self-organized, since the lowest heat capacity jump ΔC_p at T_g in DSC measurements has been found for this glass composition [9]. The changes in the thickness *(d)*, as well as in the refractive index *(n)* and optical band gap (E_g), have been evaluated for films with d > 0.5 μm. A decrease in the magnitude of both PI effects, the irreversible PB and reversible PD, has been obtained with decreasing film thickness. For nanosized films (90-100 nm), low PB is established, while PD nearly disappears. No conversion to PB has been obtained. The absence of reversible PB has been discussed in comparison with previously studied nanosized films from stressed-rigid glasses from the same Ge_2S_3-AsS_3 system.

2. Experimental

Films with thicknesses of about 0.1 to 0.7 μm were prepared by vacuum thermal evaporation at 2-3x10^{-3} Pa with a rate ~5 nm/sec, from the previously synthesized $Ge_{11.2}As_{18}S_{70.8}$ glass (Z = 2.4). The thinnest films were

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♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008 evaporated with a rate of ~10 nm/sec. The thickness was controlled by a quartz oscillator MIKI-FFV during the evaporation procedure, and was measured by a Tally step profile-meter. The composition of the films was checked by electron microprobe *X*-ray analysis (Joel JSM 35 CF). It depends on the film thickness and evaporation rate, and differs from the respective glass composition (ΔZ is about ± 1%).

The films were exposed in air to a high pressure Hg lamp (500 W) through an IR cut off filter, for 45 min. The annealing was done in an Ar atmosphere for 45 min at the T_g of the parent glass (~ 210° C).

The transmission $T(\lambda)$ in the region 0.3-2.5 μm was measured using Specord UV-VIS and Specord NIR spectrophotometers, with ±0.1 % accuracy. The optical parameters and the thicknesses of the films with *d* ~700 nm were determined by the well-known method of Swanepoel. The values of the optical band gap energy were obtained from Tauc plots. For the thinnest films the changes in the wavelength values at T = 20% (measured with an accuracy of ±1 nm) were accepted as a characteristic of the changes in E_g after various treatments.

3. Results

In Fig. 1, typical transmission spectra $T(\lambda)$ are shown for a Ge-As-S film with Z = 2.43 and $d \approx$ 700 nm, in the fresh (1), illuminated (2), annealed (3) and post-illuminated (4) states. A "blue" shift of the spectrum is seen after illumination. After annealing, an additional shift to lower wavelengths is also observed. Both effects reflect an irreversible increase in the optical band gap (photo- and thermal-bleaching). The values of the photo- and thermal-bleaching (TB) are ~5.5% and ~11%, respectively. Curve (4) represents a "red" shift of $T(\lambda)$ (photodarkening), accepted as reversible (see curve (1) in Fig. 4 below). The value of PD is -6%.

The spectral dependences $n(\lambda)$ for the same "thick" films are well fitted by the Wemple-DiDomenico model [10]. In Fig. 2, the curves for *n* of a representative sample after various treatments are presented in appropriate coordinates. The determined values of the thickness, the refractive index (n_0 *at* $\lambda \rightarrow \infty$) and the optical band gap for different states are summarised in Table 1.

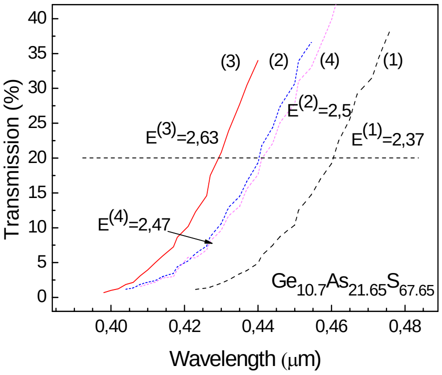

Fig. 1. Transmission curves of the film with d ~ 700 nm in different states: (1) fresh, (2) ill. (3) ann., (4) ill. after annealing. The calculated values of the optical band gap in eV are as indicated.

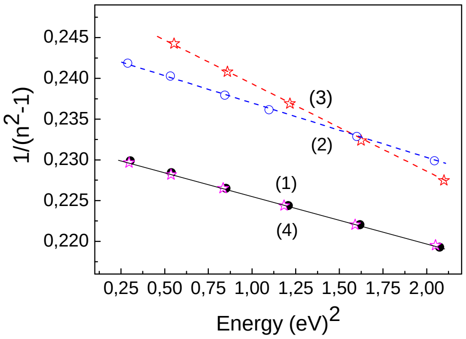

Fig. 2. Dispersion of the refractive index (n) according to the Wemple-DiDomenico model for the $Ge_{10.7}As_{21.65}S_{67.65}$ *film (d* ≈ 700 nm*): (1) fresh, (2) ill., (3) ann., (4) ill. after annealing.*

The illumination of the fresh film leads to a small increase in the thickness (~3%), accompanied by a small decrease in *n* (~2%), see Table 1 and Fig. 2. The subsequent annealing leads to an additional decrease in *n* and some recovery of the thickness. Some of these results are in good agreement with those published in [11] for thicker Ge-As-S films (~1.3 μm) with *Z* = 2.41.

Table 1. Values of the thickness, optical band gap, refractive index and Wemple-DiDomenico parameters E_d *and* E_w*.*

Ge-As-S *Z*=2.43	d, μm	E_g, eV	n_0 $\lambda \rightarrow \infty$	E_d, eV	E_w, eV
(1) Fresh	0.727	2.37	2.31	27.1	6.3
(2) Ill.	0.752	2.50	2.26	24.3	5.9
(3) Ann.	0.738	2.63	2.24	19.3	4.8
(4) Ill.	0.733	2.47	2.31	27.4	6.3

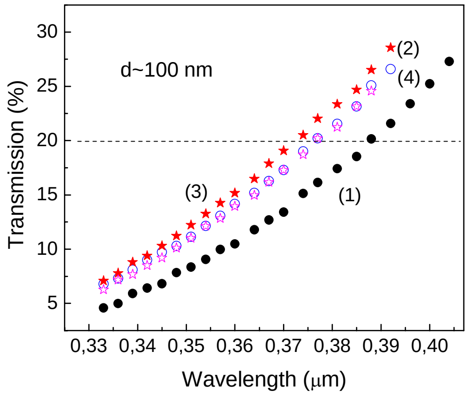

Fig. 3. Transmission curves of the thinnest film in different states: (1, ●) fresh, (2, o) ill., (3,★) ann. at 215°C,
(4, ☆) ill. after annealing.

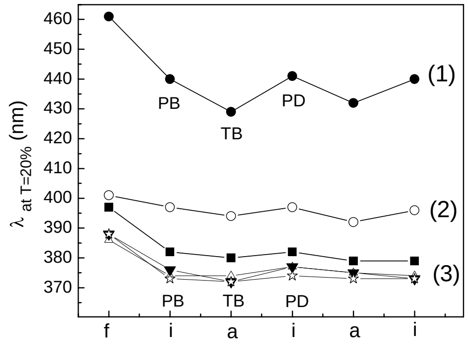

Fig. 4. Photo- and thermally-induced changes in films of $Ge_{11.2}As_{18}S_{70.8}$ glass with different thicknesses in the illuminated (i) and annealed (a) states.

Upon decreasing the film thickness to 200 nm, we observed a decrease in the irreversible PB and a weak additional TB effect. A decrease of the PD was also detected. A further decrease in the thickness down to ~100 nm did not change the character of the photo- and thermally-induced effects. These results are illustrated in Fig. 3 for a nanosized Ge-As-S film. The transmission curves present irreversible PB(curve 2), and a small additional TB (curve 3). The well annealed film shows a “red” shift of 3-5 nm (PD). The subsequent annealing-illumination does not produce a noticeable PD effect. This can be seen in Fig. 4, where repeated photo- and thermally-induced effects are shown for films with decreasing thicknesses: 700 nm (curve 1), 200 nm (curve 2) and 90-100 nm (curves 3).

4. Discussion

In the investigated Ge-As-S system around $Z = 2.4$, intermediate stress-free phases are expected, where the self-organisation of the structure dominates. We assume that for S-rich ternary glassy compositions, the S content is sufficient to form the main structural $As(S_{1/2})_3$ and $Ge(S_{1/2})_4$ units of the Ge-As-S system. For the investigated composition, as for the results in [12], numbers of S atoms can enter the network, forming a flexible connection as $(S_{1/2})_3Ge{-}(S{-}S)_n{-}As(S_{1/2})_2$. It could be supposed that the fresh films under study, prepared at relatively high-evaporation rates, contain structural units like those in the parent bulk glasses. Moreover, a high density of defective units with homopolar (Ge-Ge, As-As) bonds could exist, indicating an increase in the degree of disorder.

Using the most probable and energetically favourable structural units (SU), the composition of the film with $d \approx 700$ nm can be presented as:

$$Ge_{10.7}As_{21.65}S_{67.65} \rightarrow 10.7GeS_2 + 10.5As_2S_3 + 14.75S$$

The Ge- and As- SU are connected by the extra content of S atoms (S_n chains predominantly), and hence a compact energetically stable and more flexible network than that of the stressed rigid glasses is developed. It can be also supposed that S atoms form $S{=}As(S_{1/2})_3$ units in the self-organized structure, similar to the quasi-tetrahedral units in the backbone of Ge-As-Se [4].

It is known that illumination of the fresh films causes photodarkening in As_2S_3 and photo-bleaching in GeS_2 films. An equal amount of As_2S_3 and GeS_2 building units are presented in the studied Ge-As-S samples, in accordance with the above consideration. Some competition between PD and PB processes could take place. As a result, the irreversible PB ~5.5% is much lower than the obtained irreversible PB ~27% in films with Z around 2.7, where the high free volumes additionally facilitate the PI effects [5-8]. The obtained low photoexpansion (~3%) in illuminated $Ge_{10.7}As_{21.65}S_{67.65}$ films may be due to the same opposed processes - photoexpansion (in Ge-S) and photocontraction (in the As-S based parts of the network). The observed TB effect is well expressed and may be attributed to the lower effectiveness of photo- than of thermally-induced ordering in films from self-organized glasses. In thin films with $Z \sim 2.7$, where high stress and nanophase separation of some entities could exist, the TB is lower than the PB [6,8]. In Fig. 4, the photo- and thermally-induced changes, measured by changes in λ at $T = 20\%$, are compared for the studied films with decreasing thicknesses. We would like to mention that the low irreversible PB shown in curve (2) must be related not only to the thickness decrease ($d \approx 200$ nm) but also to the lower Ge content (and lower amount of GeS_2 entities). The detected composition of these films ($Ge_{7.9}As_{21.2}S_{70.9}$, $Z = 2.37$) differs strongly from that in curve (1). With a further decrease of the film thickness down to ~90-100 nm (Fig. 4, curves 3) the irreversible PB is better expressed. Because of the high evaporation rate (~10 nm/s) the composition of the thinnest samples is expected to be close to that of the parent glass ($Z = 2.4$). The well-annealed nanosized films show PD of 3-5 nm. This PD effect tends to disappear after subsequent annealing-illumination (Fig. 4, curves 3).

The interesting result in present study is the absence of reversible PB at $d \approx 100$ nm. Reversible PB has been found in films with the same thickness with $Z = 2.6\text{-}2.7$ from the same system [8]. In the thinnest films, the photo-induced process is governed mainly by the disordered surfaces (where photo-oxidation appears, besides PI ordering, especially when high concentrations of Ge-Ge bonds exist), which suppress the processes leading to PD. For films with $Z \approx 2.4$, nanophase separated units rich in Ge-Ge bonds are not expected, and the structure of well-annealed films in the volume as well as partly in the surface is close to the respective glass structure. As a result, PD could proceed in the volume and near surface regions, and the PB can not entirely overcome the PD. So, at $d \approx 100$ nm an effective reduction of the PB effect in comparison with that in the films from stress-rigid glasses takes place and conversion to reversible PB can not appear.

5. Conclusions

New results on photo- and thermally-induced changes in films from the self-organized $Ge_{11.2}As_{18}S_{70.8}$ glass, depending on the film thickness, have been presented. In films with $d \sim 700$ nm, an irreversible photo-induced increase in the optical band gap and the thickness was obtained, with a magnitude lower than the respective values for films from stress-rigid glasses from the same Ge_2S_3-AsS_3 system. With decreasing film thickness, the irreversible effects decreased. It was proposed that the competition between opposed PI effects in the As-S and Ge-S based parts of the compact and stable network contributes to the lowering of the PI irreversible changes. The reversible photo-darkening decreased with thickness down to 100 nm, and in nanosized films it nearly disappeared. No conversion to the reversible PB was manifested at this thickness. It is accepted that the more ordered self-organized structure prevents the full disappearance of the PD and the conversion to PB.

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[*] Corresponding author: darsova@pronto.phys.bas.bg