

PHOTOINDUCED CHANGES IN Ge-As-S THIN FILMS WITH VARIOUS NETWORK RIGIDITIES

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Photo- and thermally induced changes in the optical bandgap and thickness are investigated in thin films that belong to three lines traced through regions with different rigidities in the Ge-As-S system. The dependences of the photo- and thermally induced bleaching of the fresh films on the average coordination number, as well as of the photodarkening of the annealed films, show a global maximum in the range 2.6 - 2.7.

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1. Introduction

Photoinduced structural changes in amorphous chalcogenide films are broadly investigated more than 30 years, but their origin is still not fully understood. The renewed interest is related mainly to arising possibilities for applications (optical memories, photolithography, etc.). The photoinduced changes are due to transformations of the structure and reflect on many related properties. Since the photoinduced changes depend on the composition, it is interesting to investigate thin films from systems with large glass-forming ability and high response to the illumination. Films from the Ge-As-S system with varying compositions are suitable for these investigations.

In 1986 it has been reported on a reversible photodarkening in Ge-As-S glasses with maximal values at chemical compositions with an average coordination number $Z = 2.6$ and 2.67 [1]. Later K. Tanaka [2] has suggested that anomalies in some physical properties (including photodarkening) of the chalcogenide glasses near $Z = 2.67$ may result from a new structural phase transition involving a change of the network dimensionality. Recently, new ideas to understanding the structure of chalcogenide glasses have been put forward. Thermal properties complemented by Raman scattering measurements of binary and ternary chalcogenide glasses as a function of the mean coordination number have revealed that thermally reversing windows open between mechanically floppy and stressed-rigid phases of glasses [3]. Glass compositions in these windows define intermediate phases, which are regarded as stress-free (self-organized) phases of the disordered network. "Floppy", "intermediate" and "stress-rigid" regions in Ge-As-S system have been distinguished. [4].

For the present study compositions that belong to three lines of Ge-As-S system, traced through the mentioned above regions have been chosen. They are: line (1) - $\text{Ge}_x\text{As}_x\text{S}_{1-2x}$ (that is considered to contain "floppy", "intermediate" and "stress-rigid" glasses [4]), line (2) - $\text{Ge}_2\text{S}_3\text{-AsS}_3$, the thermal characteristics of which have been previously studied in [5], and line (3) - $\text{Ge}_2\text{S}_3\text{-As}_2\text{S}_3$ or $\text{Ge}_x\text{As}_{0.4x}\text{S}_{0.6}$ [5-8]. According to [4], both "intermediate" and "stress-rigid" compositions can exist

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among those from line (2), while compositions belonging to line (3) should all be “stress-rigid”. Photo- and thermally induced changes in the optical bandgap of thin films evaporated from Ge-As-S glasses from both lines (1) and (2) are studied for the first time. The obtained results are compared with those in [7, 8] for the $\text{Ge}_x\text{As}_{0.4-x}\text{S}_{0.6}$ films from line (3). The influence of the network rigidity of the films from different regions on the photoinduced sensibility is discussed.

2. Experimental details

Thin films from Ge-As-S glasses with compositions listed in the Table 1 were investigated. The compositions were chosen from each line (1) and (2) in order to obtain samples with an average coordination number Z lower and higher than 2.6.

Table 1. Compositions of the glasses under investigation, Z is the average coordination number, ρ [g/cm^3] - the density.

$\text{Ge}_x\text{As}_x\text{S}_{1-x}$ - line (1)			Ge_2S_3 - AsS_3 - line (2)			Ge_2S_3 - As_2S_3 - line (3)	
Composition	Z	ρ	Composition	Z	ρ	Composition	Z
$\text{Ge}_{15.4}\text{As}_{15.4}\text{S}_{69.2}$	2.46	2.81	$\text{Ge}_4\text{As}_{22.5}\text{S}_{73.5}$	2.31	2.78	$\text{Ge}_5\text{As}_{35}\text{S}_{60}$	2.45
$\text{Ge}_{20}\text{As}_{20}\text{S}_{60}$	2.60	2.96	$\text{Ge}_8\text{As}_{20}\text{S}_{72}$	2.36	2.73	$\text{Ge}_{10}\text{As}_{30}\text{S}_{60}$	2.50
$\text{Ge}_{25}\text{As}_{25}\text{S}_{50}$	2.75	3.17	$\text{Ge}_{15.4}\text{As}_{15.4}\text{S}_{69.2}$	2.46	2.81	$\text{Ge}_{14}\text{As}_{26}\text{S}_{60}$	2.54
$\text{Ge}_{30}\text{As}_{30}\text{S}_{40}$	2.90	3.40	$\text{Ge}_{26.8}\text{As}_{8.2}\text{S}_{65}$	2.62	2.81	$\text{Ge}_{24}\text{As}_{16}\text{S}_{60}$	2.64
			$\text{Ge}_{30.8}\text{As}_{5.7}\text{S}_{63.5}$	2.67	2.81	$\text{Ge}_{27}\text{As}_{13}\text{S}_{60}$	2.67
			$\text{Ge}_{32}\text{As}_5\text{S}_{63}$	2.69	2.76	$\text{Ge}_{32}\text{As}_8\text{S}_{60}$	2.72
			$\text{Ge}_{36}\text{As}_{2.5}\text{S}_{61.5}$	2.75	2.93	$\text{Ge}_{34}\text{As}_6\text{S}_{60}$	2.74
						Ge_2S_3	2.80

Films with thickness $\sim 1.5 \mu\text{m}$ were prepared by vacuum thermal evaporation from the synthesized by us glasses. The deposition rate was $\sim 8 \text{ nm}/\text{sec}$. The films were subsequently exposed and annealed. The illumination was made with a high pressure Hg lamp (500 W) for 45 min. in ambient atmosphere; the annealing - in an Ar atmosphere for 45 min. at a temperature 20° below the glass transition temperature, T_g , of the films. The values of T_g were estimated through the obtained values of the respective optical bandgap. The optical transmission of the films was measured in the region $0.3 - 2.5 \mu\text{m}$ using spectrophotometers Specord UV-VIS and Specord NIR, with 0.1 % accuracy. The absorption coefficient and the thickness were calculated by Swanepoel's method, and the optical bandgap, E_g , was obtained using a Tauc plot. The absolute error of the relative thickness changes was about 2%.

3. Results

In the present study the photo- and thermal induced changes of the optical bandgap of films from both line (1) and (2) are compared with those of films from line (3). The data for $\text{Ge}_x\text{As}_{0.4-x}\text{S}_{0.6}$ films (line 3) are taken from Ref. [8] and plotted in Figs. 1-3.

The illumination of fresh films from line (1) and line (2) leads to an increase of the optical bandgap, E_g , i.e. to photobleaching (PB). The magnitude of the obtained PB, defined by $\Delta E_g/E_g$ is displayed in Fig. 1a, where $\Delta E_g = E_{\text{ill.}} - E_{\text{fresh}}$. The PB in films from line (1) increases from $Z = 2.46$ to $Z = 2.6$ and decreases in the Z -range 2.75 - 2.9, while the PB of the films from line (2) increases strongly in the Z -range 2.31 - 2.69 and decreases from $Z = 2.69$ to $Z = 2.75$. The compositional dependence of the irreversible photoinduced changes in the optical bandgap of $\text{Ge}_x\text{As}_{0.4-x}\text{S}_{0.6}$ films (line 3) was established in [6], and studied in details in [7, 8]. For As-rich films ($x < 5$) from the line (3) low photodarkening (PD) instead of photobleaching was observed, similarly to the results reported in [9, 10]. The Z dependences of $\Delta E_g/E_g$ from all the Ge-As-S samples under investigation have a global bell-like form with a maximum in the Z -range 2.6 - 2.7 (Fig. 1a).

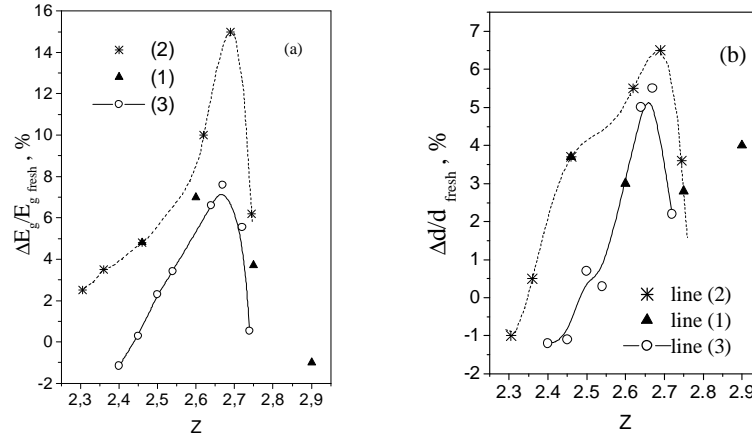


Fig. 1. Compositional dependence of the irreversible photoinduced changes in Ge-As-S films: relative changes of the bandgap, E_g , (a) and of the thickness, d , (b).

In Fig. 1b the relative change of the films thickness after first illumination is plotted in dependence on the average coordination number, Z . We have already studied the volume (thickness) changes in the $\text{Ge}_x\text{As}_{0.4-x}\text{S}_{0.6}$ films after photo- and thermal treatment [7, 8]. Large photoexpansion (PE) has been obtained around $Z = 2.67$ for the $\text{Ge}_x\text{As}_{0.4-x}\text{S}_{0.6}$ films (line 3) [8]. It is seen that the thickness of the films from line (2) increases up to 6 - 7% in the range of $Z = 2.36 - 2.69$ and then decreases to 3.5% at $Z = 2.75$. The films from line (1) manifest PE about 3 - 4% without a definite compositional dependence because of the lack of enough compositions. The films with low Ge content from lines (1) and (3) indicate absence of PE or a low photocontraction (about -1%).

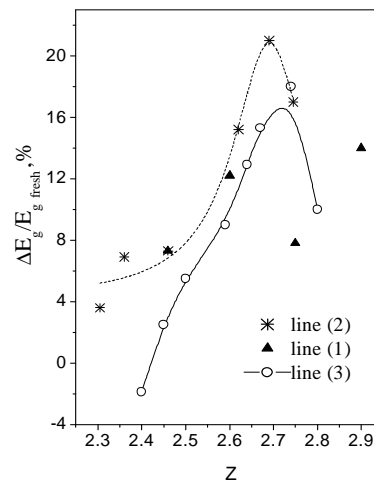


Fig. 2. Compositional dependence of the thermo-induced bandgap changes in Ge-As-S films.

$$\Delta E_g = E_{\text{ann.}} - E_{\text{fresh.}}$$

Annealing of the fresh films causes also bleaching effect. In Fig. 2 the thermoinduced bandgap changes are presented in dependence on Z . The values of the thermal bleaching ($\sim 16\%$) for the $\text{Ge}_x\text{As}_{0.4-x}\text{S}_{0.6}$ films (line 3) were twice higher than that of the photoinduced ones [8]. The films in this study were firstly illuminated and then annealed. As can be seen the films from line (2) show a strong thermal bleaching (TB) effect ($\sim 20\%$). The thermal bleaching of the films from lines (2) and (3) exhibits an asymmetric bell-like form with increasing the network connectivity (with Z). The data for the TB in the films from line (1) are scattered around 11%. It is interesting to point out that all the

investigated fresh Ge-As-S films undergo small (about 1 - 2%) negative changes in the thickness after annealing (not shown here).

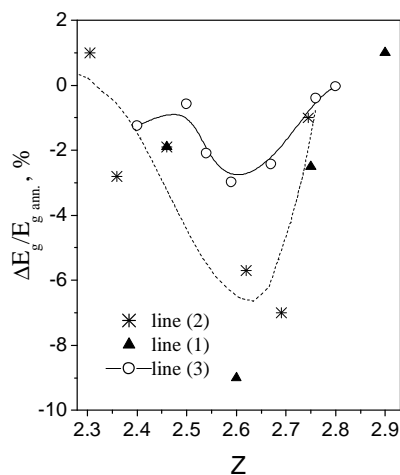


Fig. 3. Compositional dependence of the reversible photodarkening in Ge-As-S films.

$$\Delta E_g = E_{\text{ill.}} - E_{\text{ann.}}$$

The illumination of the annealed Ge-As-S films produces a decrease of the optical bandgap (photodarkening effect, PD). This PD is a reversible photoinduced effect. In Fig. 3 the Z- dependence of the reversible photodarkening in films from Ge-As-S glasses is plotted. The films with the highest and the lowest content of S have not shown PD (here the plotted changes are in the frame of the accuracy). The highest values of PD (~ 7-8 %) are obtained in the Z – range 2.6 - 2.7 (for line 2). Fig. 4 illustrates the irreversible and reversible changes in the optical bandgap of the most sensitive film of this study.

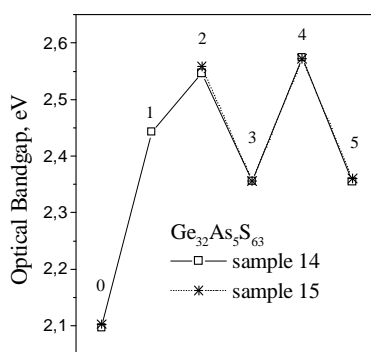


Fig. 4. Optical bandgap of two samples in 5 different states: 0 – as evaporated; 1, 3, 5 – illuminated; 2, 4 – annealed film.

4. Discussion

As it is known, the continuous floppy-to-rigid transition occurs smoothly in the property-composition dependence of glasses when the connectivity increases with their average coordination number. Around $Z = 2.4$ intermediate stress-free phases appear, where the self-organization of the structural units dominate. In the case of the investigated Ge-As-S glasses when $Z > 2.4$ the S content is insufficient to form the main structural $\text{As}(\text{S}_{1/2})_3$ and $\text{Ge}(\text{S}_{1/2})_4$ units of the respective stoichiometric compounds. With increasing of Z some additional components are possible to form simultaneously

with the main elements of the backbone. The Raman spectra of the glasses from line (3) have shown structural heterogeneity of the glassy network forming As-rich and/or Ge-rich structural units [12]. In As-rich glasses vibrations assigned to As_4S_4 have been detected, and with increasing of Ge content ($Z > 2.65$) the obtained peculiarities have been attributed to $\text{GeS}_{4-n}\text{Ge}_n$ and/or $\text{Ge}_2\text{S}_{6/2}$ ethane-like groups [12]. In Ref. [3, 4] the anomalies in some physical properties of Ge-As-S glasses have been explained with structural heterogeneity of the glassy network forming As-rich and/or Ge-rich nanophases. We assume that fresh Ge-As-S films prepared with relatively high evaporation rate contain the main structural units as in the respective bulk glasses as well as some quickly condensed fragments of a network (including defective structural units and molecules). The density of homopolar (Ge-Ge, As-As, S-S) bonds in fresh films compared to that in both well-annealed films and glasses is also higher, indicating on the high degree of disorder in them [13].

Very high photobleaching effect has been established (Fig. 1a) for fresh films from the $\text{Ge}_2\text{S}_3\text{-AsS}_3$ – line (2). The obtained PB is higher than the irreversible effect in the films from $\text{Ge}_2\text{S}_3\text{-As}_2\text{S}_3$ – line (3), regarded by us as optimal for optoelectronic applications up to now [5].

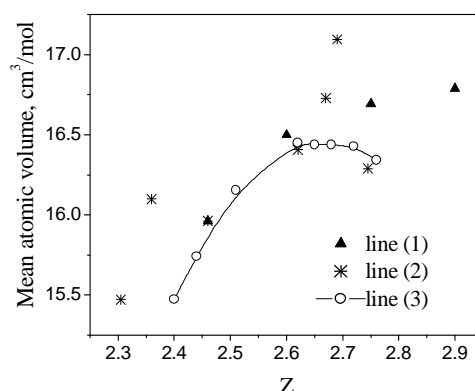


Fig. 5. Mean atomic volume of the Ge-As-S glasses.

This result is reasonable because the former system is composed from two non-stoichiometric components and the degree of disorder may be higher than the latter system. In Fig. 5 the compositional dependence of the mean atomic volume of the glasses from the three investigated lines is plotted. The values for the mean atomic volume of the $\text{Ge}_x\text{As}_{0.4-x}\text{S}_{0.6}$ glasses (line 3) are taken from [14]. The glasses from line (2) manifest the highest increase of the mean atomic volume in the range of $Z = 2.6 - 2.7$. The free volumes in the films around $Z \approx 2.67$ connected with a change of the network dimensionality may be also higher than in the case with only one non-stoichiometric component. High photoexpansion effect has been established for fresh films from the $\text{Ge}_2\text{S}_3\text{-AsS}_3$ – line (2) (Fig. 1b), too. It is worth noting that these films are evaporated from glasses that, according to [4], belong to the "intermediate" and "stressed-rigid" phases in the glass-forming region of the Ge-As-S system. Our previous DSC measurements of glasses from the $\text{Ge}_2\text{S}_3\text{-AsS}_3$ line have shown that only the composition with $Z = 2.36$ can be regarded as a real stress-free self-organized composition. The glasses with $Z = 2.31$ and $Z = 2.46$ are nearly stress-free because non-reversible effects are present in various degrees in them [11]. The films evaporated from glasses with $Z \approx 2.36$ show the lowest PB and PE (Fig 1). In glasses with $Z > 2.53$ non-reversible effects and sub- T_g endotherms are established [11] and the compositions can be accepted as stress-rigid. Giant PB and PE are found just in films from these glasses. The obtained values of the thermal bleaching of films from line (2) are higher than the photoinduced ones at Z around the maximum of the bell. They are almost the same at low Z , where stress-free phases are expected. The PD (Fig. 3) in the annealed films with low Z is also low, as can be expected for nearly self-organized glasses.

The maximal photo- and thermally induced changes are observed in the range $Z = 2.6 - 2.7$. In this region all the Ge-As-S compositions should be stress-rigid [4]. The films from glasses with $Z > 2.7$ are stress-rigid compositions, too, but their photo- and thermally induced changes are low in the

experimental conditions used in this study. In our consideration [5-8] we have explained the maximum in the photostructural changes in the $\text{Ge}_x\text{As}_{0.4-x}\text{S}_{0.6}$ films with a change of the network dimensionality. The observed in this study maximum in the range $Z = 2.6 - 2.7$ may be due to the same structural phase transition. The assumed nanophases around $Z = 2.6$ [4, 12] could facilitate the photoinduced structural transformations and structural rearrangement when the phases are layer-like arranged. For this reason the free volume becomes maximal.

The chosen compositions from the three investigated lines from the Ge-As-S system show that the photostructural transformations depend on the rigidity of the network of the parent glasses. It is evident that the magnitude of the photo- and thermally induced changes of the optical bandgap depends strongly on the chemical compositions. Giant values of the irreversible photobleaching ~15% and of the photoexpansion ~7%, as well as of the reversible photodarkening ~8%, are found in films with a coordination number 2.69 from the $\text{Ge}_2\text{S}_3\text{-AsS}_3$ system. The obtained results may be of practical interest for optoelectronic applications.

5. Conclusion

Photo- and thermally induced changes in the optical properties of Ge-As-S films from the $\text{Ge}_x\text{As}_x\text{S}_{1-2x}$, $\text{Ge}_2\text{S}_3\text{-AsS}_3$ and $\text{Ge}_2\text{S}_3\text{-As}_2\text{S}_3$ lines have been studied. The experimental results show that the photostructural transformations depend on the chemical composition and on the rigidity of the network of the parent glasses. In the frames of our experimental conditions the maximal photo- and thermally induced changes are observed in the range $Z = 2.6 - 2.7$ where the compositions are supposed to have stress-rigid phase structure. Compositions belonging to the intermediate region are less sensitive due to their self-organising ability.

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