

PHOTO- AND THERMOINDUCED CHANGES IN $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$

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The paper studies the photoinduced structural changes in the optical properties of annealed films prepared from $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ glasses. The results are discussed in terms of the compositional dependences of the density, compactness and average atomic volume of the parent glasses. The composition of the system which is most suitable for media for optical recording of information is identified.

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1. Introduction

Photo- and thermo-induced changes in the optical properties of amorphous chalcogenide thin films are the result of structural changes in these materials. These changes are of scientific interest, and are also the reason for the use of such materials as media for optical recording and processing of information [1, 2]. Under illumination with bandgap light, there are substantial changes of the optical, photoelectrical, physicochemical and other properties. Similar changes are observed after annealing of the amorphous films at temperatures close to the glass transition temperature, T_g . Investigation of the photo- and thermo-induced processes in multicomponent thin films contributes to the knowledge on their structure.

The goal of this paper is to study reversible changes in the optical properties of annealed $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ films, enabling the choice of the most suitable composition for the optical recording of information.

2. Experimental details

$\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ ($x = 0; 0.27; 0.4; 0.5; 0.75; 1.66; 4.5; 5.0$) films were prepared from powdered bulk glasses through thermal evaporation in a vacuum of approximately 10^{-3} Pa. The evaporation was performed onto glass substrates at a constant speed. The thicknesses of the films, which was between 0.6 and 1.5 μm , was controlled during evaporation. The films were annealed in an Ar atmosphere for 45 min at temperatures T_a about 20K below the glass transition temperatures, T_g , of the respective parent glasses. Then, the films were cooled to room temperature in an Ar atmosphere. With this regime, there was no oxidization of the studied samples. The annealed films were illuminated with bandgap light at a temperature of 300K, using a HBO 500 Mercury lamp.

The transmission spectra of the films were measured in the range 0.3 to 2.5 μm , using SPECORD 61 NIR and UV VIS spectrophotometers (Carl Zeiss, Jena). The thicknesses, d , the

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spectral dependences of the refractive index, $n = n(\lambda)$, and of the absorption coefficient, $\alpha = \alpha(\lambda)$, of films with different compositions were determined using the Swanepoel method [3]. The optical bandgap E_g^0 was determined according to the Tauc relationship $(\alpha h\nu)^{1/2} = f(h\nu)$. The macroscopic densities, ρ , of the parent glasses were measured hydrostatically.

3. Results

The compositional dependences of the reversible changes of the optical bandgap, E_g^0 , and the refractive index, n , of $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ films were investigated. It was found that E_g^0 decreased after illumination (photodarkening), and the refractive index increased. Fig. 1 presents the magnitudes of the changes of the bandgap, $\Delta E_g^0 = E_g^{\text{ann.}} - E_g^{\text{ill.}}$, and of the refractive index $\Delta n = n^{\text{ill.}} - n^{\text{ann.}}$ of $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ films which were illuminated after being annealed.

The magnitude of the changes in the optical bandgap and in the refractive index increased in the range of the average coordination number $2.4 < Z < 2.8$. The maxima of these changes were $\Delta E_g^0 = 0.181$ and $\Delta n = 0.166$, as found for the composition $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_{1.66}$. At an average coordination number $Z \geq 3.2$ the magnitude of the changes was essentially lower than that of films with $Z \leq 2.8$. Unfortunately, we had no films with intermediate values of Z for the present study. However, as will be pointed in the discussion, we supposed that the values of ΔE_g^0 and Δn would decrease in the range $2.8 < Z < 3.1$. The calculated normalized dependences $\Delta E_g^0/E_g^0 = f(Z)$ and $\Delta n/n = f(Z)$ exhibited curves with shapes very similar to those shown in Fig. 1.

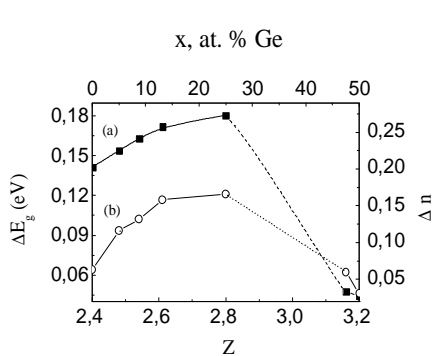


Fig. 1. Photoinduced changes in annealed $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ films: (a) of the optical bandgap; (b) of the refractive index.

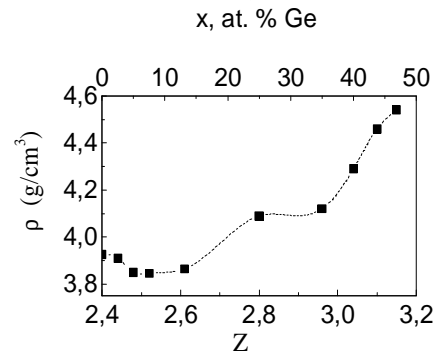


Fig. 2. Compositional dependence of the macroscopic density of $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ glasses.

In Fig. 2, the measured macroscopic densities ρ of the parent glasses $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ ($x = 0$; 0.14; 0.27; 0.40; 0.50; 0.75; 1.66; 2.70; 3.33; 4.10; 4.50; 5.00) are shown. The results from these measurements are necessary for the discussion below. It can be seen that the density decreases in the range $2.40 < Z < 2.52$ and increases strongly for larger values of the average coordination number. At $Z = 2.8$, there is a change in the curvature of the compositional dependence.

4. Discussion

The experimental results of the photoinduced changes (PIC) in the optical bandgap ΔE_g^0 and in the refractive index Δn can be used as measures of the photostructural changes of annealed films. We identify two regions of compositions with different behaviours towards the PIC in the investigated $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ films. The first region includes films with $x = 0$ -1.66 (0-25 at. % Ge), and the second is covered by films with a greater Ge content (47.4 and 50 at. %). The PICs of films from the first region were essentially greater than those from the second one. This difference leads to the assumption that the structures of the two types of film matrix are very different, not only due to the compositional variations.

The as-evaporated amorphous chalcogenide films contain a large number of defects. Their short and medium range order structures, however, contain the same main elements as those of the parent glasses. The similarities in the structures have been proved by XRD, IR, Raman and other spectroscopies. In particular, our previous Raman study of the degree of disorder in fresh and variously treated thin films from the $\text{Ge}_x\text{As}_{0.40-x}\text{S}_{0.60}$ system have proved this statement [4]. Having in mind this result, as well as several publications by other authors, we consider that the main structural units of the $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ film matrices are the same as those of the respective bulk glasses. Moreover, in this study we deal with well annealed films. Annealing at a temperature T_a (close to the glass transition temperature T_g) reduces the disorder. The structures of the annealed films become partially "repaired". Under subsequent illumination, the local atomic and electronic structures of the compositions change again, and some chemical bonds rearrange, thus increasing the disorder. Our IR spectra showed an increase in the concentration of regular heteropolar bonds after annealing, and a decrease in this concentration after subsequent illumination.

In order to obtain information about the microstructure of the $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ glasses, their macroscopic density, ρ , was measured. Using the experimental values of ρ , some structural characteristics such as average atomic volume V_a and compactness δ were calculated. The particularities in the change of the average atomic volume and the compactness have been related by some authors to changes in the topology or to chemical transitions [5, 6]. The compositional dependences $\delta = \delta(Z)$ and $V_a = V_a(Z)$ are shown in Figs. 3 and 4 respectively. It can be seen that the optimal free volume and the lowest compactness are characteristic for the glasses belonging to the first region above ($Z = 2.4-2.6$, $x = 0-0.75$). The maximum of V_a , as well as the minimum of δ , allows rearrangement of atoms and structural units. For $Z > 2.96$, the compactness is augmented and a decrease of V_a is observed, showing that the structure of the studied glasses becomes more rigid. The compositional dependence of the microhardness H showed an increase of H with Z . This confirms once more that the structure becomes more rigid with the increasing average coordination number Z .

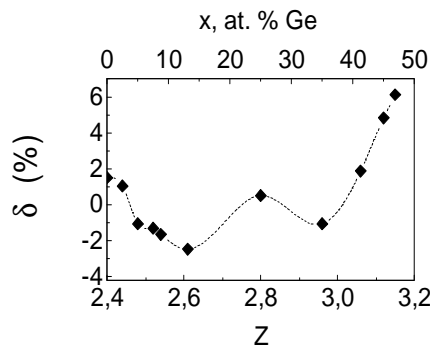


Fig. 3. Compositional dependence of the compactness of $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ glasses.

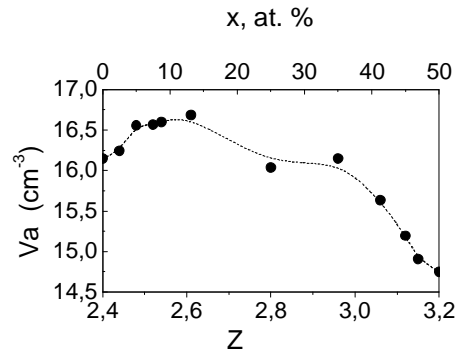


Fig. 4. Dependence of the average atomic volume V_a on the average coordination number of the glasses

The existence of elastic phase transitions has been established as a function of network connectivity. A structure-based classification of glasses as *floppy-intermediate-stressed rigid* has been advanced. Recent investigations on ternary $(\text{Ge}_2\text{X}_3)_x(\text{As}_2\text{X}_3)_{1-x}$ ($\text{X}=\text{S}$ or $\text{X}=\text{Se}$) chalcogenide glasses [7, 8] have established the presence of additional nanoscale separation in certain parts of the Ge-As-S and Ge-As-Se glass-forming regions. In Fig. 5, a ternary combined diagram, based on the results from [7] and [8], is shown. The main features of the regions surrounding the line of the glasses investigated by us are shown. For clarity, some of the regions characterizing other parts of the glass-forming regions are omitted. The hashed marked region and the region with the grey dots represent those with nanoscale separation [7, 8]. The investigated $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}\text{Ge}_x$ compositions are presented by black points. It can be seen that the first four film compositions belong simultaneously to the so called intermediate (*im*) range, and to both regions with nanoscale separation. This is why PIC in those compositions become favourable. In [9] a large number of Ge-As-S glasses have been investigated, and a compositional dependence of the free atomic volume very similar to that obtained

by us, $V_a(Z)$, was obtained. According to these authors, an inhomogeneous distribution or clustering of network-forming atoms and violation of chemical order in the chalcogenide glasses exists. We suggest that such a structure can facilitate the PIC.

The composition with $x = 1.66$ belongs to the nanoscale separated glasses, but no longer lies in the “*im*” region. This is why the properties of this composition differ somewhat from those of the films with $x = 0-1$. Finally, the compositions with great Ge contents are situated in the stressed rigid region only, and the PIC are hardly achieved in them.

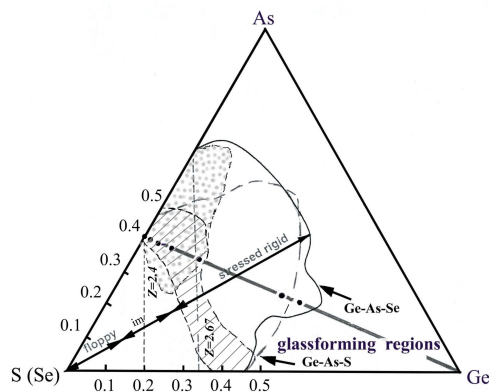


Fig. 5. Glass-forming Ge-As-S(Se) regions. The intermediate phase region, as well as the regions with nanoscale separation, are shown according to [7,8].

5. Conclusions

The theory of glass network rigidity can be applied for the explanation of the ability of different $As_2S_{1.5}Se_{1.5}Ge_x$ films to be changed by thermal treatment and/or irradiation. The existence of an intermediate phase between the floppy and the stressed-rigid phases explains the maximum of the obtained photoinduced changes. Nanoscale phase separation facilitates the process. The network structures of the films are also related to the optimal free volume and compactness that allow the rearrangement of bonds, atoms and structural units.

Acknowledgements

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