

# Structure of amorphous $(\text{GeS})_{1-x}\text{Bi}_x$ thin films ( $0 \leq x \leq 0.15$ )

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The influence of Bi additions on the structure of short-range order of amorphous  $(\text{GeS})_{1-x}\text{Bi}_x$  films ( $0 \leq x \leq 0.15$ ) has been investigated. The method of electron diffraction showed that the structure of condensates is described on the basis the model typical of solid solutions  $\text{GeS}-\text{Bi}_2\text{S}_3$ .

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## 1. Introduction

Bi-additions to the amorphous materials based on GeS are an effective tool for changing their physical properties [1-4]. Bi and Pb additives lead to inversion of the type of conductivity of these compounds. Other elements of the bismuth group, even at high concentrations in chalcogenide matrices, do not change the type of conductivity [3, 4].

But among scientists, there is uncertainty about the mechanism of entry of Bi into amorphous matrices and the coordination of Bi [2, 5]. Study of the amorphous films structure can broaden our understanding of the conductivity type inversion. This paper presents the results of studies on the short range order structure of films by the electron diffraction method.

## 2. Experimental part

We studied film compositions  $(\text{GeS})_{1-x}\text{Bi}_x$  ( $x = 0; 0.03; 0.07; 0.11; 0.15$ ) of thickness 0.3-1.2 microns. Bulk samples were obtained in ampoules by melting stoichiometric GeS with the addition of Bi of certain concentrations. The ampoules were subjected to vibration and hardening in cold water. The thin films under investigation were obtained by using a method of discrete evaporation of a fine-dispersive mixture on substrates at 293 K in a vacuum ( $10^{-4}$  Pa) followed by annealing in vacuum at  $T = 350$  K. NaCl monocrystals were used as substrates.

The comparison of results of electron probe analysis of bulk and thin films of  $(\text{GeS})_{1-x}\text{Bi}_x$  ( $x = 0; 0.03; 0.07; 0.11; 0.15$ ), which were obtained at the "Camebax" device, indicates their good correlation. The thickness of the films was measured with an optical interferometer. Electron diffraction patterns were filmed on the electron-diffraction apparatus EG-100M at accelerating voltage  $U = 80$  kV by using a rotating sector.

## 3. Results

The normalized functions of electron scattering  $i(S)$  for  $(\text{GeS})_{1-x}\text{Bi}_x$  films ( $0 \leq x \leq 0.15$ ) have a form characteristic of amorphous materials (Fig. 1, 2). In the case of amorphous objects consisting of atoms of different types, the curve of the atomic radial distribution function (RDF) is described by the equation [6]:

$$4\pi r^2 \sum_i \sum_j n_i k_i k_j \rho_{ij}(r) = 4\pi r^2 \rho_0 \left( \sum_i n_i k_i \right)^2 + \frac{2r}{\pi} \int_0^\infty Si(S) \sin(Sr) dS,$$

where  $4\pi r^2 \sum_i \sum_j n_i k_i k_j \rho_{ij}(r) dr$  is an average number of particles in a spherical shell from  $r$  to  $r + dr$ ;  $n_i$  – a concentration of component  $i$ ;  $\rho_{ij}(r)$  – a partial distribution function of the atoms of type  $i$  relative to the atoms of type  $j$ ;  $S = (4\pi \sin \theta) / \lambda$  – a vector of scattering;  $\rho_0$  – an average atomic density of particles;  $k_i, k_j$  – effective ability of the scattering of atoms  $i$  or  $j$ ;  $i(S)$  – an interference function of electron scattering.

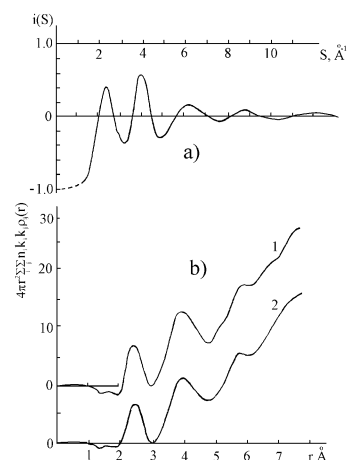


Fig. 1. Curves of electron scattering  $i(S)$  (a) and the RDF (b) from GeS amorphous films at different values of the upper limit of integration  $S_B$  (1 -  $S_B = 8.0 \text{ \AA}^{-1}$ ; 2 -  $S_B = 10.0 \text{ \AA}^{-1}$ ).

For amorphous samples the average atomic density was taken 10 % lower than the density of crystalline compounds. The normalizing factor was determined by the method [10]. Imposition of restrictions on the upper limit of integration in the Fourier transform leads to an increase of the area under the coordination peaks. We used an approach to accounting the "break effect" proposed in [7]

short-range order of the amorphous state versus the crystalline one.

Table 1. The experimental values of the radii of the coordination spheres  $r$  and the area under the first coordination peaks  $Q$  for amorphous GeS-Bi films.

Composition	$r_1$ , Å	$r_2$ , Å	$r_3$ , Å	$Q$
GeS	2.34	3.87	5.77	2.48
(GeS) <sub>0.93</sub> Bi <sub>0.07</sub>	2.40	3.99	5.89	2.46
(GeS) <sub>0.85</sub> Bi <sub>0.15</sub>	2.44	4.02	5.92	2.33

#### 4. Discussion

The experimentally obtained radii of the first coordination spheres and the areas under the first coordination peaks were compared with those calculated theoretically [7]:

$$r_{1(\partial \hat{a} i \partial)} = \frac{\sum_i \sum_j \tilde{n}_i n_{ij} R_{ij}}{\sum_i \sum_j \tilde{n}_i n_{ij}}, \quad (1)$$

$$Q_{(\partial \hat{a} i \partial)} = \sum_i \sum_j \tilde{n}_i k_i k_j n_{ij}, \quad (2)$$

where  $n_{ij}$  is the number of atoms of type  $j$  around the atom of type  $i$ ,  $c_i$  – a concentration of component  $i$ ;  $R_{ij}$  – a distance between the atoms of type  $i$  and  $j$ .

For the calculations we chose three models of the amorphous films structure:

- 1)  $n_{11} = 0; n_{12} = 4; n_{22} = 0; n_{21} = 4;$
- 2)  $n_{11} = 2; n_{12} = 2; n_{22} = 0; n_{21} = 2;$
- 3)  $n_{11} = 3; n_{12} = 1; n_{22} = 1; n_{21} = 1.$

Within these models we calculated the values of radii of the first coordination sphere  $r_{1(\text{theories})}$  and the area under the first coordination peaks  $Q_{(\text{theories})}$  (Table 2).

Table 2. The calculated values of radii of the first coordination spheres  $r_{1(\text{theory})}$  and the area under the first coordination peaks  $Q_{(\text{theory})}$  for amorphous GeS films.

Model					
1		2		3	
$r_{1(\text{theory})}$ , Å	$Q_{(\text{theory})}$	$r_{1(\text{theory})}$ , Å	$Q_{(\text{theory})}$	$r_{1(\text{theory})}$ , Å	$Q_{(\text{theory})}$
2.26	2.44	2.32	2.50	2.32	2.51

Comparison of the experimental results with the calculated ones (Table 1, 2) indicates that the structure of amorphous condensates is better described within the second model. Thus, in amorphous GeS films, the Ge atoms are covalently bonded to two Ge atoms at the

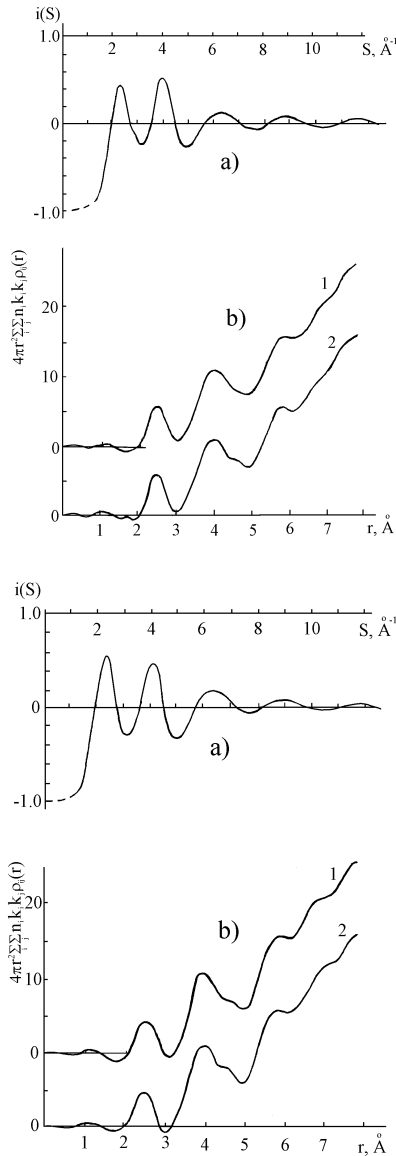


Fig. 2. Curves of electron scattering  $i(S)$  (a) and the RDF (b) from (GeS)<sub>0.93</sub>Bi<sub>0.07</sub> (left) and (GeS)<sub>0.85</sub>Bi<sub>0.15</sub> (right) amorphous films at different values of the upper limit of integration  $S_B$  (1 -  $S_B=8.0 \text{ Å}^{-1}$ ; 2 -  $S_B=10.0 \text{ Å}^{-1}$ ).

The radii of the coordination spheres were determined by the position of maxima on the curves of electron scattering (Table 1). The position of the coordination maxima determined an average interatomic distance. For GeS amorphous films the average interatomic distance was shorter than that in the corresponding GeS crystals (2.76 Å) [8]. This indicates a significant difference in the

distance of 2.44 Å and to two S atoms at the distance of 2.29 Å; the atoms of S – to two Ge atoms at the distance of 2.29 Å.

Thus, the chemical bond between the atoms in GeS amorphous films is covalent, and the structure of the first coordination sphere differs from the corresponding crystalline structure, which is characterized by a layered structure with the coordination of 3-3. The analogical conclusion is drawn by the authors [9] who investigated the structure of amorphous GeS ( $1 < x < 2$ ) by X-ray spectroscopy methods. A transition from the crystalline to the amorphous state for GeS is related to the fundamental changes in coordination of Ge atoms. It is found that the structure a-GeS is well described by the chemically ordered bond net model with coordination 4(Ge)-2(S).

The authors in [10] describe the implementation of the three-time coordination of atoms in amorphous GeS samples. By changing the conditions of condensation it is possible to modify the structure of amorphous germanium monochalcogenides [11]: the amorphous films deposited on substrates at room temperature have the coordination 4-2; the films deposited on cooled substrates are structured

by the coordination 3-3, and the structure of films at annealing relaxes to the coordination 4-2.

The adding of bismuth to GeS amorphous films changes the intensity ratio of the first and second interference peaks on the interference functions of the scattering of electrons (Fig. 2). The first diffraction peak corresponds to coherent scattering for large values of  $r$ , and, therefore, an increase in its intensity may be due to increasing the packing density of the second and higher coordination spheres or the chemical bonds of bismuth to the amorphous matrix, because of the large radius of Bi, partially fall into the second coordination sphere.

As the result of incongruent evaporation at the condensation of amorphous films in their structure there can form clusters, whose structure corresponds to the crystalline phases GeS, GeS<sub>2</sub> and Bi<sub>2</sub>S<sub>3</sub>, and compounds not typical of the crystalline structures. The comparison of the binding energies of atoms (Table 3) shows that the Bi-S bonds are energetically more favourable than the Bi-Ge and Bi-Bi bonds. Most likely, we can speak about the lack of Bi-Ge bonds and a small probability of Bi-Bi bonds at the bismuth additives to 15 at. %.

Table 3. Bond energy of atoms.

Source	Type of bond / bond energy, kJ/mol								
	Se-Se	S-S	Ge-Se	Ge-S	Ge-Bi	Bi-Se	Bi-S	Bi-Bi	Ge-Ge
[3]	184	213	216	232	132	170	193	-	-
[12]	225	280	230	265	-	-	-	-	185
[13]	332	-	476	547	-	280	315	188	-

The average coordination number, calculated from the area under the first coordination peak, decreases when adding Bi but corresponds to the neighbour coordination of atoms of the initial GeS amorphous matrix: to the fourfold coordination of germanium and twofold coordination of chalcogen. Interpretation of the structure of amorphous  $(\text{GeS})_{1-x}\text{Bi}_x$  is based on the following assumptions: a) Bi-S bonds are energetically more favourable for Bi atoms than Bi-Bi or Bi-Ge; b) due to incongruent evaporation during film condensation, clusters enriched in one or two elements of the alloy can be formed. It should be noted that most authors do not admit the existence of Ge-Bi bonds at adding bismuth to chalcogenides of germanium.

Calculation of the area under the first maximum and of the radii of the first coordination sphere was done by the formulas (1), (2) in the assumption of a double coordination of S atoms, tetrahedral coordination of Ge atoms and a triple coordination of Bi atoms. Therefore, additional conditions were imposed on the calculation:

$$\begin{aligned} c_i n_{ij} &= c_j n_{ji}, \\ n_{11} + n_{12} + n_{13} &= 4, \\ n_{21} + n_{22} + n_{23} &= 2, \\ n_{31} + n_{32} + n_{33} &= 3, \end{aligned}$$

where subscript "1" refers to Ge, "2" – to Se and "3" – to Bi.

Theoretical calculations were done on the assumption of covalent bonds for the following models of the amorphous condensates structure:

- 1) a heterogeneous model, with clusters of Bi atoms ;
- 2) a model with a random distribution of Bi bonds;
- 3) a model where Bi atoms have bonds typical of compounds  $A^V_2B^{VI}_3$ .

Within the proposed models, we calculated the areas under the first maxima and the radii of the first coordination spheres (Table 4). The coincidence of the results of the theoretical calculations with the experimental data proved the validity of the model. The results of the CARD interpretation best correlate with the experimental data within the third model, i. e. assuming the triple coordination of Bi atoms which form structural units of the pyramidal type  $\text{BiS}_{3/2}$ , connected to each other or to the atoms of the main matrix through sulphur atoms. When adding Bi the structure of amorphous films is modified, so that along with the main structural fragments of a-GeS (tetrahedral coordination), the amorphous matrix contains clusters of atoms similar in composition and coordination to quasicrystalline complexes  $\text{Bi}_2\text{S}_3$ , which agrees with the data [14].

Table 4. The calculated values of the radii of the first coordination spheres  $r_{1(\text{theory})}$  and the area under the first coordination peaks  $Q_{(\text{theory})}$  for amorphous (GeS)<sub>1-x</sub>Bi<sub>x</sub> films.

Composition	Model					
	1		2		3	
	$r_{1(\text{theory})}$ , Å	$Q_{(\text{theory})}$	$r_{1(\text{theory})}$ , Å	$Q_{(\text{theory})}$	$r_{1(\text{theory})}$ , Å	$Q_{(\text{theory})}$
(GeS) <sub>0.93</sub> Bi <sub>0.07</sub>	2.36	2.60	2.47	2.42	2.37	2.52
(GeS) <sub>0.85</sub> Bi <sub>0.15</sub>	2.42	2.54	2.49	2.30	2.42	2.39

## 5. Conclusions

At Bi-additions to amorphous GeS films (0-15 at. %), their structure is modified, so that along with the main structural fragments of a-GeS (tetrahedral coordination), the amorphous matrix contains clusters of atoms similar in composition and coordination to quasicrystalline complexes Bi<sub>2</sub>S<sub>3</sub>.

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