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Synergetics of the instability and randomness in formation of gradient modified semiconductor structures

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Abstract. The criteria for formation of an inhomogeneous structure based on vitreous Ge_2S_3 with modifiers Al, Bi, Pb, Te that are identified due to changes in the condensed medium (evaporation temperature, condensation velocity, increasing or decreasing the intensity of the fluctuations of the active field) have been determined. The article analyzes the obtained equations describing formation of inhomogeneous amorphous structures and taking into account the dynamics of the concentration of modifier owing to the source of the atomic flow of a chemical element, structural heterogeneity (availability of vacancies, micropores) and particle diffusion. Computer simulation of the source of the atomic flow of the modifier has been carried out, which makes it possible to form gradient structures with the predicted distribution of the chemical element according to the film thickness. Morphology of gradient structure surfaces and the mechanism of condensation of modifiers Al, Bi, Pb, Te with the amorphous matrix of Ge_2S_3 have been ascertained.

Keywords: computer modeling, heterogeneous modified structures, morphology of gradient structures surfaces, non-crystalline state, self-organizing processes, synergetics.

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1. Introduction

The current state of development of materials science and information technology sets the research task to purposefully create crystalline and non-crystalline materials with structural-sensitive properties [1, 2]. Amorphous chalcogenides (S, Se, Te) and their multicomponent alloys are very interesting objects with wide practical applications. Due to the transparency in the near, medium and far infrared regions, their significant non-linearity, chalcogenide semiconductor materials are used as active and passive elements in optics and sensor devices [3, 4], telecommunications [1] as a thermal image and generation of nonlinear light [3-5]. Intensive and reverse crystallization observed in some thin-film systems of chalcogenides is the basis for using these materials in creation of non-volatile memory [3, 5-6]. The mentioned applications of the chalcogenide materials of As(Ge)-S(Se, Te) systems could not be realized without the knowledge of the basic properties and processes occurring in these unique materials [4, 6-10]. In addition, the fundamental research into the influence of random processes on formation of the structure of modified semiconductor systems by using synergetics and computer simulation is extremely important [11-13]. From this perspective, the study of formation processes in ordered structures in thin-film systems continues to arouse lasting and constant interest in the synergetic approach and their practical application [13-15].

This paper presents the complex theoretical and experimental research of thin-film semiconductor structures made of As(Ge)-S(Se, Te) with using computer modeling. The aim of the research is to establish the possibility to form a controlled distribution of the modifier concentration in the thin film gradient structures Ge_2S_3:X (X = Al, Bi, Pb, Te) and the corresponding implementation of anticipated structural-sensitive properties.

2. The computer modeling: initial equations and conditions

An example of using computer modeling to form thin-film inhomogeneous modified structures is shown in Fig. 1. Application of computer modeling implies the iterativeness and "formation" of the model in the cycle: 1 – physical model, 2 – mathematical model, 3 – calculation methods, 4 – algorithm and program for model calculations, 5 – testing and model research, 6 – comparison of calculation results with experimental data and subsequent refinement of the model. This cycle is repeated a required number of times approaching the real object (phenomenon). Each step of computer modeling (Fig. 1) will be considered.

The first stage is the physical model. A physical model for inhomogeneous modified structures is a model of an open system, for which the transition to a non-crystalline state can be considered as a cooperative self-organized process by using the principles of synergetics. Indeed, the conditions necessary to form self-organized structures in open systems are as follows [11, 12]:

- The system should be thermodynamically open, *i.e.*, there should be the exchange of mass, energy, and information with environment.
- The system is at a significant deviation from equilibrium.
- The self-organization of structures has a threshold character; the behavior of a significant number of subsystems belonging to the system must be consistent.
- Dynamic equations describing the behavior of the system are nonlinear and stochastic.

The following part of the paper analyzes how these conditions are fulfilled in formation of the investigated structures:

- The technological process for obtaining inhomogeneous modified structures (for example, in the process of cooling the fusion, sedimentation of layers) occurs in a thermodynamically open system that exchanges mass and energy with the surrounding medium.
- Such structure is formed at significant deviation of the system from equilibrium (for example, fusion, charged material), which corresponds to homogeneous or quasi-homogeneous distribution of physical quantities. The inhomogeneity can be given by distribution of atoms in different phase states (for example, soft (vacancies, pores, dislocations) and rigid (matrix frame) configurations). The degree of deviation is determined by the order parameter, calculated as deviation of the part of atoms from the homogeneous distribution of the thermodynamically equilibrium state.

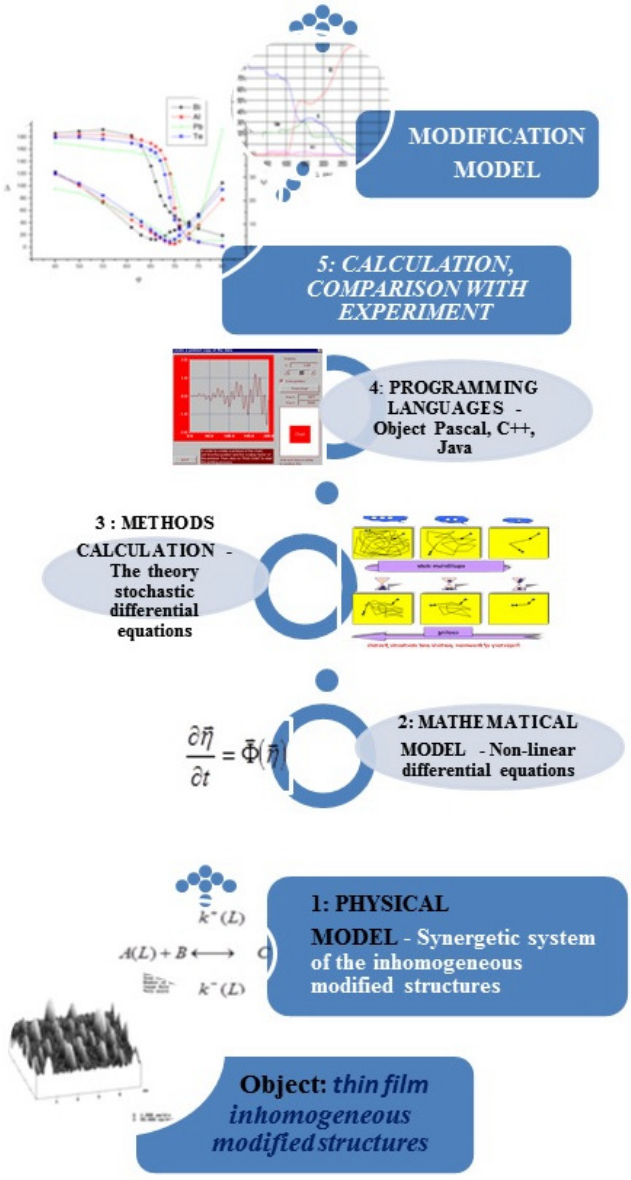

Fig. 1. Computer modeling of the gradient non-crystalline structures.

- Formation of modified films has a threshold character and is realized at certain values of the external control parameter (*e.g.*, cooling rate, deposition rate). In the process of transition to the vitreous condition, there is self-consistent interaction of different subsystems, which determines the nonlinear nature of the system behavior. The system is characterized by stochasticity, *i.e.*, the time reliance of the system depends on the reasons that cannot be predicted with absolute precision.
- The inhomogeneous modified structure has features of a dissipative structure that is characterized by much higher space-time correlation of the motion of atoms and their groups than that of the initial homogeneous system [15].

3. Modified non-crystalline structures based on the systems As(Ge)-S(Se, Te) and self-organization processes

A non-crystalline system that contains N particles (atoms, molecules), a part N_{mod} of which is components of the modifier (the atoms of the chemical elements Al, Te, Bi, *etc*.), and a part N_{mat} includes components of the matrix (elements of the vitreous Ge_2S_3), which is considered in [2, 8, 14]. The process of modified non-crystalline structure formation can be described by the following physical-chemical reaction:

$$A(L)+B \underset{k^-(L)}{\overset{k^+(L)}{\longleftrightarrow}} C. \qquad (1)$$

Here the symbol $A(L)$ identifies the components of the modifier in the spatial domain that consists of L particles (hereinafter the size of the domain will be understood as the number of particles), B identifies the components of the matrix (Fig. 2). Reactions (1) suggest that the domain is growing or decreasing (in relation to velocity $k^+(L)$, $k^-(L)$ by joining or separating individual modifier particles in the matrix. Behavior of the domain set with the size L in time will be described by means of the size distribution function $g(L,\vec{r},t)$, where $\vec{r}=\vec{r}(x,y,z)$ is the radius vector, which spatial coordinate z is perpendicular to the plane (x, y).

The dynamics of the change in the distribution function $g(L,\vec{r},t)$ is given by the Fokker–Planck equation [16]:

$$\frac{\partial g(L,\vec{r},t)}{\partial t}=-\frac{\partial I(L,t)}{\partial L}, \qquad (2)$$

where $I(L,t)=V(L)g(L,\vec{r},t)-\frac{\partial}{\partial L}\left(D(L)g(L,\vec{r},t)\right)$ is a flux, the density of which is set by the velocity of component evaporation, $V(L)=k^+(L)-k^-(L)$, $D(L)=\left(k^+(L)+k^-(L)\right)/2$ – growth velocity and diffusion coefficient in the space of sizes. The initial and boundary conditions are as follows: $\partial g(L,\vec{r},t)/\partial L\big|_{z=0}=0$, $g(L=1,\vec{r},t=0)=\rho_s$, $\sum_L g(L,\vec{r},t=0)=1$ (ρ_s – the density of dislocations, micropores). Thus, the equation (2) can be rewritten in the form:

$$\frac{\partial g(L,\vec{r},t)}{\partial t}=-\frac{\partial}{\partial L}\left[V(L)g(L,\vec{r},t)\right]+D(L)\nabla^2 g(L,\vec{r},t)$$

Here,

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}=\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right)+\frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2}+\frac{\partial^2}{\partial z^2}$$ is

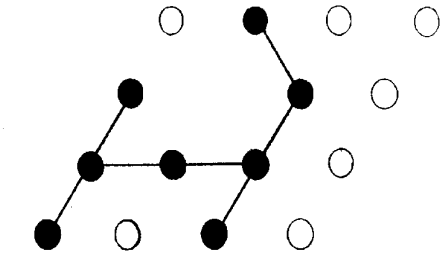

Fig. 2. An example of forming an amorphous layer (a matrix consisting of $n=15$ elements links between modifier atoms visually single out the domain $L=8$); ○ – matrix's components, ● – modifier's components.

Laplacian in the cylindrical coordinate system (ρ,φ,z). The growth velocity of domains will be approximated by the following expression: $V(L)=(D_a/L)\cdot N_{\text{mod}}$, $D_a=D/a^2$, where a is the interatomic distance, D – diffusion coefficient of particles, and diffusion in the space of sizes $D(L)=\beta_0/L^2$, where β_0 is the diffusion constant (for metals Al, Bi, the diffusion coefficient depending on temperature $D=10^{-10}\ldots10^{-15}$ cm^2/s, $\beta_0\approx0.2$, $a=(2\ldots4)\cdot10^{-8}$ cm [8, 17].

The change dynamics in the number of particles of the components of the system modifier N_{mod} under the action of source G during time τ_p is considered in the following part. The change in the number of particles in the size interval $L, L+dL$ is determined by correlation $V(L)g(L,\vec{r},t)$ and the total number of particles $4\pi\int_0^\infty L^2V(L)g(L,\vec{r},t)dL$. The atomic particles flux $G=g_{\text{source}}\cdot\exp(-mz)$. g_{source}, m are constants of particle source; here, the transition from time dependence to space dependence is taken into account according to correlation $t\Rightarrow z/V$ (V is the velocity of layer growth) that may change with time according to a certain law (in this case, an exponential change law is considered) [18-20]. Thus, the dynamics of changing the number of particles is given in the equation:

$$\frac{\partial N_{\text{mod}}}{\partial t}=G-4\pi\int_0^\infty L^2V(L)g(L,\vec{r},t)dL+D_a\nabla^2N_{\text{mod}}. \qquad (3)$$

The equation of continuity $N_{\text{mod}}\big|_{z=0}=N_{\text{mod}s}$, $\frac{\partial N_{\text{mod}}}{\partial z}\big|_{z=0}=0$, $\frac{\partial N_{\text{mod}}}{\partial z}\big|_{z=d}=0$ (d is the layer thickness). The first summand in (3) determines the change in the number of components of the modifier due to the source of the molecular flow, the second – due to structural inhomogeneity (available vacancies, micropores), the third one – the diffusion of particles. Equations (2) and (3) enable describing the dynamics of system behavior. The following part of the paper considers the cases of homogeneous and inhomogeneous sources.

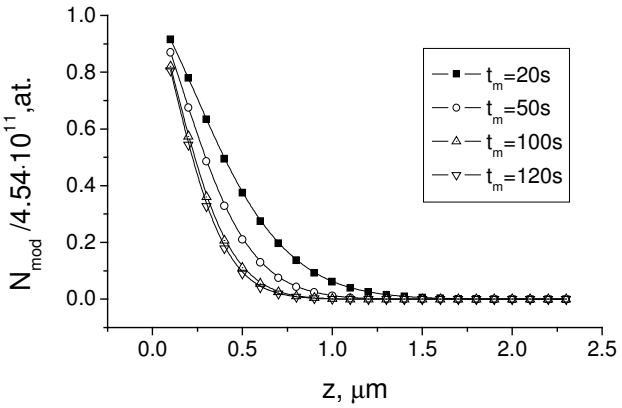

Fig. 3. Modification of modifier distribution with temperature change for Bi from $T_{evap} = 750$ °C till $T = 730$ °C during the time intervals t_m ($t_{m1} = 20$ s, $m_1 = 0.27029$, $g_1 = 2.786 \cdot 10^{11}$; $t_{m2} = 50$ s, $m_2 = 0.67572$, $g_2 = 2.786 \cdot 10^{11}$; $t_{m3} = 100$ s, $m_3 = 1.35143$, $g_3 = 2.786 \cdot 10^{11}$; $t_{m4} = 120$ s, $m_4 = 1.62172$, $g_4 = 2.786 \cdot 10^{11}$).

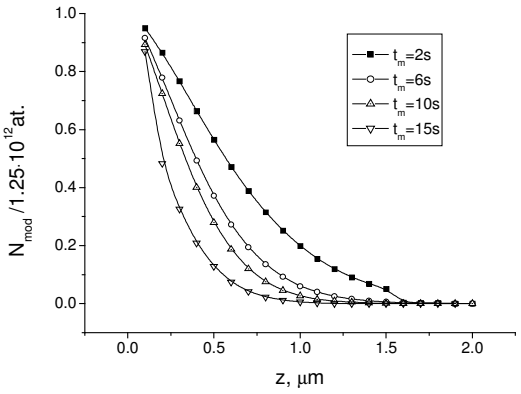

Fig. 4. Changing the modifier distribution when changing temperature for Al from $T_{evap} = 765$ °C till $T = 740$ °C during time intervals t_m ($t_{m1} = 2$ s, $m_1 = 0.03323$, $g_1 = 2.786 \cdot 10^{11}$; $t_{m2} = 6$ s, $m_2 = 0.09968$, $g_2 = 2.786 \cdot 10^{11}$; $t_{m3} = 10$ s, $m_3 = 0.16613$, $g_3 = 2.786 \cdot 10^{11}$; $t_{m4} = 15$ s, $m_4 = 0.24919$, $g_4 = 2.786 \cdot 10^{11}$).

The equations (2) and (3) in the stationary case $\left(\frac{\partial N_{\text{mod}}}{\partial t} = 0,\ \frac{\partial g}{\partial t} = 0\right)$ acquire the following form:

$$-\frac{\partial}{\partial L}\left[V_s(L) g_s(L,r,t)\right] + D(L)\nabla^2 g_s(L,r,t) = 0, \tag{4}$$

$$g_{\text{source}} \cdot \exp(-mz) -$$
$$-4\pi \int_0^{\infty} L^2 V_s(L) g_s(L,r,t) dL + D_a \nabla^2 N_{\text{mod}\,s} = 0.$$

The stationary solutions of the equation (4) in the homogeneous case ($G = g_{\text{source}}$) are determined by the correlations:

$$N_{\text{mod}\,s}^{\text{hom}} = \text{const} \approx g_{\text{source}} / \left(4\pi\rho_s D_a \overline{L}^2\right),$$

$$g_s^{\text{hom}} = \rho_s \overline{L} \cdot \delta\left(L - \overline{L}\right). \tag{5}$$

In the inhomogeneous case $G = g_{\text{source}} \cdot \exp(-mz)$, taking into account that φ = const and solutions of the equation $N_{\text{mod}}, g \approx R(\rho) Z(z)$, the following equations are obtained:

$$N_{\text{mod}\,s}^{\text{inhom}} = N_{\text{mod}\,s}^{\text{hom}} \cdot \exp\left(-\gamma z\right),$$

$$g_s^{\text{in hom}} = g_s^{\text{hom}} \cdot \exp\left(-\gamma z\right),$$

$$\gamma^2 = \left(4\pi\rho_s \overline{L}^2 D_a N_{\text{mod}\,s}^{\text{hom}} - G\right) / D_a. \tag{6}$$

The equations (6) describe formation of amorphous structures of inhomogeneous thicknesses. In particular, the inhomogeneous distribution of the modifier component at z causes formation of a structure with the gradient of the distribution function of the modifier domains according to sizes in the spatial scales $\propto \frac{1}{\gamma}$ [19]. In this case, the atomic flow of the modifier is described by the expression:

$$G_N = 3.513 \cdot 10^{22} \frac{a_1 P_{\text{evap}}}{\sqrt{M_{\text{evap}} T_{\text{evap}}}} \left[\text{cm}^{-2}\text{s}^{-1}\right], \tag{7}$$

where P_{evap} is the equilibrium saturated vapor pressure of the evaporated substance (Al, Bi, Pb, Te), $P_{\text{evap}} \approx 10^{-4}$ mmHg, a_1 – evaporation coefficient (in case of a clean surface of the evaporating substance $a_1 = 1$) [21, 22], M_{evap} – molecular weight of evaporated elements – modifiers, T_{evap} – evaporation temperature. In order for the vapour molecules to freely evaporate, the pressure P_{evap} should not exceed $\approx 10^{-2}$ mmHg, and the area of evaporator should be no more than several square centimeters (in our case, the area of the evaporator depends on the modifier type and is approximately 10^{-4} cm^2) [2, 14].

To determine the parameter m of an inhomogeneous source of the atomic flow of the modifier (see Eq. (6)), the following approximation is used. Supposing at time $t = 0$, the source of the atomic flow of the modifier is determined by the temperature of the modifier vaporization: $G_1 = G_1\left(T_{\text{evap}}\right)$. In the interval of time $t = t_m$, when the evaporation temperature changes from T_{evap} to T, the source of the modifier's atomic flow will be equal to $G_2(T) = G_1\left(T_{\text{evap}}\right) \cdot e^{-mt_m}$. Hence, the parameter m is determined in the following way:

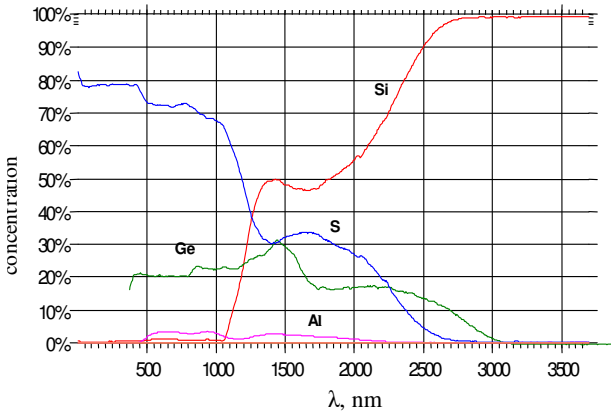

Fig. 5. Distribution of elements over the thickness of the film: ⟨Ge_2S_3:Al⟩.

$$m = \frac{1}{t_m} \ln \frac{G_1(T_{evap})}{G_2(T)}.$$

Otherwise, taking into account the correlation (7), the following equation is obtained:

$$m = \frac{1}{2t_m} \ln \frac{T}{T_{evap}} \ [s^{-1}]. \qquad (8)$$

From the correlations (6) to (8), calculation has been performed of the atom distribution of modifiers Bi and Al according to the thickness of the inhomogeneous films based on the vitreous Ge_2S_3 by changing the source of the modifier's atomic flow, structural inhomogeneity (vacancy, micropores), and particle diffusion. Figs. 3 and 4 show the dependence of the change, calculated in accordance to (6), in the number of atoms Bi and Al in the action of the source of atomic flow at time intervals (t_{m1} to t_{m4}), during which the temperature changes from T_{evap} to T.

4. Gradient thin-film structures: obtaining and determining the concentric distribution of components

The obtainment of gradient films based on vitreous Ge_2S_3 with modifiers Al, Bi, Pb, Te has been carried out by the method of thermal evaporation in a vacuum using the results of computer modeling [12, 22]. Due to the change of the constant control parameter (evaporation temperature) a necessary flow of the modifying element (Al, Bi, Pb, Te) has been created. The dynamics of the particle number of the modifier components N_{mod} under the influence of the inhomogeneous source of atomic flow G (see the formula (6)) provides the required distribution of introduced modifier over the thickness of deposited film within 0.5…3 μm (see Figs. 3 and 4).

The studied films were deposited on glass and silicon substrates. The control of the chemical and quantitative composition of the obtained gradient films ⟨Ge_2S_3:X⟩ (X = Al, Bi, Pb, Te) was performed using the method of mass-spectrometry with post-ionized neutral particles. The quantitative analysis enabled to construct the distribution of elements over the thickness of film (Fig. 5). The ordinate axis corresponds to the atomic percent of components, and the abscissa axis manifests the value of depth from the surface of the film.

As it can be seen from the diagrams, the films ⟨Ge_2S_3:Al⟩ (Al – 2 at.%), ⟨Ge_2S_3:Bi⟩ (Bi – 14 at.%) have an alternating composition with a continuous distribution of constituent components over the thickness. The repeatability of the results concerning the distribution of the introduced modifier over the thickness of the film is satisfactory dependent on the type and concentration of the introduced chemical element (Al, Bi, Pb, Te) and comprises ~90%. In addition, technological regimes of obtaining thin-film inhomogeneous structures with different modifiers (evaporation temperature, condensation rate, fluctuations of technological environment) play an important constructive role in the repeatability of the results.

5. Calculation of distribution of composite components in modified structures: comparison with experimental data

In order to check the correctness of the chosen approach that allows calculating the critical values of parameter fluctuations, in which the structural characteristics of the studied layers are not sensitive to changing conditions for their obtaining and to predict formation of qualitatively new structures at allocated intensities of noise, calculation of the distribution of constituent components over the thickness of the film and comparison with experimental data has been performed.

The difference between internal system fluctuations and external environmental fluctuations should be noted. Unlike internal fluctuations, the stochastic nature of the environment does not have the microscopic origin; the intensity of environmental fluctuations can be increased in a controlled manner in order to investigate its influence on the system behavior. With the corresponding experimental modification of the conditions for obtaining inhomogeneous structures, the noise level can be reduced but it is impossible to eliminate it completely. It constitutes another difference of noise from internal fluctuations, which makes it more flexible guided in the hands of the experimenter. The external noise is never strictly equal to zero, and therefore it must be taken into account: either the presence or absence of the influence.

Table 1. Technological parameters for obtaining modified structures.

Composition	Thickness z, μm	Condensation velocity υ, Å/s	σ_υ, Å/s	T_{evap}, °C	σ_T, °C
⟨Ge_2S_3:Te⟩	1.03	2.70	0.02	726	±5
⟨Ge_2S_3:Pb⟩	2.26	5.84	0.02	747	±5
⟨Ge_2S_3:Bi⟩	1.26	3.50	0.02	750	±5
⟨Ge_2S_3:Al⟩	2.4	6.20	0.02	765	±5

Table 1 represents the technological parameters of obtaining modified structures (condensation velocity, evaporation temperature, thickness) and the values of fluctuations of the condensation velocity σ_υ and the evaporation temperature of the layer σ_T.

Two-parameter approximation of the data of experimental curves was carried out, and parameters m, g were calculated for experimentally obtained dependences of the concentration distribution of constituent components over the thickness of film (Fig. 5), taking into account the equations (6) which describe the formation of amorphous structures with inhomogeneous thicknesses.

The following part of the paper considers the two-parameter dependence $y = ge^{-mz}$, where m, g are constant parameters [12]. Consequently, the values of the constant can be calculated (Fig. 5). The concentration distribution of modifier Bi over the film thickness ⟨Ge_2S_3:Bi⟩ (Bi – 14 at.%) parameters m, g that correspond to the experimental dependences (Fig. 5). As a result of parameters calculation, the following values of constant parameters were obtained: for the composition ⟨Ge_2S_3:Al⟩ m = 0.66142, g = 3.85894, for the composition ⟨Ge_2S_3:Bi⟩ m = 0.85772, g = 10.47423.

Figs. 6 and 7 represent the dependences of the atomic distribution for modifiers Al (2 at.%) and Bi (14 at.%) over the film thickness and compositions ⟨Ge_2S_3:Al⟩ and ⟨Ge_2S_3:Bi⟩, calculation of which was carried out from the correlations (6) to (8) (theoretical curve), the approximation of the two-parameter dependence distribution of the modifier atomic flow (approximation) and the comparison with the experimental curves (exp. curve), which are obtained using the method of mass spectrometry of post-ionized neutral particles. As it can be seen from Figs. 6 and 7, satisfactory approximation of the exponential distribution of the two-parameter dependence of the modifier atomic flow over the film thickness is observed. Consequently, the given approach to calculating the distribution of introduced elements (Al, Bi, Pb, Te) and the calculation program of constant m and g allows to check the experimental distribution of the modifier on the film thickness by using the set of programs and to determine the constants of this distribution with the given accuracy [13].

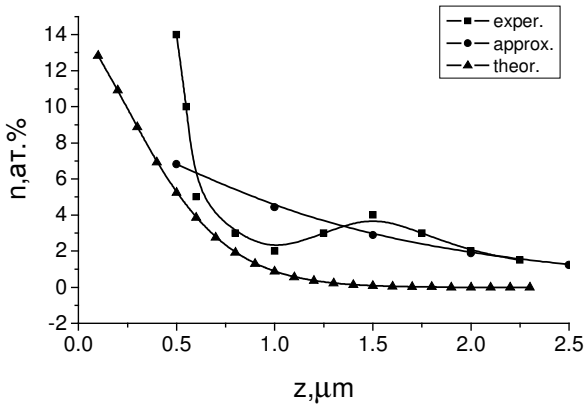

Fig. 6. Concentration distribution of modifier Bi over the film thickness ⟨Ge_2S_3:Bi⟩ (Bi – 14 at.%).

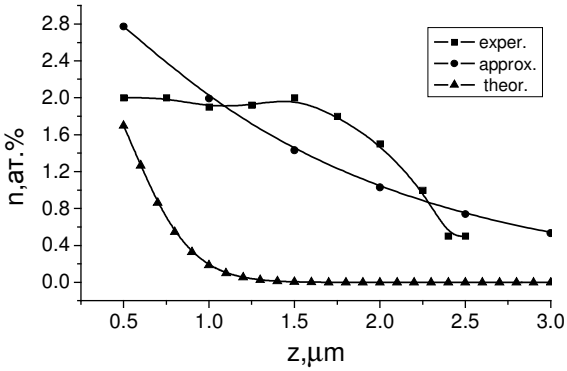

Fig. 7. Concentration distribution of modifier Al over the film thickness ⟨Ge_2S_3:Al⟩ (Al – 2 at.%).

6. Research of film surface morphology

Figs. 8 to 11 illustrate morphology of investigated surfaces of inhomogeneous structures ⟨Ge_2S_3:X⟩ (X = Al, Bi, Pb, Te). The results show that surface morphology of the films is quite complex and depends on the type of the introduced modifier. Therefore, the results of studies of inhomogeneous layers ⟨Ge_2S_3:Bi⟩ (Bi – 14 at.%) are shown in Fig. 8.

It has been found that with introduction of elements-modifiers of bismuth and lead, the condensate formation occurs in the form of vapor-liquid-solid phase with coalescence. It is characterized by formation of channels and merging of small islets into larger ones. Table 2 presents the main parameters characterizing the surface of the films. The height of the surface roughness of the gradient structure with the bismuth is within the range of 0.4…2.5 nm [8, 23, 24].

Fig. 9 shows the axonometric image and the structural analysis of the inhomogeneous film ⟨Ge_2S_3:Pb⟩ (Pb – 12 at.%).

Similar to Bi, the mechanism of condensate formation occurs in the form of vapour-liquid-solid phase with coalescence. The height of surface roughness reaches 1.2…5.4 nm.

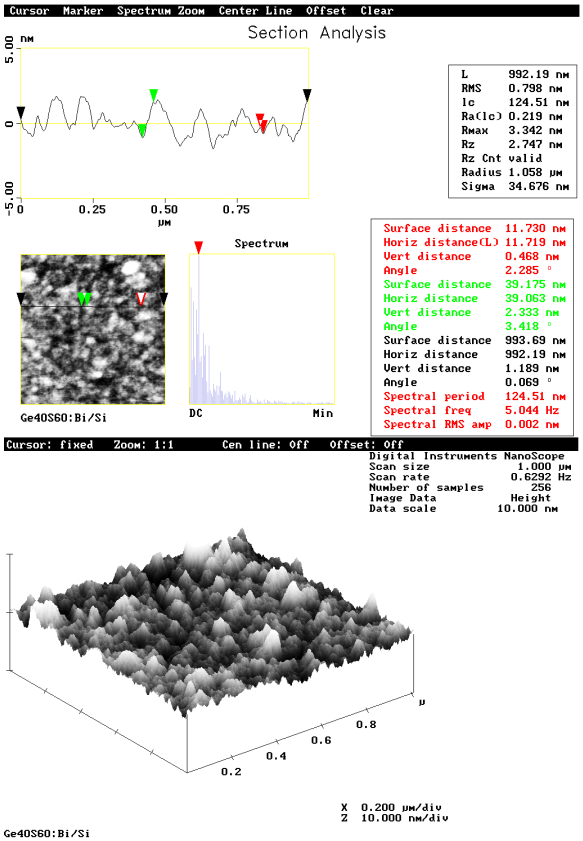

Fig. 8. Axonometric image and sectional analysis of the gradient film surface ⟨Ge_2S_3:Bi⟩ (Bi – 14 at.%), obtained using AFM.

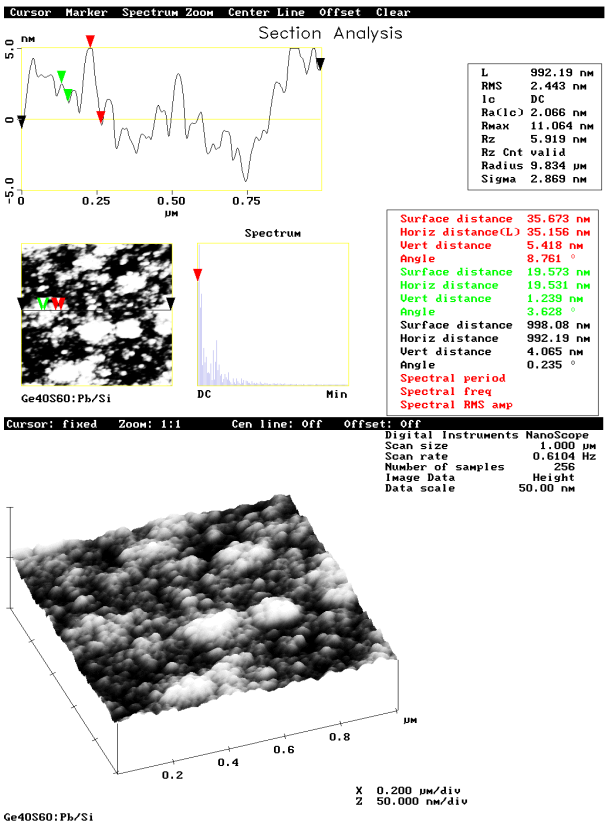

Fig. 9. Axonometric image and sectional analysis of the gradient film surface ⟨Ge_2S_3:Pb⟩ (Pb – 12 at.%), obtained using AFM.

Table 2. Main parameters characterizing the film surface.

Composition	RMS, nm	R_a, nm	R_{max}, nm	h, nm
Ge_2S_3	0.62	0.1	0.99	0.4–0.5
⟨Ge_2S_3:Bi⟩ (14 at.%)	0.80	0.22	3.34	0.4–2.5
⟨Ge_2S_3:Te⟩ (30 at.%)	6.93	5.45	21.84	2.3–36.9
⟨Ge_2S_3:Al⟩ (2 at.%)	1.53	1.03	8.07	1.4–6.3
⟨Ge_2S_3:Pb⟩ (12 at.%)	2.44	2.06	11.06	1.2–5.4

RMS – mean-square deviation vertically,
R_a – arithmetic mean deviation,
R_{max} – maximum deviation,
h – roughness height.

Having analyzed Fig. 10 for the structure ⟨Ge_2S_3:Te⟩ (Te – 30.7 at.%), it is clear that the parameters characterizing the roughness value are significantly different from the previous results [24]. This difference in the values for structures with Te is explained by the presence of two halogens with different structural parameters in the film, resulting in possible substitution of sulfur by tellurium, which leads to a partial disordering of an amorphous matrix frame on the basis of vitreous Ge_2S_3, formation of obtained condensates at given concentrations of solid solutions according to the mechanism of vapor-solid phase, with formation of a large number of large-sized islets. The height of the roughness reaches 37 nm.

Analyzing Fig. 11 for the structure ⟨Ge_2S_3:Al⟩ (Al – 2 at.%), it has been established that formation of condensate occurs according to the vapor-solid phase mechanism with densely filled islets of small sizes, which is not observed in structures with modifiers Bi, Pb.

Thus, the main feature of obtaining amorphous gradient structures in the solid phase with modifying elements is that they are always formed in non-equilibrium conditions, in which the minimum potential energy of the system is not achieved. The high energy of an amorphous state affects the values of ionic or atomic radii and the bond angles, but, first of all, on the methods of stacking structural units of solids, which are extremely large in this case [24]. The process of growth and the structure of amorphous condensates of inhomogeneous modified structures is significantly influenced by the vapor composition, energy state of its particles, condensation rate, temperature of the substrate, and evaporator.

Thus, as it can be seen from the AFM figures, the surface roughness of the studied films is negligible (Table 2), it lies within 1…7 nm at the thicknesses of structures of 500…3000 nm, and only for Te the roughness reaches the values of 37 nm, that is, the film surface is rather smooth. It is an important conclusion for the following interpretation of optical film research data.

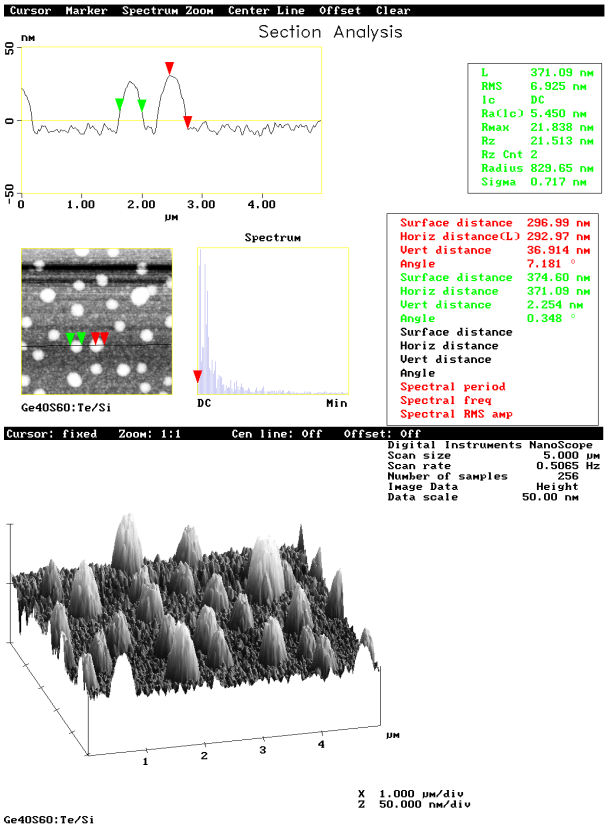

Fig. 10. Axonometric image and sectional analysis of the gradient film surface ⟨Ge_2S_3:Te⟩ (Te – 30.7 at.%).

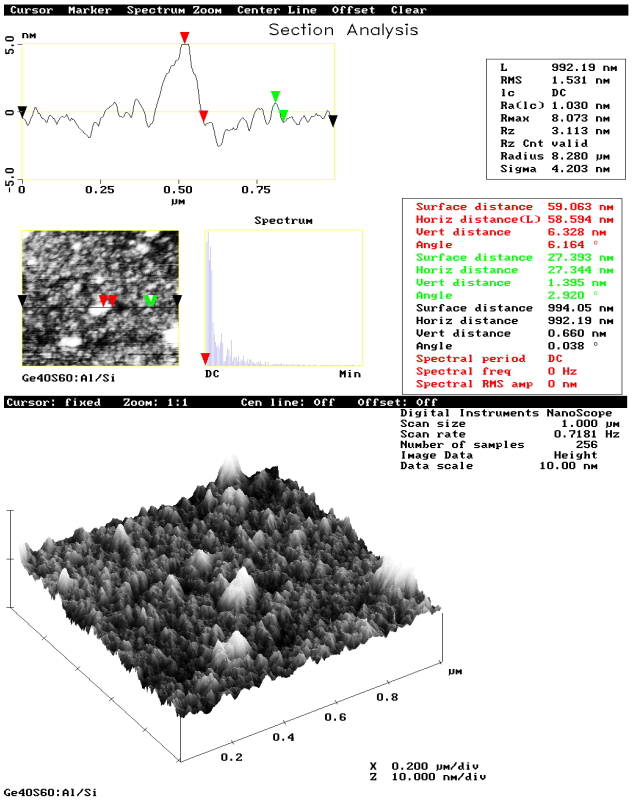

Fig. 11. Axonometric image and sectional analysis of the gradient film surface ⟨Ge_2S_3:Al⟩ (Al – 2 at.%).

7. Conclusions

Computer simulation of the source of the atomic flow of the modifier has been carried out, which makes it possible to form gradient structures with the predicted distribution of chemical elements accord to the film thickness. The equations describing formation of inhomogeneous amorphous structures and taking into account the dynamics of the number of modifier particles owing to the source of the atomic flow of a chemical element, structural heterogeneity (availability of vacancies, micropores and particle diffusion) have been obtained.

The criteria for formation of an inhomogeneous structure on the basis of vitreous Ge_2S_3 with modifiers Al, Bi, Pb, Te that are identified due to changes in the condensed medium (evaporation temperature, condensation velocity, increasing or decreasing the intensity of the fluctuations of the active fields) have been investigated. The possibility of obtaining qualitative modified gradient structures with a given distribution of components by the method of thermal deposition in vacuum and the possibility of studying the concentration thickness distribution by using mass spectrometry of post-ionized neutral particles has been shown.

The mechanism of interaction of the selected chemical modifiers (Al, Bi, Pb, Te) of the determined maximum concentration with the glassy matrix Ge_2 S_3 has been established. Morphology of the surfaces of the gradient structures Ge_2S_3:X (X = Al, Bi, Pb, Te) has also been investigated. It has been found that the film surfaces are quite smooth, *i.e.*, reflection of light from them can be described on the basis of the scattering theory of Kirchhoff's diffraction.

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