A MODEL OF THE FORMATION OF INHOMOGENEOUS MODIFIED STRUCTURES ON THE BASIS OF GLASSY Ge_2S_3

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The computer simulation of the formation of inhomogeneous modified structures based on glassy Ge_2S_3 with given concentration gradient over the thickness has been carried out. Both technological conditions and the atomic flow source of a modifier are taken into account. The formation of an inhomogeneous gradient structure is described by nonlinear differential equations which take into account the dynamics of the number of particles of the modifier at the expense of the atomic flow source, structural inhomogeneity (the presence of vacancies and micropores), and diffusion of particles.

Introduction

Because of the growing demands of science and technology, researchers have to create noncrystalline materials with structural-sensitive characteristics. To solve this problem, a fundamental research with the use of computer simulation should be developed. From this point of view, investigations of the formation of dissipative structures in frames of the synergetic approach and their practical application for noncrystalline materials are of long and permanent interest [1—4]. Dissipative structures of noncrystalline solids are defined as a way of self-organization of a system which is realized according to the production conditions through both a nonlinear interaction with the technological medium and the effect of external fields. Structural units of noncrystalline materials are considered as a result of the self-organization of a condensed medium on the corresponding levels (short- and middle- (mesoscopic) range orderings), and the hierarchy of levels (or "quantum stairs") is also as a result of the previous self-organization. The spatial correlation region of physical parameters and the life time of a dissipative structure are the quantitative characteristics of each level. By the given approach, it is possible to investigate models of the formation of dissipative structures in chalcogenide glasses [4] and in the film structures with composition gradient based on glassy germanium chalcogenides.

1. Concentration Dependence and Inhomogeneous Distribution of Modified Structures on the Basis of Glassy Ge_2S_3

Let us consider the system which contains N particles (atoms, molecules). In this system, N_{mod} particles are components of a modifier (atoms of metals Al, Bi, etc.), and N_{mat} particles are components of the matrix (elements of glassy Ge_2S_3). The process of formation of an amorphous state C can be described by the following physical chemical reaction:

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

Here, the symbol $A(L)$ identifies components of a modifier in the spatial region which consists of L particles (here and below, we treat the size of a region as the number of particles), B — components of the matrix (Fig. 1). Reactions (1) foresee that the region grows or diminishes (rates $k^+(L)$ and $k^-(L)$, respectively) by joining or the separation of some modifier particles in the matrix [5]. The behaviour of the ensemble of regions of size L in time will be described by the size distribution function $g(L,\vec{r},t)$, where $\vec{r}=\vec{r}(x,y,z)$ — radius vector, whose spatial coordinate z is perpendicular to the plane (x,y).

The dynamics of changes in the distribution function $g(L,\vec{r},t)$ is described by the Fokker—Planck equation [5—7]

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

where $I(L,t) = V(L)g(L,\vec{r},t) - \frac{\partial}{\partial L}(D(L)g(L,\vec{r},t))$ — flux, whose density is defined by the evaporation rate of components, $V(L) = k^+(L) - k^-(L)$ and $D(L) = (k^+(L)+k^-(L))/2$ are the growth rates and the diffusion coefficient in the configuration space. The initial and

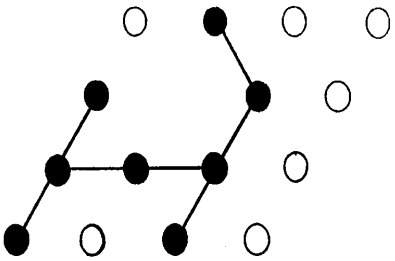

Fig. 1. Formation of the amorphous layer in the case of a matrix with $N = 15$ (lines between atoms of modifier mark the region with$L = 8$). Open symbols — matrix components, black ones — modifier components

boundary conditions are: $\partial g(L,\vec{r},t)/\partial L|_{z=0} = 0, g(L = 1,\vec{r},t = 0) = \rho_s$, $\sum\limits_L g(L,\vec{r},t = 0) = 1$ (ρ_s — density of dislocations, micropores). So, the Eq. (2) can be rewritten as

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

Here, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial z^2}$ – Laplace operator in the cylindrical coordinate system(ρ,φ,z). We approximate the growth velocity of regions by the expression $V(L) = (D_a/L)N_{\text{mod}}$, ($D_a = D/a^2$, a — interatomic distance, D — diffusion coefficient of particles) and describe diffusion in the configuration space by $D(L) = \beta_0/L^2$ (β_0 — diffusion constant). For metals Al and Bi, the diffusion coefficient $D = 10^{-10} \div 10^{-15}$ cm^2/s depending on the temperature, $\beta_0 \approx 0.2$ and $a = (2 \div 4)\cdot 10^{-8}$ cm [8].

Let us consider the dynamics of changes in the number of particles N_{mod} of a modifier of the system under the action of a source G for time τ_p. A change of the number of particles in the size range $L, L + dL$ is determined by the expression $V(L)g(L,\vec{r},t)$, and the full number of particles is $4\pi\int\limits_0^\infty L^2 V\left(L\right)g\left(L,\vec{r},t\right)dL$. The atomic flow of particles can change with time according to a certain law (in this case, we consider the exponential law of changes)

$$G = g_{\text{source}}\exp(-mz) \tag{3}$$

where g_{source} and m are constants of a source of particles (here, we have taken into account the transition from the dependence on time t to that on the z coordinate according to the expression $t \Rightarrow z/V$, V is the of layer growth rate). So, the dynamics of change in the number of particles is defined by the equation

$$\frac{\partial N_{\text{mod}}}{\partial t} = G - 4\pi\int\limits_0^\infty L^2 V\left(L\right)g\left(L,\vec{r},t\right)dL + D_a\nabla^2 N_{\text{mod}}. \tag{4}$$

The continuity equation is $N_{\text{mod}}|_{z=0} = N_{\text{mod}s}$, $\frac{\partial N_{\text{mod}}}{\partial z}|_{z=0} = 0$, $\frac{\partial N_{\text{mod}}}{\partial z}|_{z=d} = 0$ (d — thickness of a layer).

The first term in (4) determines a change in the number of modifier's components at the expense of the molecular flow source, the second one — at the expense of structure inhomogenity (due to vacancies and micropores), the third one — at the expense of diffusion of particles. By the Eqs. (2) and (4), we can describe the dynamics of the system. Let us consider the situations with homogeneous and inhomogeneous sources.

Equations (2) and (4) in the stationary case ($\partial N_{\text{mod}}/\partial t = 0$, $\partial g/\partial t = 0$) become

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

$$g_{\text{source}}\exp(-mz) -$$

$$-4\pi\int\limits_0^\infty L^2 V_s\left(L\right)g_s\left(L,\vec{r},t\right)dL + D_a\nabla^2 N_{\text{mod}s} = 0. \tag{5}$$

Stationary solutions of Eq. (5) in the homogeneous case ($G = g_{\text{source}}$) are determined by the expressions

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

$$g_s^{\text{hom}} = \rho_s\bar{L}\delta(L - \bar{L}). \tag{6}$$

In the inhomogeneous case, $G = g_{\text{source}}\exp(-mz)$. Taking into account that $\varphi = \text{const}$ and solutions of the equation $N_{\text{mod}}, g \approx R(\rho)Z(z)$, we obtain

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

$$\gamma^2 = (4\pi\rho_s\bar{L}^2 D_a N_{\text{mod}s}^{\text{hom}} - G)/D_a. \tag{7}$$

Equations (7) describe the formation of amorphous structures which are inhomogeneous in thickness. In particular, the inhomogeneous distribution of modifier's components along z determines forming a structure with a gradient of the distribution function of modifier's regions over sizes on space scales of the order of $1/\gamma$.

In this case, the atomic flow of the modifier can be described as [9, 10]

$$G_N = 3.513\cdot 10^{22}\frac{a_1 P_e}{\sqrt{M_e T_e}}, \quad \text{cm}^{-2}\text{s}^{-1}, \tag{8}$$

where P_e — equilibrium pressure of saturated vapours of the evaporated substance (Al, Bi, Pb, and Te), $P_e \approx 10^{-4}$ Torr, a_1 — evaporation coefficient (in the case of the clean surface of an evaporated substance, $a_1 = 1$), M_e — molecular weight of the evaporated elements–modifiers, and T_e — evaporation temperature. To allow molecules of vapour to freely evaporate, the pressure P_e should not exceed 10^{-2} Torr, and the evaporator area should be not more than few squared centimetres (in our case, the evaporator area depends on a modifier type and is about 10^{-4} cm^2).

For the determination of the parameter m of the inhomogeneous source of modifier's atomic flow [see Eq. (3)] we use the following approximation. At the initial moment of time $t = 0$, let the source of modifier's atomic flow be determined by the evaporation temperature of the modifier, $G_1 = G_1(T_\mathrm{e})$. During the time interval $t = t_m$ under the evaporation temperature change from T_e to T, the modifier's atomic flow source is $G_2(T) = G_1(T_\mathrm{e})e^{-mt_m}$. Hence, we can determine the parameter m as

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

Taking into account relation (8), we obtain

$$m = \frac{1}{2t_m} \ln \frac{T}{T_\mathrm{e}}, \quad \mathrm{s}^{-1}. \qquad (9)$$

By relations (7)—(9), we calculated the distribution of modifier's Bi atoms across the film.

Fig.2 shows the variation in the number of Bi atoms calculated by (7) under the action of the atomic flow source for periods ($t_{m1} \div t_{m4}$), during which temperature is changed from T_e to T.

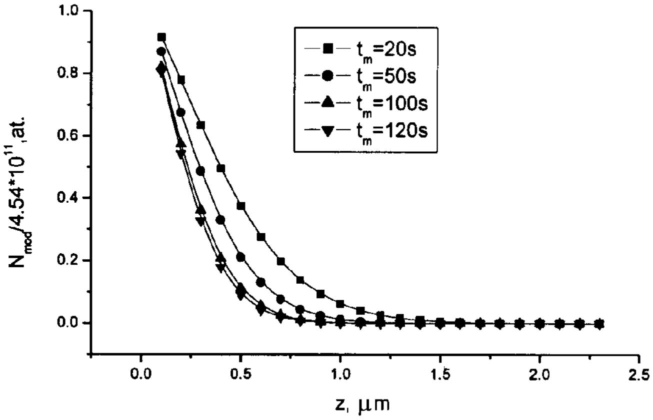

Fig. 2. The change of modifier distribution at temperature change for Bi from T_e=750 °C to T = 730 °C for time intervals t_m (t_{m1}=20 s, m_1=0.27029, g_1=2.786·10^{11}; t_{m2}=50 s, m_2=0.67572, g_2=2.786·10^{11}; t_{m3}=100 s, m_3=1.35143, g_3=2.786·10^{11}; t_{m4}=120 s, m_4=1.62172, g_4=2.786·10^{11})

2. Calculation of the Distribution of Modified Structures and Comparison with Experimental Data.

Gradient films based on glassy Ge_2S_3 with modifiers (Al, Bi, Pb, and Te) were obtained by discrete thermal evaporation in vacuum [11] using the results of the computer simulation. Forming a gradient film was carried out by simultaneous evaporation of both the Ge_2S_3 matrix content in the stationary regime and a modifier. Glassy Ge_2S_3 was evaporated from a Knudsen effusive cell at a constant temperature of the evaporator. Developed effusive cells ensured the constancy of a stoichiometric composition of the initial material and film. By varying the control parameters (the temperature of evaporation and the condensation rate), the necessary flow of a modifying component was created. The dynamics of the number of particles of modifier's components N_mod under the operation of the inhomogeneous source of an atomic flow G [see formula (3)] provided the necessary distribution of a modifier over the thickness of a deposited film. Depending on the evaporator temperature, the structure growth rate was in the range from 2 to 7 Å/s. Investigated films were deposited on glass and silicon substrates.

As an initial material, we used chalcogenide glass Ge_2S_3 prepared from chemically pure Ge of B-6 grade and from chemically pure S 17—4 grade which were synthesised by fusion of the elementary components.

In the Table, the technological parameters of the production of modified structures (condensation rate, evaporation temperature, and thickness) and fluctuations of the condensation rate σ_e and the vaporization temperature σ_T of the layer are presented.

For the experimental data on the concentration distribution of components across the film thickness of Ge_2S_3:Bi (Bi—14 at.%) [11] by taking into account Eqs. (7) which describe the formation of the gradient

Technological parameters of the production of modified structures

Composition	Thickness d, microns	Condensation rate v, Å/s	σ_e, Å/s	T_e, °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

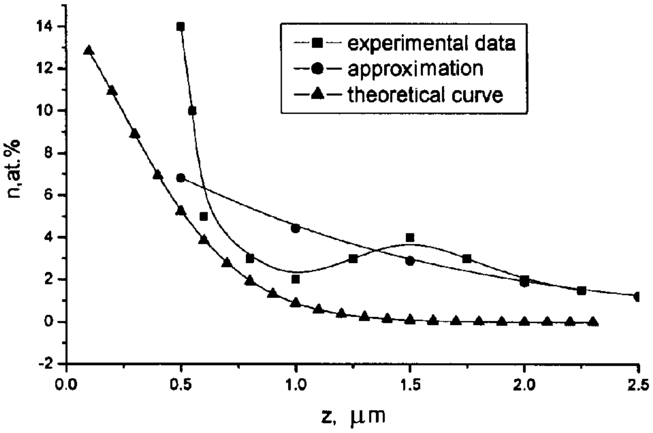

Fig. 3. Concentration distribution of the modifier (Bi — 14at.%) over the Ge_2S_3:Bi film thickness

structures inhomogeneous in thethickness, we used the two-parameter approximation $y = g_0 e^{-m_0 z}$ of experimental curves and estimated the parameters m_0 and g_0.

As a result of the calculations for a Ge_2S_3:Bi gradient film, we have obtained the following values of the parameters: $m_0 = 0.85772; g_0 = 10.47423$.

In Fig. 3, the dependence of the atomic distribution of the modifier Bi (14 at.%) over the Ge_2S_3:Bi film thickness, calculated from relations (7)—(9) (theoretical curve), is depicted. Also you can see both the approximation of the distribution by a two-parameter dependence (approximation curve) and the experimental curve obtained by mass-spectrometry of post-ionized neutral particles (experimental curve) [11]. As is seen from Fig. 3, a satisfactory approximation by the two-parameter exponential distribution of a modifier over the film thickness is observed. So, the given approach to the calculation of the distribution of changes in the number of Bi and the constants m_0 i g_0 allows us to verify and compare the obtained experimental distribution of a modifier over the film thickness and to estimate constants of the necessary distribution with desired accuracy.

Thus, the developed computer model of formation of inhomogeneous gradient structures based on glassy Ge_2S_3 takes into account the technological conditions of the production and allows obtaining structures with a predefined distribution of components.

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МОДЕЛЬ ФОРМУВАННЯ НЕОДНОРІДНИХ МОДИФІКОВАНИХ СТРУКТУР НА ОСНОВІ СКЛОПОДІБНОГО Ge_2S_3

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Резюме

Проведено комп'ютерне моделювання формування неоднорідних модифікованих структур із заданим градієнтом концентрації по товщині на основі склоподібного Ge_2S_3, яке враховує технологічні режими одержання та джерело атомного потоку модифікатора. Формування неоднорідної градієнтної структури описано нелінійними диференціальними рівняннями, які враховують динаміку числа частинок компонент модифікатора за рахунок джерела атомного потоку, структурну неоднорідність (наявність вакансій, мікропор) та дифузію частинок.