Kovove Mater. 61 2023 175–188
DOI: 10.31577/km.2023.3.175

The resonance between the mixing energy and the elastic strain energy as the reason for the composition modulation effect appearance during the spinodal decomposition of GaInPAs solid solutions

Pavel Moskvin[1], Sergii Skurativskyi[2]*

[1] *Zhytomyr Polytechnic State University, Zhytomyr, 103, Chudnivska str. 10005, Ukraine*
[2] *The Institute of Environmental Geochemistry of National Academy of Sciences of Ukraine, Kyiv, Academician Palladin Ave. 34A, Ukraine*

Received 9 April 2022, received in revised form 11 March 2023, accepted 28 March 2023

Abstract

In the research, to describe the spinodal decomposition of A^3B^5 semiconductor solid solutions, in which the substitution of the main components occurs simultaneously in each of the sublattices of the sphalerite crystal structure, the Cahn-Hilliard concepts are extended. The resulting system of differential equations is applied to describe the effect of composition modulation in $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solutions grown on InP substrates. In this case, the elastic deformation energy of a thin layer of $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution is calculated on the assumption of its coherent conjugation with a massive InP substrate. The excess mixing energy of the components in the solid phase is evaluated in accordance with the simple solution model. The temperature-concentration ranges, in which the conditions for the occurrence of an oscillatory mode of relaxation of the supersaturated metastable state of the solid phase are realized, are found by analyzing phase portraits of the system. The performed analysis shows that the effect of modulation of the material composition is connected with the resonance of total entire excess energy and elastic energy. The parameters of the oscillatory process are compared with data on the effect of composition stabilization, which is experimentally observed in the growth of elastically stressed heterostructures $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ – InP substrate.

Key words: semiconducting III-V materials, solid solutions, phase equilibrium, spinodal decomposition, stresses, crystal structure

1. Introduction

To improve the operational characteristics of semiconductor modern optoelectronics devices, it is necessary to use ultra-thin layers of material in them with increased structural perfection. At present, A^3B^5 quaternary solid solutions are used as the material for the active layer of an optoelectronic device based on a heterojunction. An increase in the number of components in the solid solution made it possible to independently control both the crystallographic and optical parameters of the heterostructure. This promoted the creation of highly efficient optoelectronic devices based on heterojunctions with properties of the perfect interface.

At the same time, the decrease of the layers' growth temperature is limited by the possibility of the figurative point leaving the region of the primary crystallization of the solid solution as it moves along the phase diagram during the growth process. This statement becomes especially relevant for multicomponent materials in accordance with the following thermodynamic considerations. Indeed, an increase in the number of components in a solid solution inevitably leads to a decrease of the size of the primary crystallization phase space on the multidi-

---

*Corresponding author: e-mail address: skurserg@gmail.com

mensional state diagram of the multicomponent system.

Indeed, the total number of mole (atomic) fractions of the initial components of the multicomponent system is equal to one. For binary systems, this number of mole fractions of a substance is distributed between the two initial components of the system. As the number of components in the system increases, the same unit is distributed over more and more components. In this case, the composition of the phases (concentration axis) on the state diagram from the line for a binary system is transformed into a triangle for a ternary system, for a quaternary system – into a tetrahedron, and so on.

However, for all types of geometric interpretations for the concentration space of phase diagrams, the sum of the lengths of the sides of the spatial figures describing the composition of the solution in accordance with the normalization condition for mole fractions is equal to one. As a result, it turns out that the sizes of possible areas of change in concentrations for each component, at which the existence of the required phase is ensured, decrease. This reasoning is a theoretical substantiation of the well-known requirement in practice to increase the accuracy of controlling the composition of the initial growth medium and other parameters of the technological process when obtaining multicomponent solid solutions with specified parameters.

An increase in the number of solid solution components leads to an increase in the number of thermodynamic degrees of freedom in the growth system. Therefore, in the case of the decomposition processes in multicomponent systems, the stated problem is formulated as a problem touching upon the influence of an increase in the degrees of freedom of the system on the process of spinodal decomposition in unstable multicomponent materials. The answer to the question about such an effect is difficult to find experimentally because of the need to conduct a large number of precision experiments. The use of theoretical models for this and the implementation of numerical simulations on their basis will allow us to evaluate the influence of this factor on the process of spinodal decomposition of the A^3B^5 multicomponent solid solutions.

The transition of the system to the region of thermodynamic instability of the phase is accompanied by its spinodal decomposition, which often results in the formation of a structure with micro-fluctuations in the solid solution composition. Such oscillations were found experimentally in ternary and quaternary A^3B^5 solid solutions. This effect is known as the effect of modulation of the solid solution composition [1–4]. The appearance of inclusions of new phases leads to a change in the optoelectronic properties of the hetero-composition. According to the data of [4], these oscillations of the composition appearing in the $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solutions grown on the InP substrate at temperatures below 600 ℃ were responsible for the decrease of the charge carriers' mobility in the material. An increase in the synthesis temperature brought the growth system out of the region of thermodynamic instability of the solid phase, eliminated its spinodal decomposition, and ensured the growth of the material with a composition constant over the layer. The latter increased the crystallographic perfection of the layer due to the departure of the system from the state of spinodal decomposition. In this case, the effect of the mechanism of scattering of charge carriers on the inhomogeneities of the composition of the solid solution became insignificant. This explained the increase in the mobility of charge carriers in layers grown at higher temperatures.

The processes accompanying spinodal decay led to the formation of a structure that is periodic in composition and optoelectronic properties. Such a structure with a superlattice is formed naturally and can have unique electrical and optical parameters [1, 3, 5, 6]. This stimulates a theoretical analysis of the process of its formation. Moreover, the purpose of such modeling is to find methods for controlling the amplitude and period of these oscillations when creating a composition-modulated structure for optoelectronic devices.

The possibility of realizing such a situation in ternary and quaternary A^3B^5 systems was analyzed in several theoretical works [3, 5–9]. The results of these theoretical studies were confirmed in the description of experimental data on composition modulation effect in A^3B^5 ternary and quaternary solid solutions. The use of the analytical method to describe this effect in ternary solutions made it possible to explain the appearance of micro-oscillations in the composition of the layers [3, 5, 6]. A direct numerical solution of the Cahn-Hilliard spinodal decomposition equation made it possible to show that the phenomenon of resonance between the mixing energy of the components and the energy of elastically deformed inclusions of a new solid phase into which the material decomposes is responsible [7–9]. This effect is responsible for a significant increase in the amplitude of oscillations in the composition of the material to a value that can be experimentally detected.

Among A^3B^5 quaternary solid solutions, the $Ga_xIn_{1-x}P_yAs_{1-y}$ system occupies a special place. The thermodynamic properties and technological processes of its production are now thoroughly studied. One of the main features of these materials is the fact that, under the most typical temperature conditions of the growth process, the most important compositions of these materials are located in close proximity to the decomposition spinodals on the phase state diagram of the system [1, 9–12]. According to the theoretical data of many authors, the lattice-matched conditions of $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solutions to InP substrates pass most closely near the spinodal surface when the material composition is designed to operate at a wavelength of 1.4 mkm. At the same time, the compositions of material most important in practical terms, used in optoelectronic devices for fiber-optic communication lines, operate at 1.3 and 1.55 mkm wavelengths. For such compositions of the material and at typical temperatures of their synthesis, the thermodynamic situation in the system is very close or even lies within the boundaries of absolute phase instability. Obviously, a further decrease in the growth temperature will inevitably aggravate the situation with the thermodynamic stability of the material. It should also be noted that, due to the practical importance of the indicated compositions of these solid solutions, the technological processes for obtaining the material and its properties in this range of compositions have been studied quite intensively by researchers. This made it possible to detect micro-oscillations in the composition of the solid solution, i.e., the composition modulation effect for this class of materials.

The assertions mentioned above allow one to form the main purposes of the theoretical studies of the process of spinodal decomposition of $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ quaternary semiconductor solid solutions:

– to extend the approach of Cahn and Hilliard to the description of the process of spinodal decomposition of $\mathrm{A}^3\mathrm{B}^5$ quaternary solid solutions;

– using this extension and the model of simple solutions to obtain the system of differential equations describing the spinodal phase decomposition;

– to perform an analysis of equations to state the thermodynamic conditions under which the system of equations possesses periodic solutions;

– under the conditions of the existence of periodic solutions of equations to simulate the effect of composition modulation of the solid solution, which occurs due to the spinodal decomposition of the material.

Thus, we start from the derivation of a system of differential equations for the decomposition of quaternary solid solution, in which the substitution of components is carried out both in the metallic and in the metalloid sublattices of the sphalerite structure.

2. Adaptation of the Cahn-Hilliard equations to the description of the spinodal decomposition of A^{3}B^5 semiconductor quaternary solid solutions

For the thermodynamic description of the process of spinodal decomposition, we used the approach developed by Cahn and Hilliard [13, 14]. The adaptation of the Cahn-Hilliard decomposition equation for the thermodynamic description of the process of spinodal decomposition of quaternary solid solutions of semiconductors was carried out in the following way:

Let us consider the process of spinodal decomposition as a process occurring in two energetically weakly coupled subsystems, which are created by the metallic and metalloid sublattices of the sphalerite structure. Then the variations in the composition of the solid solution in each sublattice can be related to the change in the free energy of the entire solid phase. In this situation, the final (stationary) composition distribution in each sublattice obeys the following system of differential equations [9, 15]:

$$\begin{aligned} \frac{\partial G\left(x,y\right)}{\partial x} - \beta_1 \frac{\mathrm{d}^2 x}{\mathrm{d}z^2} - \mu_1 = 0, \\ \frac{\partial G\left(x,y\right)}{\partial x} - \beta_2 \frac{\mathrm{d}^2 y}{\mathrm{d}z^2} - \mu_2 = 0, \end{aligned} \tag{1}$$

where $G(x,y)$ is the Gibbs free energy of a quaternary solid phase depending on the current composition x, y, the parameters β_1 and β_2 stand for expansion coefficients in a power series of the Gibbs free energy in a compositionally inhomogeneous solid solution [13, 14], and z is the coordinate along the selected crystallographic direction in the solid solution crystal.

The presented Eqs. (1) were obtained by mathematical transformations, which are described in detail in [6]. The difference between the above formulas is that they form a coupled system of equations that describe variations in the composition of a decomposing solid solution in two sublattices of the sphalerite crystal structure. The quantities μ_1 and μ_2 represent the constants of integration of the Cahn-Hilliard equations for the stationary state. They are interpreted in [16] as chemical potentials in the corresponding sublattice (subsystem) of the solid phase crystallizing in the sphalerite structure.

To apply these equations to the description of the process of spinodal decomposition, an analytical form of the dependence of the excess Gibbs energy on the composition of the material is required.

The most fruitful method for describing the energy state of the solid phase of $\mathrm{A}^3\mathrm{B}^5$ semiconductors is based on the model of simple solutions. According to these concepts, the excess energy of the quaternary solid phase with simultaneous substitution of components in two sublattices of the sphalerite structure is written in the form [17]:

$$\begin{aligned} G^{\mathrm{m}} = RT[x\ln x + y\ln y + (1-x)\ln(1-x) + \\ (1-y)\ln(1-y)] + \alpha_{12}^{\mathrm{S}}x(1-x) + \\ \alpha_{34}^{\mathrm{S}}y(1-y) + \alpha_{\mathrm{C}}xy, \end{aligned} \tag{2}$$

where α_{12}^{S} and α_{34}^{S} are reduced mixing energies (interaction parameters) between metallic and metalloid components in the corresponding sublattices of the sphalerite structure, α_{C} is the combination of energies of pair interactions between nearest tetrahedrally coordinated atoms located in different sublattices, R

and T are the gas constant and temperature, respectively.

According to the simple solution model, the parameter α_C can be evaluated via the formula [17]:

$$\begin{aligned}\alpha_\mathrm{C} = \Delta S_{14}^\mathrm{F}(T_{14}^\mathrm{F} - T) + \Delta S_{23}^\mathrm{F}(T_{23}^\mathrm{F} - T) - \\ \Delta S_{13}^\mathrm{F}(T_{13}^\mathrm{F} - T) - \Delta S_{24}^\mathrm{F}(T_{24}^\mathrm{F} - T) + \\ 0.5(\alpha_{13}^\mathrm{l} + \alpha_{24}^\mathrm{l} - \alpha_{23}^\mathrm{l} - \alpha_{14}^\mathrm{l}),\end{aligned} \tag{3}$$

where ΔS_{ij}^F and T_{ij}^F stand for the entropy and melting point of the compound ij being a part of the solid solution; α_{ij}^l are the parameters of interaction between the components ij of a binary compound in the liquid phase.

In Eq. (3), as applied to the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution, the following indexing is used: Ga – 1; In – 2; P – 3; As – 4.

To calculate the component of energy of solid-phase interaction α_C in expression (2), its relationship with the melting parameters of the corresponding compounds is used. Despite the fact that the vast majority of modern technologies for the synthesis of solid solutions of the $\mathrm{A}^3\mathrm{B}^5$ system involve crystallization from a gas phase, the use of thermodynamic functions describing the process of material melting in the problem under consideration seems to be justified. The main reason for this approach is that the thermodynamic data on the description of the interaction of components in the liquid phase are found with significantly higher reliability than similar parameters for synthesis reactions from the gas phase [17, 18].

It is worth noting that the energy of interchange between atoms of metallic components depends on the composition of the nonmetallic sublattice and vice versa. To take this effect into account in the quaternary system $\mathrm{A}_x\mathrm{B}_y\mathrm{C}_{1-x}\mathrm{D}_y$, the parameters α_{ij}^S should be considered as linear functions of the composition [17]:

$$\begin{aligned}\alpha_{12}^\mathrm{S} = y\alpha_\mathrm{AC-BC}^\mathrm{S} + (1-y)\alpha_\mathrm{AD-BD}, \\ \alpha_{34}^\mathrm{S} = x\alpha_\mathrm{AC-AD}^\mathrm{S} + (1-x)\alpha_\mathrm{BC-BD}.\end{aligned} \tag{4}$$

This approach allowed one to successfully simulate the energy state of the solid phase and quite satisfactorily describe p-T-X phase equilibria not only in $\mathrm{A}^3\mathrm{B}^5$ multicomponent systems, but also in $\mathrm{A}^2\mathrm{B}^6$ systems [18–21].

The consequence of spinodal decomposition is the appearance in the parent lattice of inclusions of a new phase, crystal lattice parameter (CLP), which differs from the CLP of the original material's matrix. The resulting elastic energy of coherently conjugated phases is taken into account in the expression for the total energy balance of the system. To calculate this component of the energy of the solid phase, the expressions from [3, 18] are used, where they were obtained for different crystallographic orientations of coherently conjugated layers.

Since the effect of composition modulation in layers of $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solutions grown on an InP (111) substrate will be simulated in this work, the expression for calculating the molar energy for a layer of the indicated crystallographic orientation is given only:

$$\begin{aligned}G^\mathrm{el} &= \frac{6C_{44}(C_{11} + 2C_{12})}{C_{11} + 2C_{12} + 4C_{44}} N_0 \frac{a(a - a_\mathrm{S})^2}{4} \\ &= \lambda_{111}\frac{a(a - a_\mathrm{S})^2}{4},\end{aligned} \tag{5}$$

where C_{ij} are elastic moduli, a and a_S are current and averaged CLP of the layer (CLP of the initial matrix of the solid solution or CLP of the substrate, depending on the conditions of coherent phase conjugation in the structure), N_0 is Avogadro's number, and λ_{111} is the combination of elastic moduli for a given layer orientation [3, 18].

Thus, the joint consideration of the mixing energy of the components and the energy of elastically stressed precipitates of a new phase allows us to arrive at the following form of stationary equations for the analysis of concentration fields after a spinodal decomposition:

$$\begin{aligned}\beta_1\frac{\mathrm{d}^2x}{\mathrm{d}z^2} &= RT[x\ln x + (1-x)\ln(1-x)] + \\ &\quad \alpha_{12}^\mathrm{S}x(1-x) + \alpha_\mathrm{C}xy + \\ &\quad \lambda_{ijk}a(a-a_\mathrm{S})^2/4 - \mu_1 = F_1(x,y), \\ \beta_2\frac{\mathrm{d}^2y}{\mathrm{d}z^2} &= RT[y\ln y + (1-y)\ln(1-y)] + \\ &\quad \alpha_{34}^\mathrm{S}y(1-y) + \alpha_\mathrm{C}xy + \\ &\quad \lambda_{ijk}a(a-a_\mathrm{S})^2/4 - \mu_2 = F_2(x,y).\end{aligned} \tag{6}$$

To close the problem, we take into account the relations for the average concentration of each of the components in the corresponding sublattice of the quaternary solid solution:

$$\begin{aligned}\bar{x} = \frac{1}{L}\int_0^L x(z)\mathrm{d}z, \\ \bar{y} = \frac{1}{L}\int_0^L y(z)\mathrm{d}z,\end{aligned} \tag{7}$$

where L is the period of composition variation.

The last equations are the consequence of the mass conservation laws during the redistribution of components after the decomposition of a supersaturated solid phase.

The final formulation of the problem under consideration for calculating the distribution of the composition of a solid solution over the thickness of the

Table 1. Crystal lattice parameters of the initial binary compounds of $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solution at $T = 298$ K and thermodynamic parameters of binary and ternary systems forming the Ga-In-P-As system [3, 18]

Compound	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	CLP (mm)	T^F (K)	ΔS^F_{ij} (J mole^{-1} K^{-1})	α^l_{ij} (J mole^{-1})
GaP	141.2	62.6	70.5	0.54509	1740	72.4	8876–18.6 T
InP	102.2	57.6	46.0	0.58688	1511	69.67	21604–38.35 T
GaAs	118.1	53.2	59.4	0.565325	1343	63.64	19963–20.14 T
InAs	83.3	45.3	39.6	0.60586	1215	60.80	16161–41.87 T
				α^S_{i-j} (kJ mole^{-1})			
$\alpha^S_{GaP-GaAs}$		1.67		$\alpha^S_{InP-InAs}$		1.67	
$\alpha^S_{GaP-InP}$		14.65		$\alpha^S_{GaAs-InAs}$		12.56	

deposited layer assumes the choice of boundary conditions.

The classical boundary conditions for such problems are the conditions that determine the values of the initial concentration of each component and the value of its derivative at the point $z = 0$.

The choice of the initial content of the component in the solid solution will make it possible to set the concentration interval in which the solution of the boundary value problem will be searched. The values of the derivatives $\frac{dx}{dz}(z = 0) = 0$ define the point's position for which the value of the initial concentration of the component is set. If we assume that the value of the desired derivative is equal to zero, then this will mean that the maximum possible deviation of the composition of the solid solution from its average value is set at the boundary. Following the above considerations, the final formulation of the boundary value problem includes the following additional conditions:

$$\begin{aligned} x_{\text{boundary}} &= x_0 = \text{const}, \\ y_{\text{boundary}} &= y_0 = \text{const}, \\ \frac{dx}{dz_{(z=0)}} &= \frac{dy}{dz_{(z=0)}} = 0. \end{aligned} \tag{8}$$

Thus, differential Eq. (6) with boundary conditions (Eq. (8)) and mass conservation laws (Eq. (7)) form a boundary value problem that completely characterizes the redistribution of the composition in quaternary semiconductor substitutional solid solutions of class A^3B^5, which are synthesized under thermodynamic conditions close to the boundary of the material spinodal decomposition.

The relations derived for calculating the redistribution of components over corresponding sublattices of the solid solution are a system of integro-differential nonlinear equations. This problem's formulation makes it quite complex and interrelated. Therefore, this system of equations is solved using numerical methods. Issues related to the development of a mathematical tool for solving the problem are given special attention in the work.

3. Initial thermodynamic parameters for modeling

From the thermodynamic assertions presented above, it follows that the distribution of the concentration of components over the layer of the solid solution after its spinodal decomposition is determined by the set of excess mixing energies of the components in the solid phase α^S_{ij}, the parameter α_C and elastic parameters of the solid solution matrix, i.e., elastic constants C_{ij}.

Thermodynamic parameters and the elastic constants, used at modeling, for the initial semiconductor compounds forming $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solutions are presented in Table 1. The elastic parameters of the solid solution and CLP for each of its current compositions are modeled using linear approximations written for each of the material parameters.

An important stage in solving the problem is taking into account the temperature dependences of all parameters. The available data on their changes with temperature show that the variations of the indicated parameters of the material do not exceed a few percent in the transition from synthesis temperatures to room temperature [10, 18]. Taking into account the existing inaccuracy both in the experimental determination of the parameter values and their temperature coefficients, it was decided in the research to neglect the change in the values with temperature and use their values at room temperature in the analysis.

The data on the melting temperatures and entropies of the initial compounds and the parameters of the liquid-phase interaction for the components of their constituents are generally well-known. The data on these parameters, which were obtained by various authors, are in good correlation with each other. This serves as a justification for their use in the thermodynamic calculations of these studies.

The choice of the parameters α^{S} of the solid-phase interaction between the main components of the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution is fundamentally important.

These parameters characterize the excess mixing energy in the solid phase and is closely related to the critical temperature of spinodal decomposition and the position of the unstable regions boundaries on the composition-temperature diagram [3, 22, 23]. At the same time, the position of these boundaries is determined by the intervals of thermodynamic parameters, where the application of this analysis is justified, and the results of its application are the most informative.

As a rule, these parameters and their temperature dependence are found by processing data on phase equilibria in the system. For the most important temperature ranges, where the spinodal decomposition of solid solutions is most probable, the values of the interaction parameters averaged for these temperatures were used in the calculations. This means that the energy state of the solid phase is modeled by the strictly regular approximation of the simple solution theory. The use of parameters found from averaging over a wide temperature range up to the melting temperature of the initial compounds for modeling the thermodynamic situation in the low-temperature part of the phase diagram cannot be considered justified. The use of interaction energies for their averaging over such a wide range often leads to unreasonably sharp temperature dependences, which are difficult to physically interpret. Therefore, in subsequent calculations, the solid-phase interaction parameters from [10] were used, which are presented in Table 1 and satisfy the specified requirement.

The value of the critical temperature of decomposition of the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution corresponding to the accepted interaction parameters was $T_{\mathrm{c}} = 1156\,\mathrm{K}$ with the composition of the material $x_{\mathrm{c}} = 0.515$ mol.fr and $y_{\mathrm{c}} = 0.55$ mol.fr.

The results of calculations of the critical temperature value clearly confirm the previously stated statement that for $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solutions lattice matched to the InP substrate, the thermodynamic conditions of layer growth turn out to be very close to the boundaries of the unstable state of the solid phase.

According to the experience of modeling the process of spinodal decomposition in the system $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$, when choosing the intervals of the system parameters for calculations, special attention should be paid to the parameters that are located near the spinodal line. It is for these compositions the experimental observations of the solid solution composition modulation effect are most probable. The theoretical justification for such an assertion will be discussed further.

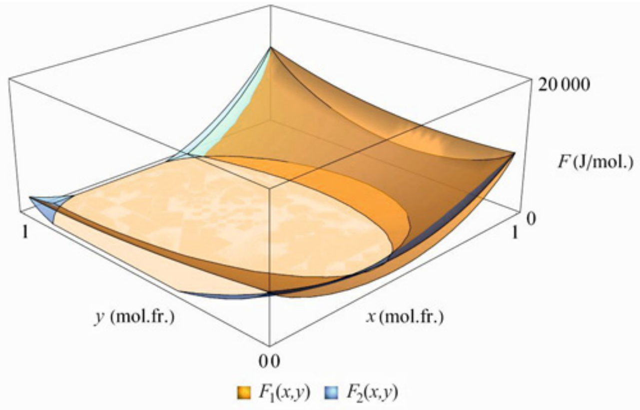

Fig. 1. The surfaces of the functions $F_1(x,y)$ and $F_2(x,y)$ defined by Eq. (6) at a temperature 873 K depending on the composition of the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution coherently conjugated to the InP (111) substrate. Here $\mu_1 = 2300\ \mathrm{J\ mole}^{-1}$ and $\mu_2 = 2340\ \mathrm{J\ mole}^{-1}$. Blue areas correspond to the intersection of the indicated functions of planes $F_1(x, y) = F_2(x, y) = 0$.

4. Search of the conditions providing the periodic solutions existence and the other mathematical tools to solve the problem

As it was mentioned above, Eq. (6) describing the distribution of the composition of the solid phase, the thermodynamic state of which is near the boundary of spinodal decomposition, form the nonlinear system of second-order differential equations. To find special domains of the system's parameters providing the periodic solution existence, qualitative analysis methods were used.

Based on these methods, the stationary points of Eq. (6) and the system's behavior in the vicinity of these points are considered. Figure 1 shows a typical form of the excess energy functions $F_1(x, y)$ and $F_2(x, y)$ for elastically deformed solid solutions, the thermodynamic state of which is close to the boundary of spinodal decomposition. Naturally, the energy of elastic deformations of the layers was calculated with respect to the CLP of the InP (111) substrate.

It is worth note that, as in the case of the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ ternary system coherently conjugated to the GaAs substrate, the elastic strain energy of the layers significantly exceeds the excess mixing energy of the solid phase. Therefore, the main contribution to the energy balance of the system is formed precisely due to the elastic deformation energy of the thin layer. This also explains the absence of extremum points (minimum and maximum) on the dependence of the excess energy of the system on composition (Fig. 1), which are typical for a phase that is in a thermodynamically unstable state. We also note the important feature of the mutual location of the isoenergetic cross sections for dependences $F_1(x,y)$ and $F_2(x,y)$ (Fig. 2)

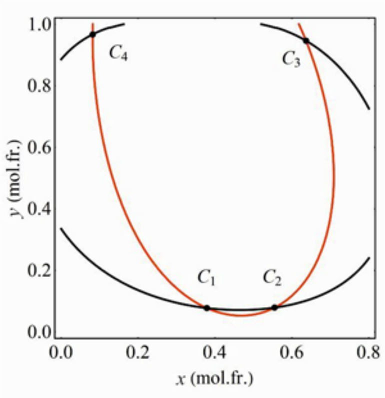

Fig. 2. Isotherms $F_1(x,y) = F_2(x,y) = 0$ of the system's energy functions at a temperature 873 K for the $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solution coherently conjugated with the InP (111) substrate (sections that are highlighted in blue in spatial Fig. 1). The points C_i, i =1, 2, 3, 4 stand for the positions of the stationary points of the system (6). Red curve corresponds to $F_1(x,y)$, black line – $F_2(x,y)$. Curves 1 and 2 stand for solid solution compositions the lattice matched to the InP and GaAs substrates. The parameters for calculations are the same as for Fig. 1.

relative to the spinodals and the binodals of the solid solution $Ga_xIn_{1-x}P_yAs_{1-y}$ decomposition. A direct comparison of the position of zeros of the excess energy functions, which are used in equations (4), with the lines of the state phase diagram of the material, is illegal, because these energies relate to different thermodynamic processes. The position of the spinodals and binodals of decay in Fig. 1 is set only by the values of the excess mixing energy of the components in the solid phase. The process of spinodal decomposition assumes participation in the interaction of the elastic energy of inclusions of a new phase. In this respect, the positions of the zeros of the functions are better suited for describing the positions of the coherent spinodals of the system.

The comparison performed is useful since it follows from this that the ranges of compositions, where fluctuations in the composition of the solid solution and the effect of composition modulation should be observed, are located precisely in the regions between the spinodals and binodals of material decomposition. This predetermines the shift in emphasis in further studies to the compositions of the solid solution that are in the metastable region, i.e., between the binodal and spinodal of solid phase decomposition at the chosen temperature.

We should recall an important feature of the thermodynamic situation that develops during the deposition of a $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solution on an InP substrate. Comparison of the position of the spinodal curve from [1–3] with the position of zeros of the functions F_1 and F_2 shows that at typical temperatures of layer's synthesis, they are located in close proximity and even cross the line of lattice matched of solid solution to the InP substrate. This should be considered as a theoretical substantiation of the possibility of realizing the effect of composition modulation in layers grown under such thermodynamic conditions. However, the noted fact cannot be considered as a sufficient condition for the occurrence of composition oscillations in the layer.

From Fig. 2 it follows that in the general case for the considered system of equations there are four stationary points C_i for which the conditions $F_1(x,y) = F_2(x,y) = 0$ are simultaneously satisfied. An analysis of the behavior of these functions in the vicinity of points C_1 and C_4 showed that the sign of the first derivative of these functions with respect to the composition of the solid solution is positive. This means that if the system in its thermodynamic evolution turned out to be in the vicinity of these points, then the only possible way to change the composition towards a stable equilibrium state of the system would be to change them according to an aperiodic process. In such a situation, the conditions for the appearance of oscillations of the composition of the solid solution, i.e., there are no conditions for the appearance of the composition modulation effect. Therefore, these states of the system were not considered.

A different situation develops when the system is in states close to points C_2 and C_3. For these states, the sign of the derivatives is negative. This means that when the system deviates from its equilibrium state, thermodynamic forces arise in it, which tend to return it to its original state. These forces are associated with the appearance of elastic deformations in newly formed inclusions of the solid phase. The state C_3 is characterized by a very significant deviation of the composition and, accordingly, of the CLP of the solid phase from the CLP of the substrate. The magnitude of this discrepancy reaches a few percent, which is very large. There is no reason to hope that, at such values of the CLP mismatch, coherent phase conjugation will be preserved in the heterostructure.

An estimate of the critical film thicknesses, at which its coherent conjugation with a massive substrate is still possible, shows that this value is much smaller than the thicknesses of layers deposited even by nanotechnologies. Therefore, the state of the system corresponding to the point C_3 cannot be implemented in practice, and it should also be excluded from consideration. This means that the state of the system in the vicinity of the point C_2 is of the greatest interest. Therefore, the further system's studies are carried out in the vicinity of this state.

The above considerations about the implementation of the decomposition process allow us to conclude about the possible amplitudes of fluctuations in the composition of the solid solution. Taking into account the magnitude of critical strains in the film, the application of the written equations should be limited to sufficiently small oscillation amplitudes in the vicinity of the stationary point. At the same time, it is known from experiments on studying the composition modulation effect in solid solutions that the shape of composition oscillations differs significantly from harmonic and is quite close to rectangular (concentration domains). The appearance of such types of oscillations is possible only in a situation where non-linear components in the initial equations are significant. This is possible in a situation where the oscillation amplitudes are large enough, and the dependence of the elastic and thermodynamic properties of the solid phase on its composition is clearly manifested.

The most effective method for the final search for intervals of the initial parameters of the system (x_0, y_0, μ_1, μ_2), when oscillatory solutions with a large amplitude will be observed in it, is based on constructing a phase portrait for the system of differential Eq. (6), i.e., the dependence of the value of derivatives $\mathrm{d}x/\mathrm{d}z$ and $\mathrm{d}y/\mathrm{d}z$ on the composition of the solid solution $x(z)$ and $y(z)$. This approach proved to be effective when searching for the conditions for the occurrence of composition oscillations in the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ ternary system [6, 7].

It is worth note that from a mathematical point of view, the parameters $\beta_{1,2}$ provide a scale transformation of the x and y profiles, leaving the oscillation type of the system's behavior unchanged. Therefore, at this stage of the analysis, we can put $\mu_{1,2} = 1$. The parameter forming the set of level lines (isoenergetic lines) is the value of the total system energy $E_{\text{total}} = E_{\text{el}} + E_{\text{ex}} + \mu_1 + \mu_2$, and the input parameters for their formation are the quantities μ_1 and μ_2.

Calculations show that in the vast majority of cases, which corresponds to an arbitrary choice of the values of the integration constants, the phase trajectory turns out to be open. This means that to obtain the conditions for periodic changes in the composition, i.e., to observe the effect of composition modulation, is possible only in strictly defined ranges of variations of these parameters. Such phase portraits, both with broken and closed phase trajectories, were observed for the Ga-In-P ternary system [6, 7].

The phase portrait for system (6) is a spatial pattern. The typical phase portrait of the periodic system's trajectory is shown in Fig. 3. Such phase trajectories can be observed if the system evolves in the immediate vicinity of the stationary state C_2. For clarity, projections of the functions under consideration onto the coordinate planes of the solid phase composition are also presented there.

The resulting phase portraits have fundamental differences from the phase portraits for the ternary system. According to the theory of differential equations, system (4) is characterized by quasi-periodic solutions, for which the oscillation period is not constant and is a weakly changing quantity [24]. The absence of an exact period in such interrelated oscillatory processes can be easily explained using the representations of a classical oscillatory system, where nonconservative forces act. Indeed, energy losses in such an oscillatory system led to a change (increase) in the period of its own oscillations. In the case of two coupled oscillation subsystems, a continuous energy exchange occurs between the metallic and metalloid sublattices of the sphalerite structure, and the appearance of continuous variations in the oscillation period of the compositions is inevitable. Mathematically, this effect is primarily associated with the appearance in the initial equations of the energy component as a function of the composition of each of the sublattices: $\alpha_{\mathrm{C}}xy$. It is also necessary to point out the dependence of the reduced mixing energies of the components in one of the sublattices on the composition of the other. This feature of the energy interaction in the system was considered in the dependences of the parameters α_{12}^{S}

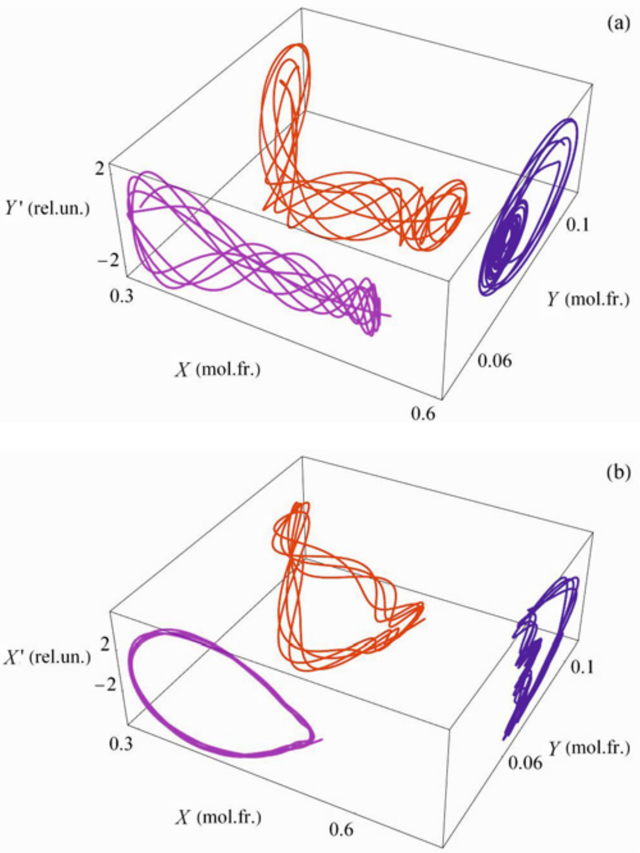

Fig. 3. Phase trajectories and their projections (side panels) for Eq. (6) when the thermodynamic state of the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution is localized in the vicinity of the stationary point C_2. Temperature 873 K, InP (111) substrate. The thermodynamic parameters for calculations are the same as for Fig. 1.

and α_{34}^{S} on the composition of the solid solution. To what has been said, one should add the existence of dependences of the elastic constants and, consequently, the elastic energy in each sublattice on the composition of the other interacting with it. It is the complex interchange of energy between the subsystems that is reflected in the quasi-periodicity of oscillations in the composition of the solid solution.

This effect is reflected in the shape of the phase portraits of oscillations in the system. The absence of a strict period for the considered oscillatory processes leads to the fact that the phase portrait is not stationary. Thus, Fig. 3 shows a typical form of spatial dependences for the phase trajectories of composition oscillations in sublattices during 5 periods of the process, when the effect of composition modulation should be observed in the system. These phase trajectories and their projections on the composition planes correspond to the conditions when the decomposition of a supersaturated solid solution occurs according to a periodic law. If the analysis of the projection forms of phase trajectories on the plane of compositions shows that they are quite close to closed forms, then the consideration of spatial patterns shows their complex variations. This effect is clearly illustrated by the 3D images of the phase curves in Fig. 3, which show the dependences of derivatives on the composition of the solid solution on the composition of the material itself. As already mentioned, the interval for which the evolution of the phase portrait was calculated in Fig. 3, was limited to 5 oscillation periods. Careful consideration of the phase portrait shows that the phase trajectory in the space of material compositions is open.

However, due to the relatively not very strong energy interaction between the oscillatory subsystems, the variations in the period of oscillatory processes are still not very large. Therefore, the phase trajectories are located close enough to each other. This makes it possible to interpret such a solution of the system of equations as a quasi-periodic one. The observed effect is reflected in the smearing or thickening of the lines on the graph of the phase trajectory projections for the variable x when its phase trajectories somewhat change their position on the graph in Fig. 3a. For the same conditions, the oscillatory process in the metalloid sublattice of the sphalerite structure in Fig. 3b follows a rather complex form, which corresponds to the complex form of the oscillation itself. However, even in this case, its phase trajectory changes its position from one oscillation cycle to the next insignificantly: changes in the vicinity of its stationary state. These features of interrelated oscillatory processes are attributes of quasi-periodic oscillations [24].

The absence of a strict periodicity in vibrations introduces some uncertainty in the calculations of the average compositions of the solid solution in accordance with Eq. (3) due to the uncertainty in the value of the period L. At the same time, such data are necessary to compare the calculated and experimental results on the composition of the solid solution. The problem was solved by averaging the composition of the solid solution, which changes as a result of the composition modulation effect, over 5 periods. Increasing the accuracy of calculating the average compositions and, accordingly, the average mismatch of the CLP in the heterostructure seems to be inappropriate due to the accuracy of the experimental measurement of the indicated quantities themselves.

To specify the phase trajectory, parameters μ_1 and μ_2 are used. These parameters are responsible for the position of the energy function with respect to the composition plane x-y and set the amplitude of composition oscillations in its sublattice of the solid phase. Studies of the influence of parameters $\mu_{1,2}$ on the shape of trajectories have shown that their absolute values determine the position of the point C_2, in the vicinity of which oscillatory solutions of the equations are observed, and the difference between them controls the oscillation amplitude. In this case, the initial concentrations x_0 and y_0 should be chosen slightly to the left of point C_2.

Calculations show that even with small variations in the initial parameters leading the system away from point C_2, the phase trajectories are not closed. At the same time, the closeness or equality to zero of the excess energies in each sublattice of the sphalerite structure from the physical point of view means that the system has the most favorable conditions for the complete transition of the excess mixing energy, which initiates phase decomposition, into the energy of elastic deformations of the precipitating new phase. In this case, the complete equality of the indicated energies means the appearance of the effect of a kind of resonance. Calculations show that this phenomenon is observed in a very narrow range of both parameters $\mu_{1,2}$ and initial composition x_0, y_0 of the solid solution for which the decomposition is modeled.

According to our studies, a variation in the total energy of the system, even by less than 1 %, can lead the system away from the desired mode of formation of intense oscillations.

Obviously, the study of the behavior of solutions of the system of Eqs. (6)–(4) under these conditions is of particular interest since it is in this range of initial values that all the previously stated conditions for the manifestation of composition modulation effect with a complex character of oscillations are realized. An analysis of the position of point C_2 at a temperature of 850 K on the thermodynamic phase diagram shows that this point is in close proximity to the decay spinodal and falls into the region of the metastable state, which lies between the lines of the spinodal and the corresponding binodal. We point out that, near the boundaries of unstable states, we previously observed the appearance of regions with an anomalously high sensitivity of the compositions of $Ga_xIn_{1-x}P_yAs_{1-y}$ quaternary solid solutions grown on an InP substrate to small changes in the parameters of the growth process [10, 18, 19]. A similar situation is observed in the case under consideration. When the initial concentration is located somewhat to the left of point C_2, the solution of the boundary value problem shows a sharp increase in the oscillation amplitude in the composition distribution over the film thickness. This allows us to hope that in oscillations with such initial parameters, the nonlinear properties of the system of Eqs. (6)–(4) will clearly manifest themselves.

The above considerations and the experience of computational work for a similar problem in the ternary system $Ga_xIn_{1-x}P$ made it possible to construct the following algorithm for solving the integro-differential problem (Eqs. (6)–(4)). The solution of the problem began with the calculation of the thermodynamic and elastic properties of the $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solution for a given average composition of the material. Then, for a preliminary assessment of the possible values of the initial compositions x_0, y_0, and parameters $\mu_{1,2}$ in the "manual" mode, the position of the graph of the total energy of the system was analyzed with the search for zeros of the functions F_1 and F_2. According to the preliminary analysis, the set of input data of interest from physical considerations for calculations should be chosen somewhat to the left of the point C_2 on graph. This provided a search for a solution to the boundary value problem in the required concentration range. The chosen values (x_0, y_0) allowed us to start solving the system of differential equations. For integrating the equation, the in-built functions of the software *Mathematica* are used. Further, the obtained dependences $x(z)$ and $y(z)$ entered the block for finding their average value, which was calculated by integrating the found dependences over the average oscillation period in accordance with formulas (3). If the obtained average did not coincide with the previously specified one, then at the next cycle of solving the problem, a correction was made to the value $(x_0; y_0)_i$. Correction and calculation of a new, current value, was performed by the secant method. The result of the work of such a computational cycle was the value of the average concentrations $\bar{x}$, $\bar{y}$, which were self-consistent both in solving the differential equation and in calculating the thermodynamic and elastic properties of the material. The developed algorithm formed the basis of software for modeling the process of spinodal decay, i.e., the effect of composition modulation during the formation of a heterostructure based on a $Ga_xIn_{1-x}P_yAs_{1-y}$ quaternary solid solution and an InP substrate.

5. Simulation of the composition modulation effect for the $Ga_xIn_{1-x}P_yAs_{1-y}$ – InP heterostructure formation

The developed thermodynamic ideas about the process of spinodal decomposition were applied to the conditions for the formation of a heterostructure based on a $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solution – InP (111) substrate. For this system of solid solutions, there are experimental results on the discovery of the effect of modulation of the material composition, some data on its parameters of composition oscillations are reported, information is given on the technological process of their synthesis by various epitaxial methods in slightly different temperature-time regimes [4, 11, 12, 20, 22, 23].

At the first stage of modeling, the search for model parameters was carried out that would provide the best agreement between the calculations and the available experiments. As already noted, the fitting parameters of the model are the parameters $\beta_{1,2}$ of the power-law expansion of the free energy of a solid solution inhomogeneous in composition, the constants $\mu_{1,2}$, and the initial composition of the material (x_0,y_0). The constants $\beta_{1,2}$ specify only the period of oscillations in the composition of the solid solution in each of the sublattices of the sphalerite structure. The parameters $\mu_{1,2}$ set the position of the zeros of the energy functions $F_{1,2}$ and control the amplitude of the oscillatory processes in their sublattice. Naturally, the choice of the values of these parameters was carried out in accordance with their indicated physical meaning.

To estimate the parameters $\beta_{1,2}$, we used experimental data on the oscillation period of the composition and CLP in the layers of the $Ga_xIn_{1-x}P$ solid solution deposited on the GaAs (111) substrate from its own liquid phase [5], and in the heterostructure based on the $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solution and substrates InP (111). According to the experimental data [1, 2, 4, 11, 22, 23], the grown layers had an average period of change in their composition at the level of 200–300 nm. This result on the oscillation period is reported for both ternary and quaternary solid solution. Based on the low accuracy of the indicated data on the oscillation period, and also taking into account the incompleteness of the reported information, for example, on the temperature-time conditions for the synthesis of layers, in further modeling of the spinodal decomposition, it was decided to accept $\beta_1 = \beta_2 = 1.4 \times 10^5$ J nm^2 mole^{-1}, as in [5] for systems $Ga_xIn_{1-x}P$. Since the temperatures of material synthesis on GaAs and InP substrates are different and amount to about 750 ℃ in the first case and 650 ℃ in the second case, then under this assumption it is automatically assumed that the parameters $\beta_{1,2}$ in these calculations do not depend on temperature.

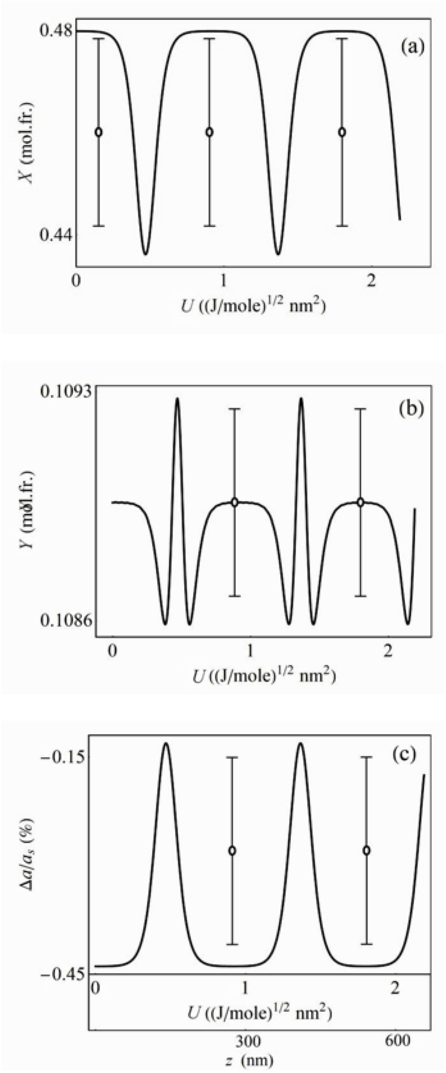

Fig. 4. Distributions of the composition (a), (b) and the lattice parameters mismatch (c) over the layer of $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution coherently conjugated to the InP (111) substrate. Temperature is 873 K, $\mu_1 = 2700\ \mathrm{J\ mole}^{-1}$, $\mu_2 = 3200\ \mathrm{J\ mole}^{-1}$; average solid solution composition $\bar{x} = 0.472$ mol.fr.; $\bar{y} = 0.109$ mol.fr.; initial compositions $x_0 = 0.480854$ mol.fr., $y_0 = 0.108791$ mol.fr.; the average mismatch between the layers in the structure is – 0.39 %. Experimental data on the amplitudes of composition oscillations are taken from [12, 22, 23].

According to the fundamental works [13, 16], the parameters $\beta_{1,2}$ are the coefficients of the expansion of the Gibbs free energy of the solid phase in terms of its composition and, naturally, depend on temperature. However, it seems that at the current stage of the theoretical study of the effect of composition modulation in semiconductor materials, nevertheless, such a simplification of the problem is quite justified, since only such an approach makes it possible to obtain quantitative data on the effect under study.

The main results of modeling the composition modulation effect in a heterostructure based on a $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution and an InP (111) substrate are shown in Figs. 4 and 5.

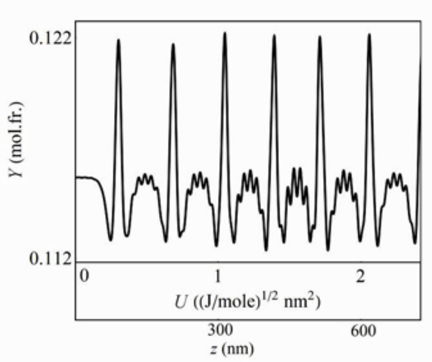

Fig. 5. Distribution of phosphorus over the layer of $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}_y\mathrm{As}_{1-y}$ solid solution coherently conjugated to the InP (111) substrate. Temperature is 873 K, $\mu_1 = 2700\ \mathrm{J\ mole}^{-1}$, $\mu_2 = 3300\ \mathrm{J\ mole}^{-1}$; average layer composition: $\bar{x} = 0.468$ mol.fr. and $\bar{y} = 0.115$ mol.fr.

Among all possible compositions of the material for calculations, we chose compositions that, in terms of the CLP, are close to the lattice of the InP substrate.

In this case, the band gap of the material of this composition ensures its optical sensitivity at a wavelength of about 1.55 μm. Modern fiber communication lines operate in this wavelength range.

A typical distribution of the composition and mismatch between the crystal lattices parameters in a heterostructure is given both depending on the mathematical parameter $U = \beta^2 z$, and on the actual coordinate directed perpendicular to the (111) plane.

From Figs. 4 and 5 one can see the quasi-periodic structure of the distribution of the composition of the solid solution. Careful comparison of the oscillation modes of the composition makes it possible to find differences between the parameters of even neighboring oscillations. So, in Fig. 4, the variation of the oscillation periods is quite clearly visible. Indeed, the length of the oscillation half-wave near $U = 1.0$ turns out to be somewhat larger than, for example, the half-wave at $U = 2.0$.

If the shape of the curves for the variation of the composition in the metal sublattice (function $x(z)$) in different parts of space turn out to be approximately the same, then for the oscillatory process in the metalloid sublattice (function $y(z)$) not only different values of the maximum deviations of the composition are observed, but also a difference in the form of oscillations as they propagate through the crystal. Indeed, in the vicinity of $U = 1.0$, the values of three local maxima, which are located at the minimum content of phosphorus in the solid solution, differ significantly from their analogs, which are located at $U = 2.0$. Naturally, the complex form of the oscillatory process in the metalloid sublattice of the solid phase, i.e., the complex form of the function is also reflected in the peculiar and complex form of the phase portrait for changing this parameter of the system in Fig. 3b.

The concentration profiles of the solid solution components in the metallic and metalloid sublattices of the sphalerite structure $x(z)$ and $y(z)$, which are obtained as a result of calculations, differ significantly from the form corresponding to harmonic oscillations. Their shape is more reminiscent of rectangular pulses for oscillations $x(z)$ or the result of the superposition of two rectangular pulses for $y(z)$. Therefore, it can be argued that the calculated result in Figs. 4, 5 illustrates the process of formation of concentration domains in the solid phase when it is in the thermodynamic state close to the boundaries of spinodal decomposition. Note that the found input parameters for the calculations in Figs. 4, 5 (see the caption) in the square of the material compositions are located somewhat to the left of the point C_2, i.e., lie on the surface describing the resonance between the excess mixing energy, which causes the decomposition of the solid solution, and the elastic energy, created by the inclusions of the new final phase.

It is important to note once again that the desired solution with respect to the initial composition x_0, y_0 in the problem under consideration is close to a sharp resonance maximum. Therefore, even a small variation of the parameters $\mu_{1,2}$ leads to a significant change in the calculated shape of the composition oscillations. Thus, Fig. 5 shows the calculated dependence for variations in the composition of the metalloid sublattice of the solid solution, when the parameter μ_2 was changed with respect to the data in Fig. 4 by only 100 J mole^{-1}. Even such a small change in the integration constant significantly changes not only the amplitude of oscillations, but it was also reflected in the appearance on the graph of additional vibrational modes inherent in a nonlinear system.

Figures 4 and 5 also show data on the amplitude of composition oscillations, which were observed experimentally in [5]. The agreement between the calculated and experimental values in terms of oscillation amplitudes was achieved by a proper choice of the parameters $\mu_{1,2}$. When solving this part of the problem, it was noticed that the concentration interval between points C_1 and C_2 (Fig. 2), in essence, set the amplitude of the oscillatory process. It should be noted that such an arrangement of the total energy graph relative to the equilibrium position of the system can only be provided by a special relationship between the mixing energy, elastic energy, and chemical potentials of the system. If the maximum of the total energy is located in such a way that the points C_1 and C_2 are significantly spaced relative to each other, then the oscillation amplitude will be large. A significant composition variation in such a process will cause the appearance of large mismatches on the CLP of coherently matched materials. In such a situation, the parameters of the system can exceed their critical values with the formation of dislocation networks and disruption of the coherent state of the phases. The latter will inevitably lead to the disruption of the oscillatory process, and in this case, the model under consideration is not applicable. This reasoning suggests that the effect of composition modulation must manifest itself quite rarely during the synthesis of semiconductor solid solutions.

It is of interest to compare the value of the temperature range in which modulation effect can be detected in quaternary and ternary solid solutions. The appearance of composition oscillations in a solid solution is associated with the condition that the initial figurative point for the thermodynamic state of the system is located in the vicinity of its spinodal on the phase diagram. According to the notation adopted in the work, this is point C_2 in Fig. 2 for the quaternary system. The position of point C_2 is set by the value of the excess energy of mixing of the solid phase and the value of the elastic energy of the newly formed inclusions. The elastic energy must be calculated with respect to the CLP of the initial matrix of the solid phase in which these inclusions are formed. If a thin layer is grown on a massive substrate, as occurs when creating a heterostructure, then the elastic deformations must be calculated with respect to the CLP of the substrate. If a solid solution layer is synthesized on an amorphous substrate or on a substrate that does not provide coherent conjugation of the contacting phases, then the elastic deformations should be calculated with respect to the average CLP of the initial matrix of the solid phase. Naturally, the magnitude of the elastic energy in the mentioned cases of synthesis will be different. This means that the position of the point C_2 cannot be identified with the position of the chemical spinodal of the system when only the chemical component of the mixing energy is taken into account in the analysis. Most likely, it is located on the coherent spinodal, but it is only necessary to indicate with respect to which lattice parameter the elastic energy in the system is calculated.

The computational programs developed by us, which simulate the spinodal decomposition in ternary and quaternary A^3B^5 semiconductor solid solutions, make it possible to estimate the temperature range near the decomposition spinodals, when intense oscillations are still possible. In practice, this means that it is possible to evaluate the influence of the number of components (the number of degrees of freedom of the system) on the possibility of experimental observation of the effect of composition modulation in semiconductor solid solutions.

The solution of this problem was carried out according to the following algorithm. For systems

$Ga_xIn_{1-x}P$ – GaAs (111) substrate and $Ga_xIn_{1-x}P_yAs_{1-y}$ – InP substrate (111) for their typical crystallization temperatures, the conditions for the appearance of an oscillatory mode of solving the decay equations were found. The systems were located in the vicinity of figurative points, which ensure the appearance of resonance between excess energies in the systems. Then the decay equations were solved with simulation of the composition modulation effect. After that, the temperature in the simulated process changed and its value was fixed at which the oscillations disappeared. Calculations have shown that the temperature interval in which the oscillatory regime is detected for a ternary system is larger than for a quaternary system by about 20 K. This means that the effect of composition modulation is easier to experimentally detect in ternary systems than in quaternary systems when the range of system parameters that provides effective spinodal collapse narrows.

At the same time, the need to create heterostructures for optoelectronic devices operating at 1.3–1.55 μm a wavelength predetermined intensive and precision studies of the synthesis process and the properties of $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solutions lattice-matched to the InP substrate. A large number of high-precision experiments on layers growth, carried out under conditions of proximity of the growth system to the boundaries of thermodynamic instability, made it possible to experimentally detect the discussed effects for the quaternary system. We also add that quite often, the growth of $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solutions is carried out with continuous cooling of the initial liquid phase. The decrease in temperature of the system increases the probability of passing the figurative point in the vicinity of the resonance point (point C_2 in the work) and thereby realizes the conditions for the occurrence of the composition modulation effect. This method of obtaining layers was used in [2, 4, 10–12], when a layer of solid solution was grown from a supersaturated liquid phase with its continuous subsequent cooling (supercooling method).

According to the available experimental results [10–12, 18, 19, 23], the concentration profiles of the components in the composition modulation effect have a pronounced rectangular shape. In this case, the lengths of each of the half-waves of the oscillations are approximately the same. According to the performed calculations, sufficiently extended concentration domains should be formed in the material, which are separated by relatively thin walls. This result corresponds to the theoretical concepts of the domain structure of the material after its spinodal decomposition [10, 11].

In this regard, the presence of a contradiction between the calculated representations and the available experimental data on the distribution of the composition of the material in different regions of the domain structure should be recognized. The high "off-duty ratio" of the concentration profiles, which follows from the calculations, nevertheless seems to be closer to reality. The appearance of a domain structure in which the length of the interdomain wall and the size of the domain itself were approximately equal is unlikely. The solution to this issue should be postponed until new experimental results are obtained, and their relationship with the technological regimes of layer synthesis is studied.

The appearance of periodic variations in the composition with a period of tens of nanometers should be taken into account when forming ultrathin or nanostructures based on A^3B^5 solid solutions, when the thicknesses of the deposited layers become commensurate with the modulation period.

6. Conclusions

Based on the results of these investigations, the following conclusions can be drawn:

– The Cahn-Hilliard equation was adapted to describe the formation of concentration domains during the spinodal decomposition of A^3B^5 quaternary solid solutions, when the substitution of components occurs in the metallic and metalloid sublattice of the sphalerite structure.

– The obtained model representations are applied to the description of the composition modulation effect of $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solutions, which are deposited under conditions of coherent conjugation with the InP (111) substrate at temperatures close to the regions of the metastable state of the material.

– Quantitative information was obtained on the distribution of the composition of the $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solution after its spinodal decomposition depending on the composition of the solid solution and temperature. It is shown that the effect of oscillations in the composition of the solid phase is associated with the appearance of a resonance between the mixing energy of the components in the corresponding sublattices and the energy of elastic stresses arising in elastically deformed inclusions of the new phase.

– A comparative assessment of the possibility of experimental observation of the effect of composition modulation in ternary and quaternary A^3B^5 solid solutions has been carried out.

References

[1] K. Onabe, Unstable regions in type $A_{1-x-y}B_xC_yD$ III-V quaternary solid solutions calculated with strictly regular solution approximation, Jpn. J. Appl. Phys. 22 (1983) 287–291. https://iopscience.iop.org/article/10.1143/JJAP.22.287

[2] G. B. Stringfellow, Miscibility gaps and spinodal decomposition in III/V quaternary alloys of the type $A_{1-x-y}B_xC_yD$, J. Appl. Phys. 54 (1983) 404–409. https://doi.org/10.1063/1.331719

[3] V. V. Kuznetsov, P. P. Moskvin, V. S. Sorokin, Thermodynamic stability of $Ga_xIn_{1-x}P_yAs_{1-y}$ solid solutions, Neorgan. Mater. 21 (1985) 2006–2010 (in Russian).

[4] M. Quillec, J. Benchimol, S. Slempkes, H. Launois, High mobility in liquid phase epitaxial InGaAsP free of composition modulations, Appl. Phys. Lett. 42 (1983) 886–887. https://doi.org/10.1063/1.93775

[5] A. I. Kazakov, G. V. Shapovalov, P. P. Moskvin, Computer simulation for formation of critical spaces in II-VI solid solutions, J. Cryst. Growth 506 (2019) 201–205. https://doi.org/10.1016/j.jcrysgro.2018.10.017

[6] P. P. Moskvin, S. I. Skurativskyi, O. P. Kravchenko, G. V. Skyba, H. V.Shapovalov, Spinodal decomposition and composition modulation effect at the low-temperature synthesis of $A^3_xB^3_{1-x}C^5$ semiconductor solid solutions, J. Cryst. Growth 510 (2019) 40–46. https://doi.org/10.1016/j.jcrysgro.2019.01.015

[7] V. V. Kuznetsov, P. P. Moskvin, S. I. Skurativskyi, Y. A. Stepchin, Y. M. Efremov, The composition modulation effect during spinodal decomposition of $Zn_xCd_{1-x}Te$ solid solutions under conditions of energy resonance, J. Phys. Conf. Ser. 1697 (2020) 012092. https://doi.org/10.1088/1742-6596/1697/1/012092

[8] V. V. Kuznetsov, P. P. Moskvin, S. I. Skurativskyi, Composition modulation in the $Ga_xIn_{1-x}P_yAs_{1-y}$ – InP heterostructure during spinodal decomposition under the conditions of internal energy resonance, J. Phys. Conf. Ser. 2103 (2021) 012117. https://doi.org/10.1088/1742-6596/2103/1/012117

[9] P. P. Moskvin, S. I. Skurativskyi, H. B. Zasik, T. Y. Nedashkivska, Spinodal decomposition of elastically stressed phases and composition modulation effect in $Ga_cIn_{1-c}P$ solid solutions, J. Phys. Stud. 24 (2020) 1602. https://doi.org/10.30970/jps.24.1602

[10] V. V. Kuznetsov, P. P. Moskvin, Interphase Interactions During Heteroepitaxy of Semiconductor Solid Solutions, Lan', Saint-Petersburg, 2019 (in Russian). ISBN 978-5-8114-3809-9

[11] M. Quillec, H. Launois, M. C. Joncour, Liquid phase epitaxy of unstable alloys: Substrate-induced stabilization and connected effects, J. Vac. Sci. Technol. B: Microelectronics Processing and Phenomena 1 (1983) 238–242. https://doi.org/10.1116/1.582493

[12] S. Maximov, L. A. Bondarenko, V. V. Kuznetsov, A. S. Petrov, The phenomenon of automodulation of the composition of epitaxial films during crystallization from the liquid phase, Phys. Solid State 24 (1982) 628.

[13] J. W. Cahn, J. E. Hilliard, Free energy of a nonuniform system. I. Interfacial free energy, J. Chem. Phys. 28 (1958) 258–267. https://doi.org/10.1063/1.1744102

[14] J. W. Cahn, On spinodal decomposition, Acta Metall. Mater. 9 (1961) 795–801. https://doi.org/10.1016/0001-6160(61)90182-1

[15] P. P. Moskvin, S. I. Skurativskyi, O. A. Gromovyi, W. Sadowski, The composition modulation effect in GaInPAs solid solutions as a manifestation of energy resonance after material's spinodal decomposition, J. Phys. Stud. 25 (2021) 1601. https://doi.org/10.30970/jps.25.1601

[16] A. Khachaturyan, Theory of Structural Transformations in Solid, Dover Publications, New York, 2008, ISBN 9780486462806.

[17] A. S. Jordan, M. Ilegems, Solid-liquid equilibria for quaternary solid solutions involving compound semiconductors in the regular solution approximation, J. Phys. Chem. Solids 36 (1975) 329–342. https://doi.org/10.1016/0022-3697(75)90032-3

[18] I. P. Ipatova, V. G. Malyshkin, V. A. Shchukin, On spinodal decomposition in elastically anisotropic epitaxial films of III-V semiconductor alloys, J. Appl. Phys. 74 (1993) 7198–7210. https://doi.org/10.1063/1.355037

[19] I. P. Ipatova, V. G. Malyshkin, V. A. Shchukin, Compositional elastic domains in epitaxial layers of phase-separating semiconductor alloys, Philos. Mag. B 70 (1994) 557–566. http://dx.doi.org/10.1080/01418639408240230

[20] A. T. Gorelenok, V. N. Mdivani, P. P. Moskvin, V. S. Sorokin, A. S. Usikov, Phase equilibria in the In-Ga-As-P system, J. Cryst. Growth 60 (1982) 355–362. https://doi.org/10.1016/0022-0248(82)90111-7

[21] V. M. Glazov, L. M. Pavlova, Chemical Thermodynamics and Phase Equilibria, Metallurgia, Moscow, 1981. (in Russian)

[22] S. Mahajan, B. V. Dutt, H. Temkin, R. J. Cava, W. A. Bonner, Spinodal decomposition in InGaAsP epitaxial layers, J. Cryst. Growth 68 (1984) 589–595. https://doi.org/10.1016/0022-0248(84)90466-4

[23] N. A. Bert, L. S. Vavilova, I. P. Ipatova, V. A. Kapitonov, A. V. Murashova, N. A. Pikhtin, A. A. Sitnikova, I. S. Tarasov, V. A. Shchukin, Spontaneously forming periodic composition-modulated InGaAsP structures, Semiconductors 33 (1999) 510–513. https://doi.org/10.1134/1.1187719

[24] B. P. Demidovich, Lectures on the Mathematical Theory of Stability, 2nd Edition, Moscow State University, Moscow, 1998, ISBN 5-211-03641-7. (in Russian)