Composition modulation in the Ga$_x$In$_{1-x}$P$_y$As$_{1-y}$ - InP heterostructure during spinodal decomposition under the conditions of internal energy resonance

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Abstract. The Cahn-Hilliard concepts are generalized and used to the description of the spinodal decomposition of A$_3$B$_5$ quaternary semiconductor solid solutions, when the mixing of components occurs simultaneously in the metallic and metalloid sublattices of the sphalerite structure. The resulting system of differential equations for material decomposition was used to describe the effect of composition modulation observed in the synthesis of Ga$_x$In$_{1-x}$P$_y$As$_{1-y}$ - InP heterostructures. Numerical simulation of the spinodal decomposition of the Ga$_x$In$_{1-x}$P$_y$As$_{1-y}$ solid solution is carried out. The intervals of the thermodynamic parameters of the technological process of the synthesis of structures, in which the effect of modulation of the composition should be manifested, are found.

1. Introduction

Lowering of the layers synthesis temperature makes it possible to obtain a material with increased structural perfection. However, such a temperature decreasing encounters the possibility of leaving a figurative point from the region of existence of a single-phase solid solution when the thermodynamic system moves along the phase diagram during crystallization. The transition of the system to the region of thermodynamic phase instability is accompanied by its spinodal decomposition, which results in the formation of a structure with micro-oscillations of the material composition. Such composition oscillations were found experimentally in both ternary and quaternary solid solutions of the A$_3$B$_5$ system.

This phenomenon is known as the composition modulation effect of the solid solution [1-2, 12]. It is obvious that the appearance of the modulation leads to changes in the optoelectronic properties of the heterostructure [1].

The possibility of compositionally periodic structure formation in ternary and quaternary A$_3$B$_5$ solid solutions were analyzed in a number of theoretical works [4-6]. In these cases, to describe this effect in ternary and quaternary solid solutions, an analytical method for the solution of decomposition equations was used. This approach allowed one to explain the appearance of micro-oscillations in the composition of layers [4].

However, the direct numerical integration of the Cahn-Hilliard spinodal decomposition equation [5-6] shown that compositional oscillations with significant amplitudes arise only at certain relations between the component mixing energy in the corresponding sublattice and the energy of elastically deformed inclusions of a new solid phase into which the material decomposes. These relations for the
mentioned energies are responsible for a significant increase in the oscillation amplitudes and, moreover, correspond to the conditions of a kind of resonance between the indicated energies. Thus, it is observed the phenomenon of resonance that leads to the appearance of oscillations with significant amplitudes in the material composition, which can be detected experimentally.

Among the A<sub>3</sub>B<sub>5</sub> quaternary solid solutions, a special place is occupied by the Ga<sub>x</sub>In<sub>1-x</sub>P<sub>y</sub>As<sub>1-y</sub> system. One of its main features is that, for the most important material compositions ensuring the operation of an optoelectronic device at wavelengths of 1.3-1.55 μm at the most typical synthesis temperatures, the initial thermodynamic parameters of crystallization are in close proximity to the spinodal surface. A large number of precision studies of technological processes for material production, as well as material properties in this range of compositions, allowed one to detect micro-oscillations in the composition of a solid solution, that is, the effect of composition modulation [1-3, 11, 12].

The aforementioned considerations stimulate further theoretical studies of the spinodal decomposition process in quaternary A<sub>3</sub>B<sub>5</sub> solid solutions.

2. Theory and mathematical tools for solving the spinodal decomposition problem

In [5, 6], the fundamental equations of Cahn and Hilliard [7–8] were modified to describe spinodal phase transformations during the decomposition of ternary A<sub>3</sub>B<sub>5</sub> semiconductor solid solutions deposited on both oriented and amorphous substrates. In this work, we consider the spinodal decomposition of quaternary solid solutions under the conditions of their lattice-matched synthesis on a massive substrate InP when the coherent conjugation of solid phases occurs.

The joint consideration of the component mixing energy and the energy of elastically strained precipitates of a new phase leads us to the following system of stationary equations adapted to the description of spinodal decomposition in the quaternary system:

\[
\begin{align*}
\beta_1 \frac{d^2 x}{dz^2} &= RT \left( x \ln x + (1 - x) \ln(1 - x) \right) + a_{12} S_x x(1 - x) + a_{34} S_y y(1 - x) + \\
&+ \lambda_{ijk} N_0 a(a - a_s)^2 / 4 - \mu_1; \\
\beta_2 \frac{d^2 y}{dz^2} &= RT \left( y \ln y + (1 - y) \ln(1 - y) \right) + a_{12} S_y x(1 - x) + a_{34} S_y y(1 - y) \end{align*}
\]

(1)

where \( \beta_1, \beta_2 \) are the coefficients of expansion in a power series of the Gibbs free energy in a compositionally inhomogeneous solid solution [7]; \( z \) is the coordinate in the direction of layer growth; \( a_{12} S_x, a_{34} S_y \) are the mixing energies (interaction parameters) between metal and metalloid components in the corresponding sublattices of the sphalerite structure [1]; \( \alpha_\phi \) is the combination of the energies of pair interactions between the nearest tetrahedral coordinated atoms located in different sublattices [1]; \( N_0 \) stands for Avogadro's number; \( a, a_s \) are the current crystal lattice parameter (CLP) of the layer and substrate CLP; \( \lambda_{ijk} \) are the combination of elastic moduli [1].

The constants \( \mu_1, \mu_2 \) that appeared after the integration of the Cahn – Hilliard equations for the stationary state are interpreted in [9] as chemical potentials in the corresponding sublattice (subsystem) of the solid phase crystallizing in the sphalerite structure.

The problem are fully formulated after taking into account the obvious relationship for the average concentration of each components in the corresponding sublattice of the quaternary solid solution:

\[
\bar{x} = \frac{1}{L} \int_0^L x(z) dz, \quad \bar{y} = \frac{1}{L} \int_0^L y(z) dz,
\]

(2)

where L is the average period of composition oscillations.
Note that these relations represent the condition of mass conservation for substances during the redistribution of components after the decomposition of the supersaturated solid phase.

The classical boundary conditions for the problems of this kind are the relations determining the values of the initial concentration of each component and the value of their derivatives at the point \( z = 0 \). The choice of the initial component content in the solid solution identifies the concentration range in which the search for a solution to the problem will be carried out. The values of the derivatives \( dx^S_i / dz \) fix the position of the point for which the value of the initial component concentration 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 averaged value is set at the boundary. Following the above considerations, the final formulation of the problem contains the following initial conditions:

\[
\begin{align*}
\alpha \equiv x_0 &= \text{const}, \\
\frac{dx(z = 0)}{dz} &= 0, \\
\beta \equiv y_0 &= \text{const}, \\
\frac{dy(z = 0)}{dz} &= 0.
\end{align*}
\]

Thus, differential equations (1) at the initial conditions (3) and conditions of mass conservation (2) form the mathematical problem that fully characterizes the distribution of the composition in quaternary semiconducting solid solutions \( \text{A}_3\text{B}_5 \), synthesized under the thermodynamic conditions chosen nearby the boundary of material spinodal decomposition.

3. Parameters of model

From the presented thermodynamic conjectures it follows that the distribution of the component concentration over the solid solution layer after its spinodal decomposition is determined by the excess mixing energy of the components in the solid phase \( \alpha_i \) and the elastic parameters of the solid solution matrix, i.e. its elastic constants \( C_{ij} \) \[1\]. The elastic parameters of the solid solution and the CLP for its current composition are calculated within the framework of linear approximations applied for each material parameter. The elastic constants for semiconductor compounds forming a \( \text{Ga}_{x}\text{In}_{1-x}\text{P}_y\text{As}_{1-y} \) solid solution required for modeling are presented in \[1\].

The temperatures and entropies of melting for the initial binary compounds, as well as the interaction parameters for the components in the liquid phase, which are used for calculating the parameter \( \alpha_c \), are taken from \[1\]. The data on these parameters, which have been obtained by various authors, are in good agreement with each other and their reliability is beyond doubt. This serves as a justification for their application for thermodynamic calculations in this work.

It is fundamentally important to choose the parameters of the solid-phase interaction \( \alpha_{ij} \) between the main components of the \( \text{Ga}_{x}\text{In}_{1-x}\text{P}_y\text{As}_{1-y} \) solid solution. Indeed, these parameters, which characterize the excess mixing energy in the solid phase, are decisive not only in describing the composition distribution in equations (1-3), but their values are closely related to the critical temperature of spinodal decomposition and the position of the boundaries of absolutely unstable and metastable regions on the composition-temperature phase diagram \[1\]. In this case, the position of these boundaries, in essence, sets the intervals of thermodynamic parameters, where the application of this analysis is justified and the results of its application are the most informative. Thermodynamic parameters describing the solid-phase interaction between material components and are averaged over the modeling temperature interval are taken from \[1\].

The critical decomposition temperature of the solid solution \( \text{Ga}_{x}\text{In}_{1-x}\text{P}_y\text{As}_{1-y} \) corresponding to the accepted interaction parameters is \( T_c = 1156 \) K when the composition of the material is \( x_c = 0.515; y_c = 0.55 \) mol.fr. \[1\]. These estimates clearly confirm the previously stated statement that for \( \text{Ga}_{x}\text{In}_{1-x}\text{P}_y\text{As}_{1-y} \) solid solution lattice matched to the InP substrate, under the thermodynamic conditions for layer growth are very close to the boundaries of unstable states of the material solid phase.

The search for conditions under which periodic solutions of the system of equations for changing the composition of the solid solution appears is carried out by calculating the phase portraits according to the method \[5, 6\]. The use of this approach made it possible to speed up the process of searching for the
initial conditions for differential equations, which ensure the appearance of only oscillatory solutions. The numerical method for integrating the equation is based on the standard Runge-Kutta method.

4. Modeling the modulation effect of the composition in Ga$_{1-x}$In$_x$P$_y$As$_{1-y}$-InP heterostructure

The experimental results on modulation of the composition of solid solutions A$^3$B$^5$ [1-4, 11] are taken as the initial data for modeling and evaluating the model’s parameters. As already noted, the parameters of the power-law expansion of the free energy of inhomogeneous solid solution, i.e. $\beta_i$, and constants $\mu_i$ play the role of the model’s fitting parameters. In this case, the constants $\beta_i$, in essence, set only the periods of oscillations of the solid solution composition in the corresponding sublattices of the sphalerite structure. At the same time, the parameters $\mu_i$, which are interpreted as the chemical potentials of the system in the process of spinodal decomposition [9], set the values of the amplitudes of the oscillatory process in each sublattices.

We estimate the parameters $\beta_i$ on the basis of experimental data [1-3, 11] on the period of composition oscillations (200-300 nm) in layers of Ga$_{1-x}$In$_x$P and Ga$_{1-x}$In$_x$P$_y$As$_{1-y}$ solid solutions grown on GaAs and InP substrates. According to the theory the parameters $\beta_i$ is proportional to the square root of the oscillation period [5, 6, 8] and are a relatively weakly dependent functions on the input experimental data value. Proceeding from this mathematical fact and the fact that for related systems of solid solutions the periods of composition oscillations are close on magnitude, in the subsequent analysis the parameters $\beta_i$ are taken the same as in [5, 6] and equal to $\beta = 0.06$ J nm$^2$ / mol.

As for the amplitude of the oscillatory process, in almost all reported cases of the composition modulation effect in A$^3$B$^5$ solid solutions, the oscillation amplitude don’t exceed 0.02 mol.fr. [1-3, 11, 12]. Such a range of the oscillatory process is limited by the possibility of the existence of coherent conjugation of new phase inclusions and the crystal lattice of the initial solution, which are responsible for elastic stresses in the system. Indeed, higher oscillation amplitudes would inevitably provide an excess of the critical values required for the existence of an elastically deformed state of the phases. The latter would lead to the disruption of the oscillatory process. Therefore, in the calculations performed, it is found the parameters $\mu_i$ providing the indicated amplitude of oscillations. As in [5-6], to find the intervals of the indicated $\mu$ values, we use an approach based on the construction of a phase portrait for the analyzed system of equations. It is known [10] that the closed contour of the indicated portrait, which encloses the stationary point of the differential equation ($\beta_i d^2 x_i / dz^2 = 0$), limits the interval of parameters $\mu_i$ providing the periodic solution evaluation.

A typical figure of the periodicity in the change of the composition over the layer of the Ga$_{1-x}$In$_x$P$_y$As$_{1-y}$ solid solution with $x_0 = 0.5547$ mole fr.; $y_0 = 0.0789$ mol.fr., which is synthesized on an InP substrate at $T = 873$ K, is shown in Figure 1. As can be seen from Figure 1, the concentration profiles of the components differ significantly from the shape corresponding to harmonic oscillations. This is a consequence of the complex dependence of the parameters of the differential equations for the concentration distribution on the material composition.

The calculation results on Figure 1 illustrate the formation of concentration domains during the formation of a solid phase under thermodynamic conditions close to the boundaries of spinodal decomposition. Note that the selected values of the integration constants for $T = 873$ K provide solutions to the system of equations in close proximity to the stationary point. In this case the conditions of resonance between the energy causing the decomposition of the solid solution and the elastic energy created by the inclusions of the new final phase are realized. This solution is located in the immediate vicinity to the resonance state, which is characterized by a significant increase in the amplitude of oscillations and ensures the manifestation of the nonlinear properties of the initial equations.

Figure 1 also shows the experimental data on the typical amplitude of the composition oscillations, which were observed when studying the effect of composition modulation in A$^3$B$^5$ systems [1-3, 11]. Calculations show that it is possible to ensure accordance to the experiment only with special precise relationships between the values of the mixing energy, elastic energy, and the chemical potentials of the system.
Violation of these relationships will inevitably and significantly affect the change in the composition and causes the appearance of large mismatches between the parameters of the crystal lattices of coherently conjugated materials. In this situation, the system’s parameters can exceed their critical values, which will lead to relaxation of coherent phase conjugation and disruption of the oscillatory process. Then the considered model will become inapplicable. The last reasoning allows us to make the following assumption. For the occulting the modulation composition effect in a solid solution, many factors must coincide. The effect under consideration should be manifested by no means in all cases when the growth system is in a state close to the spinodal decomposition boundary. Therefore, the modulation of the composition should be recognized as an effect that should manifest itself rather rarely on the practical of quaternary solid solutions growth.

![Graph](image)

**Figure 1.** Distributions of gallium (a) and phosphorus (b) over the $\text{Ga}_{x}\text{In}_{1-x}\text{P}_{y}\text{As}_{1-y}$, solid solution layer coherently coupled with the InP (111) substrate and synthesized at 873 K. $\mu_1$ = 2300 J / mol, $\mu_2$ = 2340 J / mol; $x_0 = 0.554731$ mol. fr.; $y_0 = 0.078926$ mol. fr. Experimental data on the amplitudes of composition oscillations are taken from [1-3, 11].

It is advisable to estimate the value of the temperature range in which the effect of composition modulation in quaternary and ternary solid solutions can be detected. The problem is solved for the heterosystems $\text{Ga}_{x}\text{In}_{1-x}\text{P} - \text{GaAs} (111)$ and $\text{Ga}_{x}\text{In}_{1-x}\text{P}_{y}\text{As}_{1-y} - \text{InP} (111)$ for its typical crystallization temperatures. Naturally, the systems are thermodynamically located on the state diagram in the vicinity...
of the figurative points, which ensure the appearance of a resonance between the excess energies in the systems. Calculations have shown that the temperature range in which the oscillatory regime is observed for a ternary system is larger than for a quaternary system by about 20 K. This means that the composition modulation effect is easier to experimentally detect in ternary systems than in quaternary ones, when the requirements for the range of system parameters to provide the efficient spinodal decomposition become very stiff.

The appearance of periodic changes on the composition of the material with a period at the level of tens of nanometers should be considered in the formation of super thin or nanostructures based on $A_3B_5$ solid solutions, when the thicknesses of the deposited layers become commensurate with the modulation period.

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