Computer Simulation of Critical Phenomena in Materials of Cyber Systems Elements

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Abstract: The safety and reliability of the operation of materials on which modern cyber systems are developed and new autonomous cyber devices are created that are capable of performing tasks in modern combat conditions was considered. Mathematical modeling of critical phenomena in semiconductor solid solutions of elements of groups III – V of the periodic system under various operating conditions was performed. The properties of the $A_xB_{1-x}C_yD_{1-y}$ type semiconductor solid solutions were predicted. The spaces, in which the conditions of stable and unstable phases are satisfied, as well as areas of coexistence of several phases simultaneously, were determined on sections of phase diagrams. A computer modeling technique for the formation of critical spaces, based on the use of a differential topological approach in complex multicomponent systems, was used. A method for determining the total derivatives of the free energy of quaternary solid solutions with mixing in two sublattices from the third to the eighth inclusive using the regular solution model and standard thermodynamic functions for binary compounds was applied to describe the interaction of atoms in multicomponent solid solutions.Sections of the phase diagram of the In-Ga-As-P system, critical spaces and phase coexistence spaces in four-dimensional space for various temperatures were calculated. The possibility of forming regions of coexistence of phases of different orders in solid solutions $In_xGa_{1-x}As_yP_{1-y}$ is shown by the obtained modeling results. The results obtained are consistent with the available experimental data, in which spatial modulation of the composition of the solid solution was observed.

1 INTRODUCTION

The safety and reliability of the operation of modern cyber systems and the creation of new autonomous devices largely depends on the properties of the materials on the basis of which they are developed. The scope of use of modern automated systems has expanded significantly, especially in modern combat conditions. In this regard, interest in predicting the properties of semiconductor compounds under various operating conditions is growing. Epitaxial layers of semiconductor solid solutions grown in unstable regions exhibit, at certain temperatures and compositions, a tendency to form structures with a periodic composition distribution [1–5]. Such phase changes are extremely difficult to identify under operating conditions, since this requires complex laboratory equipment. As a consequence, the parameters of devices created on the basis of multicomponent solid solutions can change significantly and lead to errors in the operation of the systems. At the same time, new functional electronic materials that are stable under critical conditions are currently attracting significant interest. New areas of application of multicomponent semiconductor compounds for modern micro- and nanoelectronics generate interest in understanding the problem of self-organized formation of ordered structures. The study of these phenomena is important, first of all, for modern technologies of microstructures and nanoobjects. These are, first of all, multicomponent semiconductor solid solutions with a non-uniform distribution of component concentrations, such as periodic structures, superlattices, systems of “quantum dots”, etc. To analyze the processes of the emergence of self-organized ordered structures, it is possible to use computer modeling based on thermodynamic approaches. The calculation of multidimensional phase diagrams, taking into

account the possibility of the existence of bifurcation spaces, critical spaces and spaces of coexistence of phases of different orders, should be used for such an analysis [6–8]. The equation of state of matter specifies some m-dimensional manifold in the corresponding space in the thermodynamic description of phase transitions. The equation of state of matter in the thermodynamic description of phase transitions specifies some m-dimensional manifold in the corresponding space, which is assumed in this article. Thom's catastrophe theory in the case of using one order parameter is considered as a generalized form of the Ginsburg-Landau theory of phase transitions for assessing the features of the potential function of a self-organizing system. However, to describe possible phase transitions in multicomponent systems, an approach is used that allows one to analyze the features of potential functions of several order parameters, allowing one to estimate the compositions of coexisting phases.

2 PURPOSE OF THE WORK AND RESEARCH METHODS

The purpose of the work is to further develop methods for mathematical modeling of phase equilibrium in multi-component systems to predict the reliability of electronic components in modern cyber systems. Certain provisions of the theory of bifurcations and the theory of Thom's catastrophes were used to analyze phase states, allowing one to analyze the features of potential functions of several order parameters [7 - 9]. Four-component solid solutions of elements of groups III-V of the periodic table with mixing of atoms in two sublattices of the form $A_xB_{1-x}C_yD_{1-y}$ were chosen as the object of study. It is these materials that are widely used in modern microelectronics and integrated optics, in the practice of creating large and high-speed integrated circuits, as well as optoelectronic devices, and form the basis of modern optical radiation detectors (photodetectors) for a wide spectral range. Such materials have broad prospects for creating elements of cyber systems operating in critical conditions. Modeling the process of formation of critical spaces and spaces of coexistence of phases in multicomponent and multiphase systems is possible based on the use of a differential topological approach [9]. The space of the phase coexistence occurs when one stable state coexists with another stable state. The first-order phase transition corresponds to the appearance of such a space and is determined by Maxwell's principle when two (or more) global minima of the potential function have the same depth. At some points in the space under study, a stable phase may become unstable, forming a bifurcation subspace. Two phases in a certain region can be identical for certain values of the order parameter and form a critical space of order two. In the presence of three or four identical phases, critical spaces of order 3 or 4 are formed, respectively. The conditions for the existence of singularities in this case are determined by the free energy of the system G [7, 9]:

- stable phase:

$$\frac{dG}{dx} = 0 \; ; \; \frac{d^2G}{dx^2} > 0 , \quad (1)$$

- instability space or bifurcation space:

$$\frac{dG}{dx} = \frac{d^2G}{dx^2} = 0 \; ; \; \frac{d^3G}{dx^3} > 0 , \quad (2)$$

- condition for the existence of a second-order critical space:

$$\frac{dG}{dx} = \frac{d^2G}{dx^2} = \frac{d^3G}{dx^3} = 0 \; ; \; \frac{d^4G}{dx^4} > 0 , \quad (3)$$

- condition for the existence of a third-order critical space:

$$\frac{dG}{dx} = \frac{d^2G}{dx^2} = \ldots = \frac{d^5G}{dx^5} = 0 \; ; \; \frac{d^6G}{dx^6} > 0 , \quad (4)$$

- condition for the existence of a fourth-order critical space:

$$\frac{dG}{dx} = \frac{d^2G}{dx^2} = \ldots = \frac{d^7G}{dx^7} = 0 \; ; \; \frac{d^8G}{dx^8} > 0 , \quad (5)$$

where $\frac{d^iG}{dx^i}$ are the matrices of derivatives of the free energy of the system with respect to the corresponding components $x(x^1, x^2, x^3, x^4)$.

3 PRESENTATION OF THE MAIN MATERIAL

Generalization of (1-5) to the case of m-dimensional concentration space allows us to analyze possible critical spaces and spaces of coexistence of phases in multicomponent solid phases based on the study of higher derivatives with respect to order parameters xi from the free energy of the system. An analysis of the existing principles of using multidimensional matrices and obtaining matrix derivatives was carried out [9, 12]. The possibility of expanding the free energy of multicomponent systems into a

multidimensional Taylor series was considered. The method of matrix-vector differentiation of multidimensional systems using the method of direct sums was used to obtain higher derivatives of the free energy of a four-component system. Derivatives of the free energy expression with respect to the corresponding concentration parameters were calculated from the third to the eighth inclusive.

Four-component solid solutions with a mixture of atoms in the cationic and anionic sublattices of the form $A_xB_{1-x}C_yD_{1-y}$ were presented as a mixture of four hypothetical binary compounds with concentrations X_{ij}. Accordingly, the free energy of such a solid solution will be a function of four concentration parameters:

$$G=G(X_{AC}, X_{BC}, X_{AD}, X_{BD}), \quad (6)$$

and the matrix of second derivatives of free energy with respect to these parameters will have a dimension of 4 x 4. The model of a strictly regular solution (6) was used in the work, based on the assumption of a random distribution of dissimilar atoms over the sites of the corresponding sublattices. The equation for the equilibrium number of binary clusters for modeling phase states according to the chosen model was taken in the form [6]:

$$\frac{X_{AD}X_{BC}}{X_{AC}X_{BD}} = \exp\left(\frac{1}{4kT}\left(\Delta G_1 + \Delta G_2\right)\right), \quad (7)$$

where ΔG_1 (7) is the change in free energy in the substitution reaction $AD + BC = AC + BD$, taking into account the interaction in the first configuration sphere, and ΔG_2, respectively, taking into account the interaction in the first and second coordination spheres:

$$\begin{aligned}\Delta G_1 &= \mu_{AC} + \mu_{BD} - \mu_{Ad} - \mu_{BC},\\ \Delta G_2 &= \alpha_{AC-BC}\frac{X_{BC}-X_{AC}}{X_{BC}+X_{AC}} + \alpha_{AC-AD}\frac{X_{AD}-X_{AC}}{X_{AD}+X_{AC}} \\ &+ \alpha_{AD-BD}\frac{X_{AD}-X_{BD}}{X_{AD}+X_{BD}} + \alpha_{BC-BD}\frac{X_{BC}-X_{BD}}{X_{BC}+X_{BD}}\end{aligned} \quad (8)$$

On sections of phase diagrams, expressions for the concentrations of binary components to display the modeling results were written through the concentration parameters *x* and *y*:

$$\begin{aligned}&X_{AC} = (1-x)(1-y);\ X_{AD} = (1-x)\,y;\\ &X_{BC} = x(1-y);\ X_{BD} = x\,y.\end{aligned} \quad (9)$$

The determination of higher derivatives of the free energy of the system to analyze the possibility of the existence of critical subspaces was carried out as follows. Symbolic elements of the matrix of second derivatives of the free energy of a solid solution of the form $A_xB_{1-x}C_yD_{1-y}$ were used as initial relations. The result of Kroniker multiplying the matrix of second derivatives of the free energy by differentiation operators with respect to the corresponding arguments was used to obtain the third derivative of the function of m arguments. Next, block matrices of the complete third derivative using the direct sum method were obtained containing m blocks of partial derivatives of size (m × m). Calculations of derivatives of the free energy of a multicomponent system of higher orders were carried out using a similar algorithm. Symbolic differentiation and numerical calculations of derivatives were performed using the Maxima computer mathematics system [11].

4 RESULTS

Analytical expressions for the total derivatives of the Gibbs free energy of four-component homogeneous solid solutions of the type $A_xB_{1-x}C_yD_{1-y}$ were obtained in the work starting from the third derivative to the eighth inclusive. Numerical calculations of the position of the regions of existence of derivatives and zero contours of derivatives from the second to the eighth inclusive were carried out on the cross section of the existence of solid solutions of the phase diagram of the studied system $In_xGa_{1-x}As_yP_{1-y}$ for the temperature range 773K – 1023K. Thermodynamic parameters used in the calculations (8) are given in the Table 1.

Table 1: Parameters of interaction in the solid phase for quasi-binary systems (sources [12, 13, 14]).

Quasi-binary system	Interaction parameter α^{s}_{ij-jk} J/mol
GaP - InP	14665
GaAs - InAs	12570
GaP – GaAs	1676
InP - InAs	1676

The contours of the spaces of coexistence of phases of orders two, three and four were constructed on the cross section of the existence of solid solutions in the phase diagram of the system under study based on the calculations performed for different temperatures. The obtained results of calculating the position of the zero contours of the

derivatives of the Gibbs free energy of the analyzed system according to the concentration parameters are presented in Figures 1 – 4, starting from the second derivative and up to the eighth derivative inclusive.

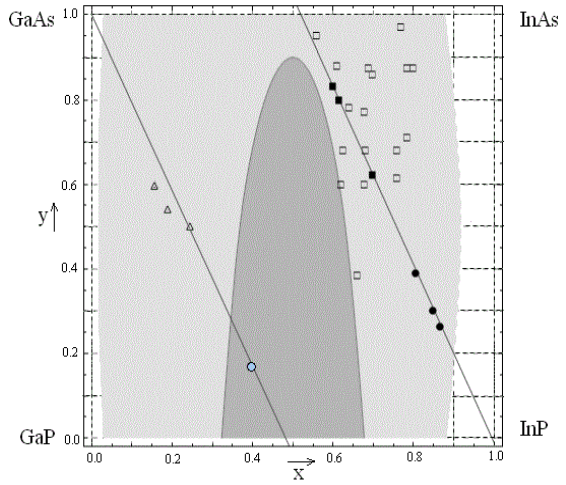

Figure 1: Cross section for the existence of solid solutions in the phase diagram of the In-Ga-As-P system. The results of numerical calculations of the second derivative of the free energy of the system are presented. Isoperiodic composition lines for GaAs and InP substrates are shown. The space of negative derivative values is shown in dark color. The space of positive derivative values is shown in light color. Temperature 773K. Sources of experimental data are: ■-[1], ● - [2], ○ - [3], Δ - [4], □ - [5].

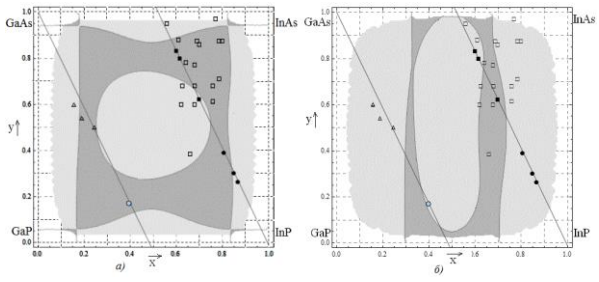

Figure 2: Cross section for the existence of solid solutions in the phase diagram of the In-Ga-As-P system. The results of numerical calculations of a) the third; b) fourth derivatives of the free energy of the system are given. The space of negative values of the corresponding derivative is shown in dark color. The space of positive derivative values is shown in light color. Temperature 773K. Sources of experimental data are: ■-[1], ● - [2], ○ - [3], Δ - [4], □ - [5].

Thus, the position of space in which the conditions of the stable phase are satisfied in accordance with (1, 9) is shown in Figure 1. The obtained positions of the zero contours for the third and fourth derivatives of the free energy of the system with respect to the concentrations of binary components for the $In_xGa_{1-x}As_yP_{1-y}$ solid solution (Figure 2) show that most of the experimental points for which composition modulation is observed fall into the region of negative values of the third derivative. These points are located in the region of positive values of the fourth derivative, which corresponds to the fulfillment of conditions (3) for the formation of spaces of coexistence of phases of order two.

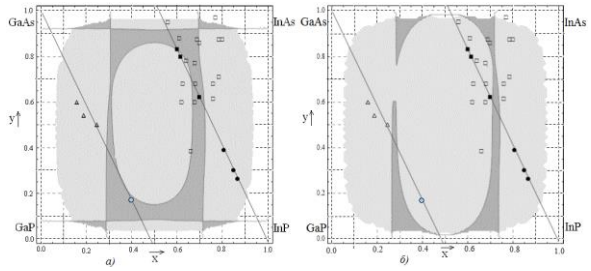

Figure 3: Cross section for the existence of solid solutions in the phase diagram of the In-Ga-As-P system. The results of numerical calculations of a) the fifth; b) the sixth derivatives of the free energy of the system are shown. The space of negative values of the corresponding derivative is shown in dark color. The space of positive derivative values is shown in light color. Temperature 773K. Sources of experimental data are: ■-[1], ● - [2], ○ - [3], Δ - [4], □ - [5].

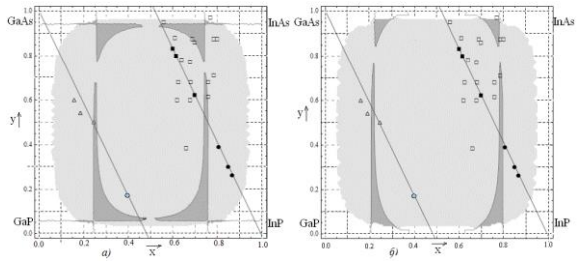

Figure 4: Cross section for the existence of solid solutions in the phase diagram of the In-Ga-As-P system. The results of numerical calculations of a) the seventh; b) the eighth derivatives of the free energy of the system are shown. The space of negative values of the corresponding derivative is shown in dark color. The space of positive derivative values is shown in light color. Temperature 773K. Sources of experimental data are: ■-[1], ● - [2], ○ - [3], Δ - [4], □ - [5].

The calculation results for a temperature of 773K are shown in Figures 1 – 4. Lines of isoperiodic compositions for GaAs and InP substrates and experimental compositions of epitaxial layers $In_xGa_{1-x}As_yP_{1-y}$, in which the formation of periodic modulated structures was observed, are shown.

These compositions were obtained using liquid-phase epitaxy on InP [1, 2] and GaAs [3, 4] substrates and gas transport epitaxy on InP substrates [5]. In works [1-5], cases of the formation of structures with simple one-dimensional modulation [1, 3], complex modulation of composition are described, such as the presence of two different concentration wavelengths in different crystallographic directions [2] and the formation of a system of alternating solid solution domains of two different compositions [4, 5]. The results of studying the structure of $In_xGa_{1-x}As_yP_{1-y}$ epitaxial layers obtained by vapor deposition on InP substrates at a temperature of 973K are presented in [5]. The formation of quasi-periodic structures of composition concentrations with a modulation wavelength from 10 – 20 nm along the {110} direction to 80 nm along the {001} direction for the concentration ranges of the resulting solid solutions ($0.2 < x < 0.53$ and $0.37 < y < 1$) was observed. As a result of additional experimental studies, it was shown that these composition modulations are not a consequence of the instability of the growth process [5]. The fact that the growth conditions of epitaxial layers do not affect the composition modulation period has also been shown [1].

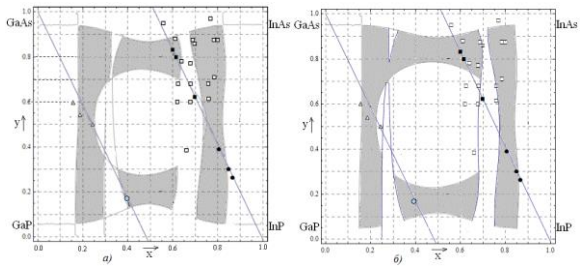

Figure 5: Cross section for the existence of solid solutions in the phase diagram of the In-Ga-As-P system. Compositions for which the conditions for the formation of phase coexistence spaces of order two are met for temperatures a) 773 K; b) 1050 K are shown in dark color.

5 CONCLUSIONS

The obtained modeling results based on the proposed approach make it possible to explain the available experimental data on the spontaneous formation of two-phase modulated structures in epitaxial layers of the $In_xGa_{1-x}As_yP_{1-y}$ solid solution. Figure 5 shows that the regular solution model used to construct the Gibbs free energy of a solid solution allows for a fairly correct assessment of the position of coexistence spaces of order 2 in phase diagrams.

An increase in temperature leads to a decrease in the resulting phase coexistence space. Based on the obtained results of modeling the position of regions of coexistence of phases of order 2, it can be assumed that the proposed model makes it possible to predict the spaces of possible appearance of periodic modulated structures in the considered solid solutions. The possibility of such a phenomenon should be taken into account in documentation on the safe use of the studied materials in modern cyber devices operating in extreme conditions.

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