Spinodal decomposition with formation of composition oscillations at low temperature GaInP - GaAs synthesis

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Abstract. The Cahn-Hillard equation is adapted to consider the spinodal decomposition process of semiconductor solid solutions. The obtained differential equation for the decomposition of a material is used to describe the composition modulation effect observed during the synthesis of $Ga_xIn_{1-x}P$-GaAs heterostructures. The numerical simulation of the process of spinodal decomposition of the $Ga_xIn_{1-x}P$ solid solution is performed. The intervals of the thermodynamic parameters for the technological process of the structures synthesis, in which the composition modulation effect should appear, are found.

1. Introduction

Modern technological processes for the synthesis of ultrathin layers of III-V semiconductor solid solutions, generally, are carried out at sufficiently low temperatures. The choice of low growth temperatures leads to the fact that the solid phase for many III-V solid solutions, which are of practical importance for modern optoelectronics, is supersaturated and close to the spinodal decomposition [1-2]. The important consequence of the supersaturated state of the solid phase, which was synthesized under conditions of thermodynamic instability, is the appearance of the effect of modulation of the solid solution composition. This effect causes the formation of micro-oscillations in the composition of the solid solution and the creation of a specific superstructure in it. This effect is quite general and it will manifest itself in solid solutions synthesized by various technologies. It is only important to have a thermodynamically unstable state of the phase, which, first of all, is determined by the temperature of material synthesis. This effect has been described theoretically during the formation of solid solutions of metals and has been detected experimentally at the synthesis of III-V semiconductor heterostructures previously [3-5].

The driving force of the spinodal decomposition process is the positive value of the thermodynamic excess mixing energy of the components of the solid solution. It makes the solid phase unstable and stimulates its decomposition. However, the transition to the steady state of such supersaturated solutions, as a rule, is accompanied by the new phases creation, the crystal lattice parameter (CLP) of which differs from the CLP of the initial material matrix. The formation of such new precipitates implies the energy costs of deformed macro states formation in the initial crystal matrix. Such deformed states will be elastic, while all interacting solid phases of different compositions are coherently conjugated.

Theoretical analysis [3-4] shows that in the result of this interaction, the entire volume of the solid phase decomposes and the structure with the periodic distribution of the components concentration occurs. In particular, periodic compositional changes in epitaxial layers both in $Ga_xIn_{1-x}P$ ternary solid solutions, grown on a GaAs substrate [5], and in $Ga_xIn_{1-x}P_yAs_{1-y}$ quaternary systems grown on InP substrates [6], were revealed by the electronmicroscopy methods.

The formation process of the composition modulated structures was considered theoretically in [3, 4]. The solution of equation for the decay of III-V semiconductor solid solutions has been found in the form of the Fourier superposition of the plane waves of various types. It should be noted that the use of slowly

converging Fourier series for describing the effect of the composition modulation implies the incorporation of a sufficiently large number of components of the corresponding series.

Direct numerical solution of the basic equations with out any additional restrictions can be useful for the thermodynamic description of this phenomenon and for the analysis of the decay effect as a nonlinear process. Thus the research of the effects occurring during the spinodal decomposition of III-V semiconductors solid solutions for the purposeful control of layers characteristics is of great importance.

2. Theory and parameters of model

The theory of spinodal decomposition has been developed in [3-4] with applications to solid solutions of metals. In the present article these ideas are adapted to the description of decomposition processes in $Ga_xIn_{1-x}P$ solid solutions. The adaptation of equation [3-4] to the description of the composition of solid solutions involves the use of the analytical form for the excess mixing energy of the solid phase. To simulate the thermodynamic state of the unstressed solid solutions, the regular approximation of the simple solutions theory is used [1-2, 7, 8].

Due to the spinodal decomposition, the new phase inclusions are formed in the parent lattice. The CLP of this new phase differs from the CLP for the initial material. The elastic energy of the coherently matched phases arising in this process should be taken into account in energy balance equation of the system. To calculate this component of the solid phase energy, the expressions obtained in [8] for different crystallographic orientations of the coherently matched layers areused.

Calculation of the mixing energy and the energy of the elastically strained inclusions of the new phase leads to the following stationary equation for analyzing the concentration fields:

$$\beta d^2x/dz^2 = \alpha^S x\cdot(1-x) + RT\,[x\ln x + (1-x)\ln(1-x)] + \lambda_{ijk}\cdot N_A a(a-a_S)^2/4 - \mu,$$

where z is the coordinate in the direction of the layer growth; β is the coefficient of power series for the free energy corresponding to the solid solution which is heterogeneous over its composition [3-4]; x is the concentration of the GaP component in the solid solution $Ga_xIn_{1-x}P$; N_A, λ_{ijk}- Avogadro number and combination of elastic modules according to [8], a, a_s - the current CLP and the CLP of the stabilizing substrate; α^s- the parameter of interaction between the components of the solid phase (GaP-InP); μ- chemical potential; R is the gas constant, T is the absolute temperature.

Together with the last equation, the mass balance equation after the decomposition is considered: $\bar{x} = \frac{1}{L}\cdot\int_0^L x(z)dz,$ where L is the period of composition variation.

The initial conditions for the problem of the solid solution composition distribution along its layer after the spinodal decomposition are the following:

$$x_{init} = x_o = const \quad \left.\frac{dx}{dz}\right|_{z=0} = 0.$$

The presented expressions with initial conditions form the integro-differential problem fully characterizing the redistribution of the composition of the $Ga_xIn_{1-x}P$ solid solutions that are close thermodynamically to the material's spinodal decomposition. Such a formulation of the problem makes it quite complex and interconnected. It is possible to solve such a system of equations only using the numerical methods.

The elastic constants and CLP used for modeling the semiconductor compounds forming $Ga_xIn_{1-x}P$ ternary solid solutions are taken from [8].

Special attention should also be paid to the choice of the parameter α^s, characterizing the solid-phase interaction between the main components of the $Ga_xIn_{1-x}P$ solid solution. This parameter is associated with the excess energy of the solid solution mixture and governs the distribution of thematerial composition after decomposition. Its value is closely related to the critical temperature of spinodal decomposition and defines the position of boundaries of absolutely unstable and metastable regions in the composition-temperature diagram [1-2, 4, 7-8]. Thus, during modeling the process of spinodal decomposition of the $Ga_xIn_{1-x}P$ solid solutions the data [7-8] were used. From the above mentioned it follows that we can assume α^s = 15200 J/mol. The critical temperature of decomposition which corresponds to the accepted interaction parameter is 913 K.

3. Mathematical tools for solving the spinodal decomposition problem

The underlying equation describing the distribution of the solid phasecomposition, which is near the spinodal decomposition boundary, is a second-order nonlinear differential equation. It is known that equations of this type have periodic solutions if the second derivative of the main variable is negative. Oscillations in the system can occur only when the thermodynamic state of the phase deviates somewhat from the equilibrium state, that is, from the point when the total energy of the solid phase is close to zero. To

satisfy this condition and select the set of parameters providing the oscillating solutions, the analysis of phase portraits of the differential equation was applied. The expression for the construction of trajectories in the plane is obtained by the analogy with [4] and is given by the first integral for the general equation. This also provides the initial data for integration of equation. The procedure outlined allows one to evaluate the problem solution in the necessary concentration range.

For numerical simulations the standard Runge-Kutta method was used. After that the average value over the period for quantity X(z) is calculated. If the obtained average value does not coincide with the previous one, then on the next cycle of the problem solving, a correction of the value X_{init} is made. The correction and calculation of the current value X_{init} is performed using the bisection method. This computational cycle results in the value of the averaged concentration, which was self-consistent both when solving a differential equation and when calculating the thermodynamic andelastic properties of the material.

4. Modeling the modulation effect of the composition in $Ga_xIn_{1-x}P$ solid solution

The validation of the developed thermodynamic concept of the process of the semiconductor solid solutions spinodal decomposition is carried out by simulating the conditions of material decomposition of heterostructure $Ga_xIn_{1-x}P$ solid solution -GaAs (111) substrate [5].

At the first stage of the modeling for providing the best fit of the calculations to the existing experiments, the assessment of the model parameters were carried out. As it was previously noted, the fitting model parameters are the parameters of the free energy of a inhomogeneous solid solution β, constant μ and X_{init}. To estimate the parameter β, experimental data on the period of composition oscillations in $Ga_xIn_{1-x}P$ solid solution layers deposited on a GaAs (111) substrate [5] were used. At this process, temperature was chosen as average over the cooling interval and put in calculations equal to 993 K. Thus, the elastic deformation of the grown layer and its deformation energy were calculated in reference to GaAs crystal lattice.

A typical distribution of the layer composition in the heterostructure depending on "z" are shown in Fig.1. In this figure, the periodic structure of the distribution of solid solution composition in the direction of the layer grow this visible. At the same time, the concentration profiles of the components differ significantly from the form corresponding to harmonic oscillations. The calculated result of Fig.1 clearly illustrates the process of structure appearance with the periodic distribution of the solid phase composition which grown under thermodynamic conditions close to the boundaries of the spinodal decomposition. It should be noted that the values μ and X_{init}, chosen at T = 993 K, correspond to the points of the curve describing the resonance between the energy that causes the solid solution to decompose and the elastic energy created by the inclusions of the new final phase. This means that the solution found is in close proximity to the resonant state, which is characterized by a significant increase in the amplitude of the oscillations and, as a consequence, the manifestation of the nonlinear properties of the system.

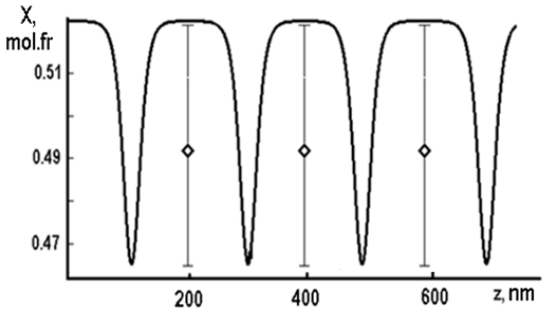

Figure 1. The distribution of the composition over a layer of $Ga_xIn_{1-x}P$ solid solution synthesized on a GaAs (111) substrate at T = 993 K with an average composition x: $\bar{X}$=0.51170 mol.fr., μ= 1910 J/mol., X_{init} = 0.52229 mol.fr. ◊- experimental data for the amplitude of oscillations are taken from [5].

Figure.1 also presents the data on the amplitude of composition oscillations, which has been observed experimentally in [5]. The good agreement of the calculated and experimental values of the amplitude of oscillations was achieved by the proper choice of parameter μ.

The analyses show that compositional oscillations in the system are caused by the special relationship between the values of the mixing energy, the elastic energy and the chemical potential of the system. At the same time significant variations of the composition in this process will cause the appearance of irrelevance of the CLP in structure. In such a situation, the system parameters can exceed their critical values and it will lead to the formation of dislocation grids and the breakdown of the coherent state of the phases. The latter will lead to the breakdown of the oscillatory process and in this case the model under consideration is not applicable.

The last argument allows us to make the following assumption. Since for the producing of the composition modulation effect many factors must coincide, the observed effect should not manifest itself in all cases when the growth system is in a state close to the border of spinodal decomposition. Therefore, the modulation effect of the composition should be regarded as an effect occurring quite rarely in the practical implementation of the process of obtaining III-V ternary solid solutions.

The clearly observed periodicity of changes in the composition makes it possible to estimate the period of the process. According to the estimation of the authors of [5], this value is equal to 200 nm. In this situation it is easy to obtain $\mu = 0.06$ J nm^2/mol.

The electron-microscopic images from [5] allow one to obtain only rectangular profiles of the distribution of contrast and do not provide any information about the shape of the oscillations. According to the available experimental results [5], the concentration profiles of the components in the effect of composition modulation have the identified rectangular shape. In this case, the lengths of each of the half-waves of oscillations are approximately the same. According to the calculations performed, the material should form sufficiently extended concentration domains, which are separated by relatively thin walls. This result corresponds to the theoretical submission which assume the formation of the set of concentration domains in material after its spinodal decomposition [4]. In this regard, it should be recognized that there is a contradiction between the calculated concepts and the available experimental data on the distribution of the composition of the material invarious areas of the domain structure. The high "porosity" of the concentration profiles, which comes out of the calculations, still seems closer to the reality. The appearance of the domain structure, in which the length of the interdomain wall and the size of the domain itself were approximately equal, seems unlikely. The solution of this issue should be postponed until the new experimental results are obtained.

$Ga_xIn_{1-x}P$ solid solution chosen for modeling is the indicative system because it has a relatively high critical temperature of decomposition, and the composition of the layer, that satisfies the condition of lattice matched substitution with GaAs, resides close in composition (X = 0.51 mol.fr.) to the top of the spinodal curve (X_{cr}= 0.5 mol. fr.). Such a combination of the properties of Ga-In-P system, together with the possibility of technological implementation of the material synthesis under these conditions, open up the possibility of detecting the effect of composition modulation in these class materials. Similar thermodynamic situation also develops in $Ga_xIn_{1-x}As$ system during its lattice matched growth on an InP substrate.

The appearance of periodic compositional changes with a period at the level of tens of nanometers should be taken into account when forming ultrathin or nanostructures based on III-V solid solutions, when the thickness of the grown layers becomes comparable with the modulation period.

Conclusion

The adaptation of the Cahn-Hillard equation is performed for describingthe process of the spinodal decomposition of ternary III-V solid solutions. The obtained model concepts are applied to the description of the composition modulation effect of $Ga_xIn_{1-x}P$ solid solutions, which are grown under conditions of coherent conjunction of a GaAs (111) substrate at temperatures corresponding to the region of the metastable state of the material. Quantitative data on the distribution of the solid solution composition after its spinodal decomposition is obtained as well.

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