Estimation of thermodynamic stability of isoperiodic epitaxial structures with GaInSbAs and GaInAsP solid solutions

E M Danilina and A S Paschenko

Federal research centre the Southern Scientific Centre RAS, 41, Chekhov st., Rostov-on-Don, 344006, Russia

Abstract. The work studied the thermodynamic stability of GaInSbAs, GaInAsP heterosystems on different substrates. The isotherms of spinodal decomposition caused by chemical changes in the internal energy of the alloy and by elastic stresses at the layer-substrate interface are obtained with the model of quasiregular solutions. It has been found that elastic stresses lead to an expansion of the region of thermodynamic stability of isoperiodic solid solutions for GaSb substrates and a decrease in the critical temperature. The developed model can be using to selection of the technological modes and parameters of epitaxial growth.

1. Introduction

Interest in multicomponent semiconductor solid solutions of III-V compounds [1-5] is due to the need to expand the spectral range and improve the structural perfection of heterointerfaces by the lattice matching of epitaxial layers and thermal expansion coefficient, which opens up possibilities for varying the photoelectric properties of the element base of devices [2].

However, in multicomponent liquid and solid solutions under suitable conditions, the formation of unstable component phases can be observed, leading to decomposition into two coexistent liquid or solid phases of different composition, respectively [3]. The experimental study of the process is labor-intensive and intends the use of precision methods of phase analysis. At the same time, information on the solubility gap of components in the solid phase is extremely important, because the immiscibility and instability of solid solutions significantly limit the range of compositions with targeted properties for use in manufacturing optoelectronic devices [4, 5].

Therefore, theoretical studies of equilibria between the liquid and solid phases in the epitaxy process are important.

2. Materials and Methods

The analysis of thermodynamic stability between the coexisting phases will be carried out using of the Prigogine-Defey criterion [6]. According to which the diffusion stability in isobaric-isothermal processes of multicomponent systems is determined by the system of inequalities

\[
\begin{align*}
\frac{\partial^2 F}{\partial x^2} &> 0; \\
\frac{\partial^2 F}{\partial x^2} \frac{\partial^2 F}{\partial y^2} - \frac{\partial^2 F}{\partial x \partial y} &\geq 0,
\end{align*}
\]

where \( F \) – Helmholtz free energy;
x, y – molar fraction of elements of III and V groups in solution, respectively.

In accordance with the approximation of a regular solution, a multicomponent solution can be represented as a set of binary compounds. Then the free energy is given by the sum of: the free energy of the mole fraction of binary components, the free energy of mixing, and the excess energy of mixing with the interaction of binary components

\[ F = F_0 + \Delta F_{\text{M}}^{\text{Sid}} + \Delta F_{\text{M}}^{\text{Sex}}. \]  

(1)

The free energy of the molar fractions of binary components determines the relationship between the nearest pairs of atoms in the first coordinate sphere

\[ F_0 = \omega_{AC} (1-x)(1-y) + \omega_{AD} (1-x)y + \omega_{BC} x(1-y) + \omega_{BD} xy, \]

where

- A, B – elements of III groups;
- C, D – elements of V groups;
- \( \omega \) – pair interaction energy between the nearest tetrahedral bond atoms in different sublattices.

The free mixing energy, model of an ideal solid solution, when the interaction energy between components is negligible

\[ \Delta F_{\text{M}}^{\text{Sid}} = RT \left( x \ln x + (1-x) \ln (1-x) + (1-y) \ln (1-y) + y \ln y \right), \]

where

- \( R \) – gas constant.

The excessive mixing energy that takes into account the interaction between the components of the solution within the quasi-chemical approximation

\[ \Delta F_{\text{M}}^{\text{Sex}} = \alpha_{AC-BC}^{\prime} xy (1-x) + \alpha_{AD-BD}^{\prime} x(1-x)(1-y) + \alpha_{BC-AD}^{\prime} y(1-x)(1-y), \]

where

- \( \alpha^{\prime} \) – solid-phase pseudo-ternary system interaction parameter.

According to [7], the sum of the energies of pair interactions can be represented in the following form, which is convenient for experimental determination

\[ \omega_{AC} - \omega_{AD} - \omega_{BC} + \omega_{BD} = \Delta S_{\text{F}}^{F} \left( T_{\text{AD}}^{F} - T \right) + \Delta S_{\text{F}}^{AC} \left( T_{\text{AC}}^{F} - T \right) + \]

\[ + \Delta S_{\text{F}}^{BD} \left( T_{\text{BD}}^{F} - T \right) + \Delta S_{\text{F}}^{BC} \left( T_{\text{BC}}^{F} - T \right) + \frac{1}{2} \left( \alpha_{AC}^{\prime} + \alpha_{AD}^{\prime} - \alpha_{BC}^{\prime} - \alpha_{BD}^{\prime} \right), \]

where

- \( \Delta S^{F} \), \( T^{F} \) – entropy and melting point of binary compound;
- \( \alpha^{\prime} \) – liquid-phase interatomic interaction parameter.

It suffices to solve the equation to find the region of spinodal decomposition

\[ \frac{\partial^2 F}{\partial x^2} \frac{\partial^2 F}{\partial y^2} - \frac{\partial^2 F}{\partial x \partial y} = 0. \]  

(2)

Equation (2) defines the boundaries of the regions of instability, which reflects the internal interatomic interaction in the lattice of the solid solution [8]. Such a spinodal is called a chemical spinodal.

Another type is a coherent spinodal, which represents the limit of metastability of a supersaturated solid solution. To calculate the coherent spinodal, it is necessary to take into account the energy of
heterogeneous deformation $F_u$, the appearance of which is a consequence of the introduction of nonperiodic microinclusions inside the unstable zone.

The energy of elastic stresses from the side of the substrate when the layer is oriented in the $\{100\}$ plane in the absence of misfit dislocations is given by the expression

$$F_u = \frac{c_{11} + c_{12}}{c_{11}} (c_{11} - 2c_{12}) N_A a_{1/4}^{1/4} \left(a_i - a_{sub}\right)^2,$$

where

$$c_{1j} = \left(c_{1j,AC}(1-x)(1-y) + c_{1j,AD}(1-x)y + c_{1j,BC}x(1-y) + c_{1j,BD}xy\right), \ j = 1, 2$$

- elastic coefficients of the solid solution layer;

$$a_i = \left(a_{AC}(1-x)(1-y) + a_{AD}(1-x)y + a_{BC}x(1-y) + a_{BD}xy\right)$$

- lattice parameter of the solid solution layer;

$a_{sub}$ – substrate lattice parameter;

$N_A$ – Avogadro’s number.

The total free energy of a solid solution is the sum of the thermodynamic energy (1) and the energy of elastic stresses (3)

$$F_{tot} = F + F_u.$$ 

The energy of elastic stresses by changing the solid solution free energy, leads to a change in the limits of solubility of the components and the boundaries of the regions of instability, which are determined by a similar formula (2).

3. Results and Discussion

We calculated the regions of existence of solid solutions of quaternary compounds on GaSb, InSb, GaAs, GaP substrates.

**Figure 1.** Isotherms of spinodal decomposition of In$_{x}$Ga$_{1-x}$As$_{y}$Sb$_{1-y}$ solution on GaSb substrate without elastic stresses, (a) $\Delta a = 0\%$ alloys lattice-matched to GaSb; (b) $\Delta a = 5\%$ to GaSb.

**Figure 2.** Isotherms of spinodal decomposition of In$_{x}$Ga$_{1-x}$As$_{y}$Sb$_{1-y}$ solution on GaSb substrate with elastic stresses, (a) $\Delta a = 0\%$ alloys lattice-matched to GaSb.
An analysis of heterophase equilibria in the Ga–In–Sb–As and Ga–In–As–P systems was carried out within the framework of the model of quasi-regular solid solutions. We also elucidated the regions of thermodynamic stability of solid solutions to spinodal decomposition caused by chemical changes in the internal energy of the alloy and elastic stresses at the layer-substrate interface.

It is shown that for \( \text{In}_x \text{Ga}_{1-x} \text{As}_{y} \text{Sb}_{1-y} \) heterosystem on GaSb substrate, compositions with a lattice mismatch of the solid solution and the substrate can exist (Figure 1 (a), (b)). In addition, it is found that \( \text{Ga}_x \text{In}_{1-x} \text{As}_{y} \text{P}_{1-y} / \text{GaAs} \) heterosystem exists in a lattice-matched composition (Figure 3 (a)) and \( \text{Ga}_x \text{In}_{1-x} \text{As}_{y} \text{P}_{1-y} / \text{GaP} \) heterosystem exists in a lattice-mismatched composition by 5% (Figure 3 (b)).

A characteristic feature is that elastic stresses lead to an expansion of the thermodynamic stability region of isoperiodic solid solutions for GaSb substrates and a decrease in the critical temperature (Figure 2). No isoperiodic compositions were found among the considered quaternary solid solutions for InSb substrates at room temperature.

The isotherms of spinodal decomposition for \( \text{Ga}_x \text{In}_{1-x} \text{As}_{y} \text{P}_{1-y} \) solution were also calculated (Figure 3). The results were compared with the technological data obtained during the growth of \( \text{Ga}_x \text{In}_{1-x} \text{As}_{y} \text{P}_{1-y} \) solid solution film on GaAs substrate (Figure 4). It shows a photograph of a heterosystem with pronounced inhomogeneities caused by spinodal decay. It is established that the growth parameters (temperature, composition) coincide with the data obtained during the simulation.

4. Conclusions
In the course of carrying out numerical experiments, it was found that the presence of elastic stresses in solid solutions leads to an expansion of the region of thermodynamic stability and a decrease in the critical temperature. Comparison of the simulation results with experimental data showed good agreement, which allows us to speak about the correctness of the calculations and the adequacy of the model, as well as the possibility of using the calculation results to substantiate the technological modes of epitaxial growth.
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