Estimation of the instable composition areas and its dependence on the thickness of GaInAsSb layers grown on different substrates

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Abstract. In this work we inform about the results of estimations of the changes of the spinodal decomposition areas and its dependence on the thickness of epitaxial layers. The calculations have been performed using the CALPHAD method and the SGTE data taking into account the elastic energy generated by the lattice mismatch between forming solid solutions and substrate. We have shown that in thin layers the elastic energy may serve both as a stabilizing factor for compositions inside the immiscibility region but lattice matched, or close, to the substrate and, on the contrary, as a reason of instability for the compositions laying in the periphery of the miscible regions.

1. Introduction
In different III-V solid solutions systems, growth within decomosition spinodal areas can produce layers with composition modulated regions [1-3] of the order of several tens of nanometers [4,5]. Such layers can serve to form low-dimensional heterostructures in the fabrication of advanced optoelectronic devices [1]. However, the instability of the solid phase inside the spinodal decomposition area can impose restrictions on the growth of alloys with certain compositions. These restrictions limit the wavelengths in which photovoltaic devices, lasers or photodetectors could be fabricated. This is clearly seen on the example of the III-V solid solutions containing Sb [2,3]. At different times, different authors have calculated spinodal decomposition areas [4-6]. However, the results of experimental studies show some disagreement with the calculated data. In addition, it was shown experimentally that instability of layers grown within the miscibility gap depend on their thickness [7].
The object of this work is to estimate the variation of the miscibility gaps when the thickness of the grown layers change, taking into account their mismatch with the substrate. The calculations have been performed for the GaInAsSb quaternary system, as an example. GaAs, InAs, InP and InSb were chosen as substrates for the formation of the layers.

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2. Calculation method

The criterion for thermodynamic stability for the quaternary III-V \( (A_xB_{1-x}C_yD_{1-y}) \) alloys is chosen as [8]:

\[
\left( \frac{\partial^2 G}{\partial x^2} \right) \left( \frac{\partial^2 G}{\partial y^2} \right) - \left( \frac{\partial^2 G}{\partial x \partial y} \right)^2 \geq 0
\]  

(1)

where \( G \) is the Gibbs free energy per mole of the solution, \( x \) and \( y \) are the molar fractions of the binary constituents.

The total Gibbs energy \( G^{\text{total}} \) of the film is given as a sum of the strain-free energy \( G^S \) of the solid phase and the elastic energy \( G^e \) due to the lattice mismatch between the solid solutions and the substrate was calculated with:

\[
G^{\text{total}} = G^S + G^e
\]  

(2)

In the case of regular solutions the Gibbs energy for \( Ga_xIn_{1-x}As_ySb_{1-y} \) is written [9]

\[
G^S = G_{GaAs}^0 x y + G_{GaSb}^0 x (1-y) + G_{InAs}^0 (1-x)(1-y) + G_{InSb}^0 (1-x)y + RT \left[ x \ln x + y \ln y + (1-x) \ln (1-x) + (1-y) \ln (1-y) \right] + x(1-x)y L_{GaAs-InAs}^0 + x(1-y) L_{GaSb-InSb}^0 + xy(1-y) L_{GaAs-GaSb}^0 + (1-x)y(1-y) L_{InAs-InSb}^0
\]  

(3)

where \( G_{ij}^0 \) are the Gibbs energies of the binary solid compounds, \( L_{m-n} \) denote the interaction parameters of the pseudobinary systems in the solid phase solutions. To calculate the strain-free energy of the solid phase we used the CALPHAD method [10]. The Gibbs energy of each binary solid compound is calculated with an expression including the sum of the enthalpies \( H_i^0 \) of the stable state of the constituting pure elements at 298.15 K and an empirical function of temperature \( GHSER_i \) [11]

\[
G_{ij}^0 = H_i^0 + H_j^0 + GHSER_{ij}
\]  

(4)

The values of the parameters used in the calculations are listed in Table 1.

In the epitaxial layers the elastic energy \( G^e \) is generated by the lattice mismatch with the substrate. To calculate \( G^e \) we used the procedure of Ohtani [12] that takes into account its dependence on the thickness, \( h \), when it exceeds the critical thickness \( h_c \)

\[
G^e = \frac{\mu (1 + \nu)}{2(1 - \nu)} N_A a^2 f^2 \quad (h < h_c)
\]  

(6)

\[
G^e = \frac{N_A a^2}{4h} \Delta \left( 1 + \ln \frac{h}{h_c} \right) \quad (h \geq h_c)
\]  

(7)

where \( a \) is the lattice parameter, \( \mu \) is the shear modulus, \( N_A \) is the Avogadro’s number. The critical thickness \( h_c \) is calculated with the equation

\[
h_c = \frac{\Delta}{2\mu f^2} \frac{1 - \nu}{1 + \nu}
\]  

(8)
using the value of 0.8 J/m$^2$ for the energy barrier $\Delta$ [13] as corresponds to the case of growth on substrates with orientation (001). The lattice misfit parameter $f$ is given by

$$f = \frac{a - a_s}{a_s}$$  \hspace{1cm} (9)$$

where $a_s$ is lattice parameter of the substrate.

### Table 1. The thermodynamic parameters used in the calculations.

| Parameters | Values (J/mol) | Ref. |
|------------|----------------|------|
| $H_{Ga,Ge}$ | 5572 | 14 |
| $H_{In,Te}$ | 6610 | 14 |
| $H_{As,Rho}$ | 5117.032 | 14 |
| $H_{Sb,Rho}$ | 5870.152 | 14 |
| $GHSE_R_{GaSb}$ | $-104352 + 265.432567T - 48.6812587\ln T - 1.1158 \times 10^{-3}T^2 + 127670 \times T$ | 12 |
| $GHSE_{InAs}$ | $-73057.2 + 236.91896T - 45.187942T\ln T - 7.73 \times 10^{-3}T^2 + 69433 \times T^{-1}$ | 12 |
| $GHSE_{GaSb}$ | $-59774.701 + 267.3096097T - 51.1966138T\ln T + 5.14355 \times 10^{-3}T^2 - 1770 \times 10^{-6}T^3 + 1.645 \times 10^{12}T^{-9}$ | 15 |
| $GHSE_{InSb}$ | $-47974.978 + 281.217555T - 55.3821132T\ln T + 8.29484 \times 10^{-3}T^2 - 1100 \times 10^{-6}T^3 + 3.53116 \times 10^{12}T^{-9}$ | 15 |
| $L_{GaSb-\text{InAs}}$ | 13360 - 5T | 12 |
| $L_{GaSb-\text{InSb}}$ | 9093 - 2.86987T | 15 |
| $L_{GaSb-\text{InSb}}$ | 24824 - 7.74301T + 4774$(X_{GaSb} - X_{GaAs})$ | 16 |
| $L_{InAs-\text{InSb}}$ | 13196.3 - 3.29157 + (20336.8 - 21.81057$(X_{InAs} - X_{InSb})$ | 17 |

### 3. Calculated results and discussions

Firstly, we have studied the influence of the layers thickness on the modification of the spinodal decomposition area for $\text{Ga}_{x}\text{In}_{1-x}\text{As}_{y}\text{Sb}_{1-y}$ compounds grown on $\text{GaSb}$ substrates (Fig 1: b – 3 nm, c – 15 nm, d – 90 nm). For comparison Fig. 1a shows the spinodal decomposition area calculated without taking in account the elastic energy $G^e$. For layers with a thickness of 3 nm (Fig. 1b), corresponding approximately to 1 ML, almost all compositions are stable, except a little region close to pure $\text{GaAs}$. In Figs. 1c and 1d it is possible to see that a band of stable compositions appears along the line of the solid solutions $(\text{GaSb})_{(\text{InAs}_{y_{0.1}}\text{Sb}_{0.9})_{1-x}}$ perfectly matched with the substrate, this bands narrows as the layer become thicker. Our calculation predicts that this band disappears at a thickness of around 1 um. In fact, several authors have already predicted the stabilizing effect of the elastic energy before [18] when

$$\left(\frac{\partial^2 G}{\partial x^2}\right)\left(\frac{\partial^2 G}{\partial y^2}\right) - \left(\frac{\partial^2 G}{\partial x \partial y}\right)^2 \geq \left(\frac{\partial^2 G^e}{\partial x^2}\right)\left(\frac{\partial^2 G^e}{\partial y^2}\right) - \left(\frac{\partial^2 G^e}{\partial x \partial y}\right)^2$$ \hspace{1cm} (10)$$

This stabilizing effect can be explained considering a competition between elastic and strain-free energies of solids. The calculations show that the positive contribution of the elastic energy increases in the less tensioned layers and decreases when the layers become thicker.
Fig. 1 also shows some experimental points [19] that represent the composition of epitaxial layers of high crystalline quality grown by SS MBE on GaSb substrates, point 1 corresponds to a 12 nm and points 2-4 to 14.5 nm thick layers. The compositions of these layers lay inside or close to the spinodal decomposition area when the elastic energy is not considered in the calculations (Fig.1a). However, they lay in the stable regions when the elastic energy is taken into account for a layer thickness of 15 nm (Fig.1 c).

![Figure 1](image)

**Figure 1.** Areas of the instable, in white, GaInAsSb compositions for the layers grown on GaSb substrate at 570 °C (a) – strain-free, b) – L= 3 nm, c) – 15 nm, d) – 90 nm); 1-4 – experimental data of Shterengas et al.

The stabilizing effect of the elastic energy can be observed also for thin GaInAsSb layers grown on other substrates. Fig.2 shows the spinodal decomposition areas in the case of layers grown at 570 °C on GaAs substrates. Fig. 2a, 2b and 2c correspond to layers of thickness 3 nm, 15 nm and 90 nm, respectively. The stabilizing effect of the elastic energy can be seen on layers with thicknesses of 3 nm and 15 nm close top right point corresponding to binary GaAs.

Also, we would like to mention another effect caused by the competition between elastic and strain-free energies for compositions on the periphery of the spinodal decomposition area. We have found that, at small thicknesses, new immiscibility regions, originated by the elastic energy, appear in stable compounds and that the immiscibility area expands in unstable compounds. Moreover, the instability is displayed only in some range of the thicknesses of the layers. So, to illustrate this effect we considered disclosing the spinodal decomposition areas in GaInAs ternary solutions in the case of growing on various substrates at 570 °C. The results are shown in fig. 3a for GaAs substrate, fig. 3b for InAs, fig. 3c for InP and fig. 3d for InSb substrates. This system is interesting because it is considered as a stable. However, the calculation demonstrated, in the case of growing on GaAs and InAs substrates, that an unstable area appears in the side close to the opposite corner to the one corresponding to the substrate and moves backwards as the layer’s thickness increases. The layers with thicknesses larger than 55 nm are stable in all compositions. When there is an important lattice mismatch between the layers and the substrate the immiscibility regions shrinks as the layer’s thickness decrease. As an example we choose for consideration the system GaInAs on InSb substrate.
It can be seen that all compositions are stable, except only the interval $0.3 < x < 0.6$ and for thicknesses up to 2 ML.

**Figure 2.** Areas of the instable GaInAsSb compositions, in white, for the layers grown at 570 °C on GaAs substrate (a) – $L= 3$ nm, (b) – 15 nm, (c) – 90 nm)

**Figure 3.** Areas of the instable GaInAs compositions, in white, for the layers grown at 570 °C grown on different substrates: a) – GaAs, b) – InAs, c) – InP, d) – InSb.
Also, at thicknesses of several monolayers, instable narrow areas appear in both sides of isoperiodical composition to InP substrate (Fig. 3c). This behavior of spinodal decomposition areas resembles the one we have observed for GaInAsSb grown on GaSb considering the stabilizing effect of the elastic energy. However, the difference is that, if we consider only the strain-free energy, GaInAs solid solutions do not contain instable areas.

4. Conclusions
Using the CALPHAD method and the SGTE data, we have estimated the changes of spinodal decomposition areas, induced by variations of the thicknesses, of GaInAsSb layers grown on InAs, GaAs, GaSb, InSb and InP substrates taking in account the elastic energy associated with the lattice mismatch. We have shown that the elastic energy may induce two opposite effects, from one side it can serve as a stabilizing factor and causes the apparition of a band of stable compositions which lay inside the spinodal decomposition area of the unstrained alloys. From the other side, the competition of elastic and strain-free energies may cause the instability of some compositions which are in the periphery of spinodal decomposition areas and even induce the apparition of immiscibility regions in normally stable alloys. The influence of elastic energy becomes stronger as the thickness of the layers decrease. We have to note that only the thermodynamic type of instability was studied in our work without considering any kinetic effects during the growth processes and the contribution of dislocations to the energy changes. Nevertheless the results are confirmed experimentally with data from the growth of actual epitaxial layers.

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