THERMODYNAMIC STABILITY OF $InSb_{1-x}Bi_x$ EPITAXIAL FILMS

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UDC 539.1

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The immiscibility region and critical temperatures of the spinodal decomposition of epitaxial thin films of a ternary semiconducting system $InSb_{1-x}Bi_x/InSb$ have been calculated taking into account both the deformation energy and the effect of plastic relaxation caused by mismatch dislocations. The relevant narrowing of the spinodal decomposition region and the reduction of its critical temperature have been demonstrated.

1. Introduction

Semiconductor devices fabricated on the basis of $A^{III}B^V$-compounds and the corresponding solid solutions find recently a wider and wider practical application in solid-state electronics. The interest in multicomponent alloys, which are potentially very important materials for the production of infra-red detectors, low-noise filters of communication systems, and continuously tunable lasers, has appreciably increased. The most accessible for today semiconductor materials for manufacturing the devices of the IR-range are alloys CdHgTe. However, the properties of those crystals depend to a great extent on a technological process which is not so perfect as, for example, that for $A^{III}B^V$-compounds and on many unforeseen factors which strongly affect the width of the energy gap [1]. Traditional alloys $A^{III}B^V$ do not give an opportunity to extend the wave range beyond the threshold of 7.5 μm (InAsSb), therefore, two alternative ways of overcoming this problem have recently appeared. The first way includes the creation of new $A^{III}B^V$-based multicomponent materials. The idea of the energy gap variation due to the stresses that arise in the corresponding superlattices and heterostructures is the essence of the second way [3]. Both the ways are not deprived of strong and weak features.

Experimental studies of the system InSb—InBi were started about 30 years ago by the classical works of Jean-Louis et al. [4—6]. The technological difficulties of the growing of the mentioned substitutional solid solution hampered its wide introduction into practice until recently. However, the recent achievements in this area [7—10] opened new prospects for its production

and application. Moreover, it is worth noting the growing interest in such fundamental characteristics as structural properties [11,12], electronic band structure [13], reorganization of chemical bonds [14], optical [15] and thermodynamic characteristics of the specified materials [16].

In spite of the fact that the issues of thermodynamic stability of the examined solid solution are of a great practical interest [17], the relevant detailed calculations have not been carried out till now.

In this work, the influence of the formation of mismatch dislocations in thin epitaxial films on the regions of thermodynamic stability has been investigated making use of the delta lattice parameter (DLP) model [18]. The immiscibility region has been determined, and the effects of biaxial deformations induced by a substrate and of the plastic relaxation caused by the generation of mismatch dislocations in the specified thin epitaxial films have been analyzed.

2. Account of Elastic Energy in Spinodal Decomposition Processes

The fact that InBi crystallizes into a tetragonal ($B10$) structure and is a semimetal, in contrast to the majority of $A^{III}B^V$-compounds which are cubic semiconductors, induced the studies of the interrelation between an abnormal crystal structure and physical properties of corresponding solid solutions [19]. The ratio of the lattice constants in InBi is $c/a = 0.9545$. The synthesized solid solutions $InSb_{1-x}Bi_x$ ($x < 12\%$) were experimentally shown to possess the sphalerite structure and to be direct bandgap semiconductors, with a transition into the zero-gap state being observed at $x \sim 11\%$ [19].

Except for the analysis of the dependences of the gap width and the lattice constants on the composition of a solid solution, it is necessary to take into account the fact that most solid solutions are unstable in a relevant range of composition. A solid solution in the region of instability tends to diminish its free energy through a decomposition, i.e. a phase transformation,

which results in a violation of the crystal macroscopical homogeneity and the appearance of a mixture of phases with different compositions. Disordered semiconductor alloys have a positive enthalpy of mixing, which leads to a decomposition and counteracts the stabilizing action of internal stresses. Moreover, disordered ternary III-V solid solutions manifest two tendencies upon phase transformations, namely, the decay and formation of superstructures [20, 21].

The regions of immiscibility and instability, which exist in many ternary and almost all quaternary $A^{III}B^V$ solid solutions, substantially limit the range of compositions which can be used for making devices. As was shown in [22], stresses and deformations in $A^{III}B^V$-alloys can lead to an extension of the solubility region. Deformation provides also an additional degree of freedom for the adjustment of a band structure and a monitored modification of optical and kinetic properties of semiconductors. Deformations and stresses in materials grown by epitaxial methods, such as molecular-beam epitaxy (MBE), organometallic chemical vapor deposition (OMCVD), etc., are caused mainly by the lattice mismatch between an epitaxial layer and a substrate. Elastic relaxation in thin films also affects phase transformations and stability [23]. It is necessary to note that, upon the spinodal decomposition, the purely coherent matching of two phases opposes the conjugation processes and can be accompanied by the appearance of mismatch dislocations [24]. A realization of each specified opportunity depends on the spinodal decomposition kinetics.

For the thermodynamic description of the pseudo-binary ternary solid solutions $InSb_{1-x}Bi_x$, consider the Gibbs free energy of mixing per mole:

$$\Delta G = \Delta H - T\Delta S \ , \tag{1}$$

where ΔH is the enthalpy of mixing, T is the absolute temperature, and ΔS is the entropy of mixing which can be written down as

$$\Delta S = -Rk\{x\ln x + (1-x)\ln(1-x)\} \ . \tag{2}$$

For the description of the enthalpy of mixing, two models are used most often: the regular solution model [25] and the DLP one [18]. It is known that the former model describes well the thermodynamic properties of the liquid phase and has some restrictions in the solid-phase case, because the interaction parameters in this model depend on the alloy composition parameter x. In the DLP model, the enthalpy of mixing ΔH depends

only on the lattice parameter a. For $AB_{1-x}C_x$ solid solutions, ΔH can be written down in the form [26]

$$\Delta H = E(\text{alloy}) - xE(AC) - (1-x)E(AB) =$$
$$= K\{a_{\text{alloy}}^{-2.5} - xa_{AC}^{-2.5} - (1-x)a_{AB}^{-2.5}\}, \tag{3}$$

where K is the model parameter equal to 1.15×10^7 (cal/mol)$\text{Å}^{2.5}$ for almost all the III—V compounds [18]. The solid solution will undergo the spinodal decomposition provided that the plot of the free energy vs the composition has an inflection point. The products of spinodal decomposition are two solid solutions with different compositions. The criterion of stability for pseudo-binary alloys can be written as $\partial^2 G/\partial x^2 > 0$. The region of instability is defined as a locus where the relation $\partial^2 G/\partial x^2 = 0$ holds.

For a bulk solid solution, besides the chemical part of the free energy, it is necessary to take into account the elastic component arising due to the requirement of coherent phase conjugation [27] with regard for a crystal anisotropy. In [28], in the framework of the regular solid solution model, it was shown that, in the quarternary solid solutions of $A^{III}B^V$-semiconductors which exhibit a positive enthalpy of formation, the coherent separation of phases occurs at certain temperatures. Such a separation is accompanied by the formation of elastic concentration domains with a solid-solution composition modulated normally to a direction of the easiest squeezing. The relaxation of elastic stresses on the epitaxial film surface was analyzed and taken into account.

In the case where the solid solution is a thin epitaxial film and the thermodynamic process runs by the mechanism of formation of mismatch dislocations, biaxial deformations will arise in the film due to a mismatch of the lattice constants of the solid solution, a_{alloy}, and the substrate material, a_{sub}. Then, $\varepsilon_{xx} = \varepsilon_{yy}$ for the deformations in the film plane, and the normal z-component of the strain tensor can be written for cubic crystals as

$$\tau_z = C_{12}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{11}\varepsilon_{zz}, \tag{4}$$

where C_{11} and C_{12} are the elastic constants of the film. Taking into account that $\tau_z = 0$ for a free (growth-related) direction of the film, relation (4) yields

$$\varepsilon_{zz} = -\frac{2C_{12}}{C_{11}}\varepsilon_{xx}(x). \tag{5}$$

The energy of such a deformation per unit volume can be written as

$$E_s = \frac{E\varepsilon^2}{1-\nu} \ , \tag{6}$$

where $\varepsilon = \varepsilon_{xx}$, E is Young's modulus, and ν is Poisson's ratio. Relation (6) was obtained in [29] as a special case. In addition, as was shown in [28] for the first time, the elastic deformation energy for an epitaxial film is changed due to the relaxation of elastic stresses on the surface. In this case, it will be more correctly to write relation (6) as

$$E_s^{'} = \left(\frac{C_{11}}{2\left(C_{11} + C_{12}\right)} \right) \frac{E\varepsilon^2}{1 - \nu} \; . \qquad (7)$$

The relative deformation of an entirely stressed epitaxial film is

$$\varepsilon\left(x\right) = \varepsilon_m\left(x\right) = \frac{a_{\text{alloy}}\left(x\right) - a_{\text{sub}}}{a_{\text{sub}}} \; . \qquad (8)$$

The dependence of the lattice constant $a_{\text{alloy}}\left(x\right)$ on the composition was described by Vegard's rule, which holds true for solid solutions $InSb_{1-x}Bi_x$ and is confirmed by experimental data [19].

Nevertheless, the described situation is observed only in the case where the thickness of a film h is smaller than the critical one h_c. But if $h > h_c$, the plastic relaxation and the formation of mismatch dislocations occur in the film. The thicker the film, the smaller its deformation. To define the influence of the specified effects on the thermodynamic stability of the considered solid solutions, we note that, according to the model of the balance of forces [30] that affect dislocations, it is possible to write down

$$\varepsilon = A/h. \qquad (9)$$

That is, when the thickness of an epitaxial film grows, the amplitude of a relative deformation decreases and the film gradually relaxes. Here, the parameter A is determined from the continuity condition of the function $\varepsilon\left(h\right)$ at the point $h = h_c$. Then, it follows from relations (8) and (9) that $A = \varepsilon_m h_c$. Most semiconductor heteroepitaxial objects are grown on surface (001) of the substrate, and here we shall examine just this orientation. An analytical expression for the critical thickness h_c can be obtained, starting from two different approximations known as the equilibrium theories of the critical thickness. The first approximation is based on the minimal energy principle and was proposed for the first time by Frank and Van der Merve; the second one known as the theory of the balance of forces belongs to Mathews and Blakeslee (see review [31]). These two approaches are equivalent and give identical values for the critical thickness. In our calculations, we used the model of the balance of forces, where the critical

thickness of an epitaxial layer (epilayer) is expressed as [30]

$$h_c = \left(\frac{b}{\varepsilon_m} \right) \frac{1}{8\pi\left(1 + \nu\right)} \left[\ln\left(\alpha \frac{h_c}{b} \right) + \beta \right], \qquad (10)$$

where $\alpha = 4$, $\beta = 1$ [17], and b is the Burgers vector modulus. Since the 60°-mismatch dislocations in plane (001) are most observable in semiconducting epilayers, the Burgers vector can be written as $\left(a/2\right)\left\langle 110 \right\rangle$, so that $b = a/\sqrt{2}$. In the dislocation core area, the stresses are too large to be described correctly in the framework of the linear theory of elasticity; therefore, the phenomenological parameter β serves as a measure of such a deviation [32].

Thus, the total Gibbs free energy of the system per unit volume is a sum of the chemical ΔG and elastic $E_s^{'}$ energies:

$$G = N_v \Delta G + E_s^{'} \qquad (11)$$

where N_v is the number of moles per unit volume of the homogeneous solid solution before the decomposition. The analysis of the Gibbs free energy as a function of the solid solution composition and the thickness of the epilayer, together with the criterion of stability, allows one to calculate the limits of solubility.

3. System $InSn_{1-x}Bi_x/InSb$

$InSn_{1-x}Bi_x$ is a very interesting substance, because it is made up of a semimetal InBi and a semiconductor InSb. For this reason, the energy gap and the lattice constant vary in wide ranges. As a result, such materials can be used for detectors in the intermediate IR range (7.4—16 μm). However, as follows from the phase diagram [2], the existence of a wide region of the decomposition of such mixed crystals predetermines significant difficulties in their growing. Therefore, the ratios of components in grown crystals will not be the same as in the solution. In [4—6], it was shown that the threshold of the equilibrium solubility for Bi is equal to 2.6 at.%, whereas the limit of its metastable solubility is 12 at.% [10]. At the same time, the reports [7—11] have appeared recently concerning the successful growing of thin $InSb_{1-x}Bi_x$-films on InSb- and GaAs-substrates, using such methods as OMCVD, MBE, and liquid-phase epitaxy (LPE).

Consider an epilayer of $InSb_{1-x}Bi_x$ on an InSb-substrate in the framework of the model described above. At low temperatures, the unstressed alloy has a positive free energy which diminishes with a temperature growth and forms two minima, which testifies for an opportunity of the spinodal decomposition. The phase diagram in
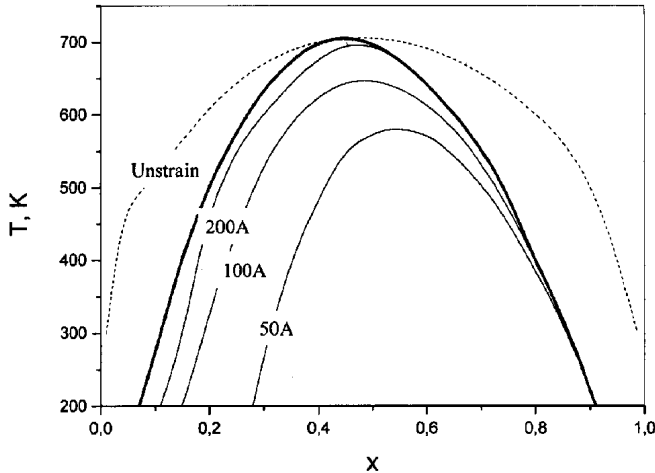
Fig. 1. Decomposition diagrams of the bulk solid solution $InSb_{1-x}Bi_x$ (dotted curve is the binodal, bold curve is the spinodal) and thin pseudomorphic films $InSb_{1-x}Bi_x/InSb$ with various thicknesses (thin curves)

Fig. 2. Dependence of the critical thickness of epitaxial films $InSb_{1-x}Bi_x/InSb$ on the composition x

this case is presented in Fig. 1 (dotted curve). From this diagram, one can see that the critical temperature $T_c = 705$ K at $x_c = 0.45$, above which the spinodal decomposition cannot occur. The calculation shows that, for an unstressed film, the limit of equilibrium solubility for Bi is 2.9%, whereas the spinodal decomposition of a solid solution begins at 11%, which nicely explains the known experimental data. Such parameters correspond to an unstressed film, which takes place if the thickness is greater than 2 μm. If the epitaxial film is quite stressed, the rapid growth of the elastic energy E'_s [in comparison with the variation of the chemical energy, which is the first term in formula (11)] with increase in the Bi content in the film gives rise to that two minima on the plot of the free energy vs the composition merge into one. This phenomenon testifies to the elastic stabilization of the film with respect to the spinodal decomposition and is possible for thin pseudomorphic films with thicknesses smaller than the critical one ($h < h_c$). However, if the epilayer thickness exceeds the critical value ($h > h_c$), the film starts to relax, i.e. the elastic energy of the film (7)—(9) diminishes with increase in the film thickness. In so doing, the region of existence for the spinodal decomposition ($\partial^2 G/\partial x^2 < 0$) remains to exist, although being narrowed (Fig. 1). The asymmetrical narrowing of the spinodal decomposition region and the reduction of the critical temperature can be explained taking into account that the critical thickness of the film depends on the composition according to (10) (see Fig. 2). The low-Bi-content border of the immiscibility region is rather sensitive to the variation of the film thickness. The
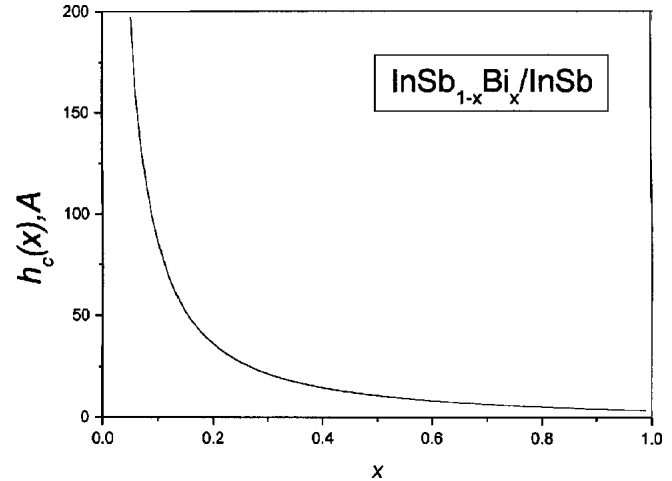
opposite border, where the Bi content is higher, depends weakly on the film thickness, being the result of both a great mismatch between the lattice constants of the film and the substrate (InSb) and, hence, the smaller critical thickness of the film. Therefore, films with practically arbitrary thicknesses are entirely relaxed in this region of compositions, and the residual stresses in them are rather small. Concerning the border in the low-Bi-content region, due to the strong dependence $h_c(x)$, the emerging epitaxial stresses are rather sensitive to the epilayer thickness. A decrease in the film thickness leads to a growth of the stresses caused by a mismatch of the lattice constants in the film and in the substrate, which results in a decrease in the critical temperature and an increase in the asymmetry of the spinodal curve (in particular, at the film thickness of 50 Å, the critical temperature $T_c = 585$ K at $x_c = 0.54$). In this case, the region of existence of the metastable solid solution expands from the side of InSb. For example, the limit of metastable solubility equals 0.31 for a film 50 Å in thickness, 0.19 for 100 Å, and 0.15 for 200 Å. Therefore, as compared to bulk alloys, the epitaxial films of $InSb_{1-x}Bi_x/InSb$ are thermodynamically more stable, with the width of the solubility region being rather sensitive to the film thickness.

4. Conclusions

The intervals of immiscibility and the critical temperatures of spinodal decomposition of the ternary semiconductor system $InSb_{1-x}Bi_x/InSb$ have been calculated. The deformation energy, the relaxation of

elastic stresses on the surface of epitaxial films, and the effect of plastic relaxation caused by mismatch dislocations have been taken into account. Their action has been shown to result in a narrowing of the spinodal decomposition region, a decrease of its critical temperature, and an increase of the decomposition curve asymmetry. Thus, thin epitaxial $InSb_{1-x}Bi_x$ films grown on InSb substrates are thermodynamically more stable in comparison with bulk specimens, which allows them to be used more widely in devices of IR-photoelectronics.

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ТЕРМОДИНАМІЧНА СТІЙКІСТЬ ЕПІТАКСІЙНИХ ПЛІВОК $InSb_{1-x}Bi_x$

В.Г. Дейбук

Р е з ю м е

Розраховано інтервали незмішуваності і критичні температури спінодального розпаду епітаксійних тонких плівок потрійної напівпровідникової системи $InSb_{1-x}Bi_x/InSb$ з урахуванням як деформаційної енергії, так і ефекту пластичної релаксації, зумовленого дислокаціями невідповідності. Показано звуження області спінодального розпаду і зниження його критичної температури.