On the spinodal decomposition of $In_xGa_{1-x}N_yAs_{1-y}$ and $GaSb_xN_yAs_{1-x-y}$ alloys

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Spinodal decomposition ranges of GaAs-enriched $GaSb_xN_yAs_{1-x-y}$ and $In_xGa_{1-x}N_yAs_{1-y}$ quaternary alloys as the result of the transformations of the bonds, strain and coherency strain energies at the phase separation are described. The alloys are represented as strictly regular solutions. The spinodal decomposition ranges of the alloys are demonstrated up to $600°C$. It is shown that $GaSb_xN_yAs_{1-x-y}$ alloys having one mixed sublattice are more promising from the standpoint of spinodal decomposition than $In_xGa_{1-x}N_yAs_{1-y}$ alloys with two mixed sublattices.

Keywords: Quaternary alloys; spinodal decomposition.

Se describen los rangos de la descomposición espinodal de las aleaciones cuaternarias $GaSb_xN_yAs_{1-x-y}$ y $In_xGa_{1-x}N_yAs_{1-y}$ enriquecidas con GaAs, como resultado de la transformación de los enlaces, las energías de deformación y de coherencia en la separación de fase. Las aleaciones se representan como soluciones estrictamente regulares. Los rangos de descomposición espinodal se mostraron hasta $600°C$. Se demuestra que las aleaciones $GaSb_xN_yAs_{1-x-y}$ con una subred mezclada son más prometedoras desde el punto de vista de la descomposición espinodal que las aleaciones $In_xGa_{1-x}N_yAs_{1-y}$ con dos subredes mezcladas.

Descriptores: Aleaciones cuaternarias; descomposición espinodal.

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1. Introduction

In the previous paper [1], the spinodal decomposition ranges of GaP-rich $GaSb_xN_yP_{1-x-y}$ and $In_xGa_{1-x}N_yP_{1-y}$ quaternary alloys were described. Spinodal decomposition is important because it allows us to know the region of the unstable states of an alloy. Besides, dilute nitride III-V alloys have attracted a lot of attention since the last decade. N concentrations around 1% and above could be easily achieved in GaAs or GaP [2]. Therefore, a dilute amount of nitrogen offers the unique feature of simultaneously reducing the band gap and the lattice parameter of a given III-V alloy [2]. In particular, when a small percentage of N is incorporated into GaAsSb, a band gap reduction [3] and a lattice contraction [4] are observed, as in other dilute III-V nitrides. Thus, the GaSbNAs quaternary alloy is another candidate for preparing strained or lattice-matched materials with low band gap on GaAs. We are going to consider the GaAs-rich $GaSb_xN_yAs_{1-x-y}$ and $In_xGa_{1-x}N_yAs_{1-y}$ quaternary alloys. The significant distinction in the atomic sizes of nitrogen and other V-group elements (As and Sb) gives rise to the substantial strain energy of such alloys. The strain energy provides the tendency toward phase separation that can lead to thermodynamically unstable states with respect to spinodal decomposition [5]. These unstable states may be produced as the transformation of a homogeneous alloy into a two-phase system [6]. At the same time, this kind of decomposition formed leads to an occurrence of the coherency strain energy due to the stress between both formed regions with different compositions and these regions and other parts of an alloy [6]. The coherency strain energy increasing the internal energy of an alloy decreases the spinodal decomposition range.

According to Gibb's classic treatment of phase stability, spinodal decomposition begins from the changes that are large in extent but small in degree [7] and develops when a negligibly small phase separation fluctuation decreases the free energy of an alloy.

$GaSb_xN_yAs_{1-x-y}$ belong to $AB_xC_yD_{1-x-y}$-type alloys where the anions (Sb, N and As) are surrounded by only one-type cations (Ga), having one mixed sublattice. Therefore, decomposition of such alloys resulting in an exchange of lattice sites between the anions does not vary the concentrations of the bonds. Accordingly, the spinodal decomposition range of $GaSb_xN_yAs_{1-x-y}$ alloys depends only on their strain and coherency strain energies. N-low content $In_xGa_{1-x}N_yAs_{1-y}$ belongs to $A_xB_{1-x}C_yD_{1-y}$-type quaternary alloys with a zinc blende. Their crystal lattice consists of the mixed cation and anion sublattices, since two kinds of the atoms fill each of them. As a result, $A_xB_{1-x}C_yD_{1-y}$ alloys have four types of chemical bonds: $A-C$, $A-D$, $B-C$ and $B-D$. A special characteristic of these alloys is the transformation of the AC and BD bonds in the AD and BC bonds or vice versa. This peculiarity is independent of the concentrations x and y. Therefore, the spinodal decomposition in these semiconductors is accompanied by the transformations of the bonds. The transformation of the bonds changes

the chemical composition and should change the free energy of the alloy [8, 9]. Therefore, spinodal decomposition range of the $In_xGa_{1-x}N_yAs_{1-y}$ alloys depends on the strain and coherency strain energies and transformation of the bonds. As it was shown in Ref. 10, the very extensive spinodal decomposition range of the $In_xGa_{1-x}N_yAs_{1-y}$ lattice mismatched to GaAs occurs due to the transformation of the bonds. The observed compositional inhomogeneity of $In_xGa_{1-x}N_yAs_{1-y}$ [11,12] confirms the theoretical results from Ref. 10.

As described above, there are two types of III-nitride quaternary alloys that can be used in the device applications. The crystal structure belonging to both of them is very strained internally. These internal strains should result in significant strain energy and, accordingly, a tendency toward spinodal decomposition. Moreover, one type of alloy has an additional origin of spinodal decomposition. However, what type of alloy has the thermodynamic preference from the standpoint of spinodal decomposition is unknown up to now. The regular solution model is the "conventional" model for the description of both types of these alloys and will be used. The aim of this study is to consider the spinodal decomposition ranges in $GaSb_xN_yAs_{1-x-y}$ and $In_xGa_{1-x}N_yAs_{1-y}$ taking into account the transformations of the bonds and strain and coherency strain energies.

2. Model

The initial stage of spinodal decomposition is accompanied by transfers of atoms over distances of the order of a lattice parameter. It was shown [13] that in cubic crystals the spinodal decomposition forms layers in a plane, where their elastic energy is minimal. Accordingly, the transfers of atoms produce a thin two-layer region with negligibly small differences in the compositions. The compositions of the layers formed at the initial stage of the decomposition can be considered to have constant values due to their small thickness. As the decomposition develops, the transfers of atoms and thickness of the layers and composition of the layers varies with their thickness. Afterwards, the difference in the mean concentrations of the phases increases continuously [14]. The initial stage of spinodal decomposition is considered to be the occurrence of two thin layers oriented in the (100) plane since the relation between the stiffness coefficients $2C_{44} - C_{11} + C_{12} > 0$ is fulfilled [15]. The stiffness coefficients of the alloys were estimated as average values of the constituent compounds. In this case, the elastic energy is minimal, due to the occurrence of these layers [13].

The phase separation leads to changes in the value of x, y or both of them in two phases occurring in the decomposed alloy. An alloy reaches the spinodal decomposition range when the variation in its free energy becomes equal to zero: $\delta f = 0$ [16]. This condition is fulfilled if one of two expressions

$$\frac{\partial^2 f}{\partial x^2}, \tag{1}$$

$$\frac{\partial^2 f}{\partial x^2} \times \frac{\partial^2 f}{\partial y^2} - \left(\frac{\partial^2 f}{\partial x \partial y} \right)^2. \tag{2}$$

becomes equal to zero [14]. The Helmholtz free energy of the homogeneous alloys grown on crystalline substrates can be represented as in Refs. 9 and 17:

$$f = f^C + u^S + u^L - Ts, \tag{3}$$

where, f^C, u^S, u^L are the chemical part, strain and lattice mismatch energies, respectively, s is the configurational entropy and T is the absolute temperature. A very detailed study of the thermodynamic stability of the quaternary alloys with respect to spinodal decomposition includes the term u^L as in Ref. 17, since the decomposition leads to an occurrence of the coherency strain energy due to the stress between the phases that appear. Then the negligibly small lattice mismatch between the alloy and substrate is introduced in order to include it in our consideration of the coherency strain energy. As $GaSb_xN_yAs_{1-x-y}$ alloys have a mixed sublattice, they contain three types of chemical bonds: GaSb, GaN and GaAs. The crystal lattice of the $In_xGa_{1-x}N_yAs_{1-y}$ alloys consists of mixed cation and anion sublattices, since two kinds of atoms fill each of them. Thus, these alloys have four types of bonds: InN, InAs, GaN and GaAs. For the sake of brevity, $GaSb_xN_yAs_{1-x-y}$ and $In_xGa_{1-x}N_yAs_{1-y}$ will be written as $AB_xC_yD_{1-x-y}$ and $A_xB_{1-x}C_yD_{1-y}$ alloys, respectively. The chemical parts of the free energy of $AB_xC_yD_{1-x-y}$ and $A_xB_{1-x}C_yD_{1-y}$ alloys are given as a sum of the energies free of the constituent compounds, respectively, as

$$f^C = x\mu^0_{AB} + y\mu^0_{AC} + (1 - x - y)\mu^0_{AD}, \tag{4}$$

$$f^C = xy\mu^0_{AC} + x(1-y)\mu^0_{AD} + y(1-x)\mu^0_{BC}$$
$$+ (1-x)(1-y)\mu^0_{BD}, \tag{5}$$

where μ^0_{AB} is the chemical potential of compound *AB*. By Vegard's law, the strain energies of $AB_xC_yD_{1-x-y}$ and $A_xB_{1-x}C_yD_{1-y}$ alloys are written, respectively, as

$$u^S = xy\alpha_{AB-AC} + x(1 - x - y)\alpha_{AB-AD}$$
$$+ y(1 - x - y)\alpha_{AC-AD}, \tag{6}$$

$$u^S = x(1-x)y\alpha_{AC-BC} + xy(1-y)\alpha_{AC-AD} \tag{7}$$
$$+ x(1-x)(1-y)\alpha_{AD-BD}$$
$$+ y(1-x)(1-y)\alpha_{BC-BD}, \tag{8}$$

where α_{AB-AC} is the interaction parameter between *AB* and *AC* compounds in the alloy. The strain energy is represented by the interaction parameters between the constituent compounds of the alloy. The interaction parameters were obtained from the strain energies of the corresponding ternary alloys estimated by the valence force field model as [1,15].

These energies were interpolated as $\alpha x(1-x)$, where α is the interaction parameter between the constituent compounds of the ternary alloy and x is the concentration of the compound. The lattice mismatch energy of the epitaxial layer on the substrate with the orientation (001) is given as [18]

$$u^L = \frac{(C_{11} - C_{12})(2C_{11} + C_{12})}{C_{11}} \left(\frac{a - a_S}{a_S}\right)^2 \quad (9)$$

where a and a_S are the lattice parameters of the alloy and substrate, respectively, C_{11} and C_{12} are given as [1]. The

configurational entropies of $AB_x C_y D_{1-x-y}$ and $A_x B_{1-x} C_y D_{1-y}$ are expressed respectively, just as in Ref. 1, by the equations

$$s = -R\left[x \ln x + y \ln y + (1-x-y) \ln (1-x-y)\right], \quad (10)$$

$$s = -R\left[x \ln x + (1-x) \ln (1-x) \right.$$
$$\left. + y \ln y + (1-y) \ln (1-y)\right], \quad (11)$$

where, R is the universal gas constant. Conditions (1) and (2) for $AB_x C_y D_{1-x-y}$ and $A_x B_{1-x} C_y D_{1-y}$ alloys taking into account (3-10) can be rewritten, respectively, as

$$-2\alpha_{AB-AD} + RT\frac{1-y}{x(1-x-y)} + \frac{\partial^2 u^L}{\partial x^2} = 0, \quad (12)$$

$$\left[-2\alpha_{AB-AD} + \frac{RT(1-y)}{x(1-x-y)} + \frac{\partial^2 u^L}{\partial x^2}\right] \times \left[-2\alpha_{AC-AD} + RT\frac{1-x}{y(1-x-y)} + \frac{\partial^2 u^L}{\partial y^2}\right]$$

$$- \left(\alpha_{AB-AC} - \alpha_{AB-AD} - \alpha_{AC-AD} - \frac{RT}{1-x-y} + \frac{\partial^2 u^L}{\partial x \partial y}\right)^2 = 0, \quad (13)$$

$$\alpha_{AC-BC} y + \alpha_{AD-BD}(1-y) - \frac{RT}{2x(1-x)} + \frac{\partial^2 u^L}{\partial x^2} = 0, \quad (14)$$

$$\left\{2\left[\alpha_{AC-BC} y + \alpha_{AD-BD}(1-y)\right] - \frac{RT}{x(1-x)} + \frac{\partial^2 u^L}{\partial x^2}\right\}$$

$$\times \left\{2\left[\alpha_{AC-AD} x + \alpha_{BC-BD}(1-x)\right] - \frac{RT}{y(1-y)} + \frac{\partial^2 u^L}{\partial y^2}\right\}$$

$$+ \left[\begin{array}{l}\mu_{AC}^0 + \mu_{BD}^0 - \mu_{AD}^0 - \mu_{BC}^0 + (\alpha_{AC-BC} - \alpha_{AD-BD})(1-2x) \\ + (\alpha_{AC-AD} - \alpha_{BC-BD}) + \frac{\partial^2 u^L}{\partial x \partial y}\end{array}\right]^2 = 0. \quad (15)$$

3. Results and discussion

$GaSb_x N_y As_{1-x-y}$ and $In_x Ga_{1-x} N_y As_{1-y}$ alloys are grown by the molecular beam and metalorganic vapor phase epitaxies at the growth temperatures of 600°C or lower [19,20]. Therefore, the spinodal decomposition ranges were estimated in the temperature interval from 0 to 600°C. The value $\mu_{InN}^0 - \mu_{InAs}^0 - \mu_{GaN}^0 + \mu_{GaAs}^0$ was estimated by

$$\mu_{InN}^0 - \mu_{InAs}^0 - \mu_{GaN}^0 + \mu_{GaAs}^0 = \Delta h - T\Delta s$$

$$+ \int_{298.15}^{T} \Delta c\, dT - T \int_{298.15}^{T} \frac{\Delta c}{T} dT, \quad (16)$$

where

$$\Delta h = h_{InN} - h_{InAs} - h_{GaN} + h_{GaAs},$$

$$\Delta s = s_{InN} - s_{InAs} - s_{GaN} + s_{GaAs},$$

$$\Delta c = c_{InN}^P - c_{InAs}^P - c_{GaN}^P + c_{GaAs}^P,$$

$$h_{InN}, \quad s_{InN}, \quad c_{InN}^P, \quad h_{InAs}, \quad s_{InAs}, \quad c_{InAs}^P,$$

$$h_{GaN}, \quad s_{GaN}, \quad c_{GaN}^P, \quad h_{GaAs}, \quad s_{GaAs}$$

and

$$c_{GaAs}^P$$

are the enthalpies, the entropies at the standard state and specific heat capacities at constant pressure of InN, InAs, GaN and GaAs, respectively. Specifically, Eq. (16) is the chemical term in Eq. (15) due to the transformation of the InN and GaAs bonds in the less thermodynamically profitable InAs and GaN bonds. Thus, the transformation of the bonds changes the chemical composition of the $In_x Ga_{1-x} N_y As_{1-y}$ quaternary alloys. The thermodynamic characteristics of the metastable cubic GaN and InN are supposed to be equal to the same characteristics of their stable hexagonal modifications. The thermodynamic, elastic and structure characteristics of the constituent compounds were taken from
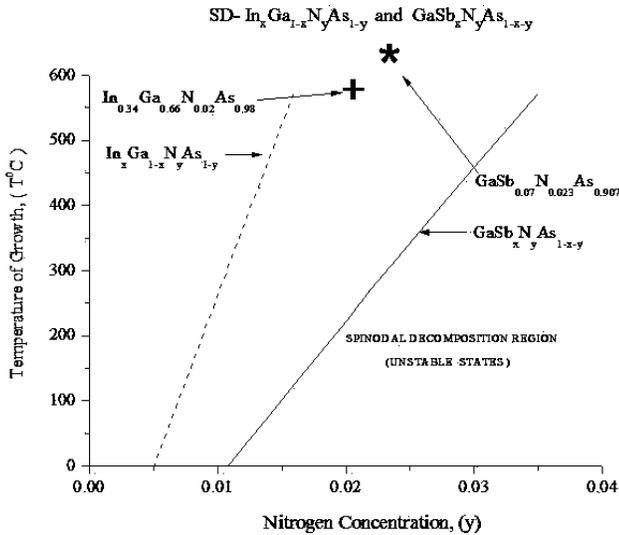
FIGURE 1. The spinodal decomposition ranges of the GaAs-enriched $GaSb_xN_yAs_{1-x-y}$ and $In_xGa_{1-x}N_yAs_{1-y}$ alloys. $In_{0.34}Ga_{0.66}N_{0.02}As_{0.98}$ and $GaSb_{0.07}N_{0.023}As_{0.907}$ are the experimental values.

Ref. 21. The interaction parameter between the compounds

$$\alpha_{GaSb-GaAs} = 22.92 \text{kJ/mole},$$

$$\alpha_{GaSb-GaN} = 409 \text{kJ/mole},$$

$$\alpha_{GaN-GaAs} = 22.81 \text{kJ/mole},$$

$$\alpha_{InN-GaN} = 45.32 \text{kJ/mole}$$

and $\alpha_{InAs-GaAs} = 18.19 \text{kJ/mole}$ were estimated from the strain energy of the corresponding ternary alloys by the approach from Ref. 22. The bond stretching and bond bending elastic constants of GaAs, GaSb, GaN, InN and InAs were taken from Refs. 23 and 24. Other interaction parameters used in the calculations were taken from Ref. 25.

The lattice parameters of $GaSb_xN_yAs_{1-x-y}$ are given as $a = xa_{GaSb} + ya_{GaN} + (1-x-y)a_{GaAs}$ and for $In_xGa_{1-x}N_yAs_{1-y}$ as

$$a = xya_{InN} + x(1-y)a_{InAs} + y(1-x)a_{GaN}$$
$$+ (1-x)(1-y)a_{GaAs}.$$

In the estimates we supposed that the lattice parameters of the alloys and the substrate are close to each other $(a \approx a_{GaAs})$. Thus, the concentrations of Sb and In in the considered $GaSb_xN_yAs_{1-x-y}$ and $In_xGa_{1-x}N_yAs_{1-y}$ alloys lattice matched to GaAs are given, respectively, as

$$x = \frac{a_{GaAs} - a_{GaN}}{a_{GaSb} - a_{GaAs}}y$$

and

$$x = \frac{y(a_{GaAs} - a_{GaN})}{a_{InAs} - a_{GaAs} + (a_{InAs} - a_{InN} + a_{GaN} - a_{GaAs})}.$$

Accordingly, the spinodal decomposition ranges of these alloys are the functions of one independent variable, which is nitrogen concentration. The spinodal decomposition ranges of the GaAs-enriched alloys are demonstrated in Fig. 1. As can be seen from Fig. 1, the $GaSb_{0.07}N_{0.023}As_{0.907}$ ($a = 5.655$Å, $\lambda = 1300$nm) alloy [26] is outside the spinodal decomposition range at its growth temperature. At the same time, the lattice mismatched $In_{0.34}Ga_{0.66}N_{0.02}As_{0.98}$ ($a = 5.767$Å, $\lambda = 1320$nm) [27] alloy is located deep in the spinodal decomposition range. Thus, from the standpoint of spinodal decomposition, $GaSb_xN_yAs_{1-x-y}$ are more promising alloys than $In_xGa_{1-x}N_yAs_{1-y}$. It is important to mention that the consideration of a wider temperature range is invalid since the GaAs-rich $GaSb_xN_yAs_{1-x-y}$ and $In_xGa_{1-x}N_yAs_{1-y}$ quaternary alloys are epitaxially grown up to 600 °C [19, 20]. Consequently, the nitrogen concentrations are very small for both types of alloys. In addition, the spinodal decomposition ranges shown in Fig. 1 begin with $y = 0.005$ and $y = 0.010$ for $In_xGa_{1-x}N_yAs_{1-y}$ and $GaSb_xN_yAs_{1-x-y}$ alloys, respectively. The bond transformation occurring during the phase separation of $In_xGa_{1-x}N_yAs_{1-y}$ leads to a dramatic increment in the temperature of spinodal decomposition. The transformation of In-As and Ga-N bonds into In-N and Ga-As bonds is thermodynamically profitable since the sum of the free energies of In-N and Ga-As is significantly smaller that that of In-As and Ga-N. The lengths of the In-N and Ga-As bonds are closer to each other than those of the In-As and Ga-N bonds. Therefore, the bond transformation reaction during spinodal decomposition is given as $nIn - As + nGa - N \rightarrow nIn - N + nGa - As$. The coherency strain energy decreases the spinodal decomposition range of the alloys considered. Therefore, in spite of the significant strain energy, the $GaSb_xN_yAs_{1-x-y}$ alloys in the large composition regions are outside the spinodal decomposition range at their growth and lower temperatures.

4. Conclusions

In summary, we have described spinodal decomposition ranges of the $GaSb_xN_yAs_{1-x-y}$ and $In_xGa_{1-x}N_yAs_{1-y}$ lattice-matched to GaAs by taking into account the transformations of the bonds, strain and coherency strain energies. The strain energy is estimated by the valence force field model with the bond stretching and bond bending elastic constants of Ga(Sb, As). From the standpoint of spinodal decomposition, $GaSb_xN_yAs_{1-x-y}$ are more promising than $In_xGa_{1-x}N_yAs_{1-y}$.

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