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Effects of elastic energy on the spinodal decomposition of InNAsP/InP heterostructures

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Spinodal decomposition of the $\mathrm{InN}_x\mathrm{As}_y\mathrm{P}_{1-x-y}$ quaternary alloys lattice-matched to the InP as the result of the internal deformation and elastic energies is described. The alloys are represented as quasiternary regular solutions. The internal deformation energy is obtained from the interaction parameters between the constituent compounds estimated by the valence force field model. Ranges of spinodal decomposition of the $\mathrm{InN}_x\mathrm{As}_y\mathrm{P}_{1-x-y}$ alloys up to $y \leq 0.109$ with and without elastic energy are demonstrated. Our results suggest that such energy prevents spinodal decomposition.

Keywords: Quaternary alloys; spinodal decomposition.

Se describe la descomposición espinodal de las aleaciones cuaternarias $\mathrm{InN}_x\mathrm{As}_y\mathrm{P}_{1-x-y}$ crecidas sobre InP como resultado de las energías de deformación interna y elástica. Las aleaciones se representan como soluciones cuasiternarias regulares. La energía de deformación interna se obtiene de los parámetros de interacción entre los compuestos que forman la aleación estimados por el modelo de campo de fuerza de valencia. Se muestran los rangos de descomposición espinodal de las aleaciones $\mathrm{InN}_x\mathrm{As}_y\mathrm{P}_{1-x-y}$ con y sin la energía elástica hasta $y \leq 0.109$. Nuestros resultados sugieren que tal energía previene la descomposición espinodal.

Descriptores: Aleación cuaternaria; descomposición espinodal.

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1. Introduction

Long-wavelength lasers emitting at 1.3 and 1.55 μm are important for optical-fiber communications and have been intensively investigated. The lasers were commonly realized with the GaInAsP/InP material system, but they have poor performance at high temperature (25°C - 85°C) and thermoelectric coolers are often required for their use in communication systems [1]. In contrast, the InAsP/InP and, more recently InNAsP/InP heterostructures have shown considerable promise for lasers and other optoelectronic devices operating at 1.06-1.55 μm [2]. Furthermore, InNAsP alloys have generated considerable interest, because incorporation of N at low concentration into the InAsP alloy layers has been shown to produce a substantial decrease in band gap [3], can partially compensate for strain due to As present in the alloy, and may possibly increase the conduction band offset [3], resulting in better electron confinement. In addition, the InNAsP/InP material system is interesting because the effects of N incorporation on material properties are not clearly understood, but appear to differ considerably from the effects of alloying with other group V elements [3].

The large difference between the atomic sizes of nitrogen, arsenic and phosphorus gives rise to the significant strain energy. Such energy provides the tendency to disintegration that can lead to the appearance of the thermodynamically unstable states with respect to the phase separation [4,5]. The phase separation was already observed earlier in the "conventional" III-V compounds alloys grown by various epitaxial methods [6,7]. The phase separation in these alloys can also be represented as spinodal decomposition in line with the theoretical study [8]. However, the nature of this phenomenon seems not entirely clear. The description of the spinodal decomposition ranges in [8] was fulfilled without the elastic energy. This energy appeared after spinodal decomposition increases the free energy of an alloy and suppresses its decomposition range [9]. Moreover, another point of view on the origin of the phase separation in these semiconductors was justified in [10], where the authors come to recognize that the phase separation observed in [6,7] appeared due to surface diffusion of atoms of growing epitaxial layers. The purpose of our study is to determine the spinodal decomposition of InNAsP quaternary alloys lattice-matched to the InP (001) substrate with and without the elastic strain energy.

2. The model

Spinodal decomposition begins if the alloy reaches the limit of stability with respect to the disintegration when the negligibly small decomposition fluctuations decrease its free energy [11]. The initial stage of spinodal decomposition is accompanied by transfers of atoms on the distances of order of a lattice parameter. Accordingly, the transfers of atoms lead to an occurrence of thin two-layer region with negligibly small distinction in the compositions and they can be considered as constant values due to their small thickness. Formation of the layers in cubic crystals oriented in the (001) planes [9], causes the elastic energy.

The elastic energy of a lattice-mismatched layer on the substrate with orientation (001) is given as [12]

$$u_E = \sum_{i=1}^{2} \gamma_i V_i Y_i \left(\frac{\Delta a_i}{a_i}\right)^2 . \qquad (1)$$

where, $V_i = a_i^3/4N_{Av}$ is the molar volume, N_{Av} is the Avogadro number, $\Delta a_i = a_i - a$, a is the lattice parameter of the substrate, $Y_i = \left(C_{11}^i - C_{12}^i\right)\left(C_{11}^i + 2C_{12}^i\right)/C_{11}^i$, C_{11}^i and C_{12}^i are the stiffness coefficients of the $i-$th $(i = 1, 2)$ phase of the decomposed alloy that are given as in Ref. 13. Finally, a_i is the lattice parameter expressed by

$$a_i = x a_{\text{InN}} + y a_{\text{InAs}} + (1 - x - y)\, a_{\text{InP}}.$$

The InN$_x$As$_y$P$_{1\text{ - x - y}}$ quaternary alloys contain three types of chemical bonds In-N, In-As and In-P. Their amounts are kept constant at the phase separation onto the two molecular layers, therefore, only the free energy of mixing of an alloy varies at spinodal decomposition.

The decomposition changes the value of x, y or both of them to form two new phases. The variation of the Helmholtz free energy of mixing at the initial stage of spinodal decomposition can be represented as

$$\delta f \approx \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[f^m + u_E\right](\delta x)^2 + \frac{\partial^2}{\partial x \partial y}\left[f^m + u_E\right]\delta x \delta y + \frac{1}{2}\frac{\partial^2}{\partial y^2}\left[f^m + u_E\right](\delta y)^2 . \qquad (2)$$

Wheref^m is the molar Helmholtz free energy of mixing of a InN$_x$As$_y$P$_{1\text{ - x - y}}$ alloy in the unstrained state. This free energy described by the regular solution model is given by [14]

$$\begin{aligned} f^m = {} & xy\alpha_{\text{InN}-\text{InAs}} + x(1-x-y)\,\alpha_{\text{InN}-\text{InP}} \\ & + y(1-x-y)\,\alpha_{\text{InAs}-\text{InP}} \\ & + RT\left[x\ln x + y\ln y + (1-x-y)\ln(1-x-y)\right]. \end{aligned} \qquad (3)$$

where $\alpha_{\text{InN}-\text{InAs}}$ is the interaction parameter between compounds InN and InAs. The boundary of the spinodal decomposition range is described by the formula $\delta f = 0$ [11]. This condition can be rewritten as

$$-2\alpha_{\text{InN}-\text{InP}} + \frac{RT(1-y)}{x(1-x-y)} + \frac{1}{2}YN_{\text{Av}}\left(a_{\text{InN}} - a_{\text{InP}}\right)^2 a = 0, \qquad (4a)$$

$$\begin{aligned} & \left[-2\alpha_{\text{InN}-\text{InP}} + \frac{RT(1-y)}{x(1-x-y)} + \frac{1}{2}YN_{\text{Av}}\left(a_{\text{InN}} - a_{\text{InP}}\right)^2 a\right] \\ & \times \left[-2\alpha_{\text{InAs}-\text{InP}} + \frac{RT(1-x)}{y(1-x-y)} + \frac{1}{2}YN_{\text{Av}}\left(a_{\text{InAs}} - a_{\text{InP}}\right)^2 a\right] \\ & - \left[\alpha_{\text{InN}-\text{InAs}} - \alpha_{\text{InN}-\text{InP}} - \alpha_{\text{InAs}-\text{InP}} + \frac{RT}{1-x-y} + \frac{1}{2}YN_{\text{Av}}\left(a_{\text{InN}} - a_{\text{InP}}\right)\left(a_{\text{InAs}} - a_{\text{InP}}\right) a\right]^2 = 0. \end{aligned} \qquad (4b)$$

3. Results and discusión

The interaction parameters between the compounds:

$$\alpha_{\text{InN}-\text{InAs}} = 1.297 \times 10^5 \text{J/mol},$$

$$\alpha_{\text{InN}-\text{InP}} = 9.407 \times 10^4 \text{J/mol},$$

$$\alpha_{\text{InAs}-\text{InP}} = 3.801 \times 10^3 \text{J/mol}$$

were estimated from the internal deformation energies of the corresponding ternary alloys [15]. The internal deformation energy of the ternary alloys was calculated by the valence-force field model [16]. The data used for the calculations were taken from [16,17].

In order to analyze the results, we considerer the works most relevant about characterization and growth of the InN$_x$As$_y$P$_{1-x-y}$ materials [2,18,19]. For example a InAs$_x$P$_{1-x}$ / InN$_x$As$_y$P$_{1-x-y}$/InP sample was grown by gas-source molecular beam epitaxy (MBE). In particular InN$_{0.01}$As$_{0.35}$P$_{0.64}$ was grown on an InP(001) substrate at a temperature of 460°C [2]. The InN$_{0.005}$As$_{0.44}$P$_{0.555}$ and InN$_{0.037}$As$_{0.59}$P$_{0.373}$ samples were grown on semi-insulating InP(001) substrates using a modified Varian Gen-II system at 460°C [18]. Precisely, this temperature was taken into account to describe the spinodal decomposition and the samples represent our experimental values.

Figure 1 shows the spinodal decomposition ranges for the InN$_x$As$_y$P$_{1-x-y}$ alloys lattice matched to InP(001) substrate $(0 < x \leq 0.11,\ y = 1 - 0.75x)$ with and without the elastic energy. A scrutinize of the curves reveals a drastic increase of the temperature of spinodal decomposition when the elastic energy is not considered. In others words, the unstable states region bounded by solid line is more extensive that the region bounded by dotted line. Since the view point of stability, the introduction of elastic energy considerably increases the region of stable states. The curves were determined by

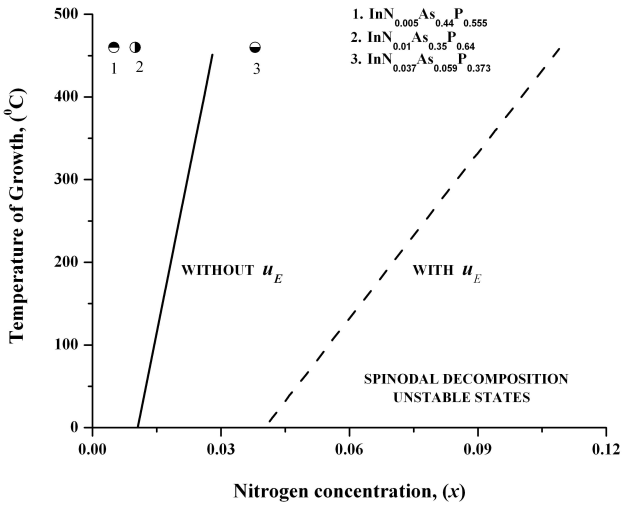

FIGURE 1. Spinodal decomposicion ranges of $InN_xAs_yP_{1-x-y}$ alloys grown on an InP (001) substrate, **1-** $InN_{0.005}As_{0.44}P_{0.555}$, **2-** $InN_{0.01}As_{0.35}P_{0.64}$ and **3-** $InN_{0.037}As_{0.59}P_{0.373}$ samples are the experimental values represented by circles.

the condition (4b) because it is fulfilled at higher temperature than (4a).

At the same time the $InN_{0.005}As_{0.44}P_{0.555}$ and $InN_{0.01}As_{0.35}P_{0.64}$ experimental values represented by circles are outside of unstable limits independently if elastic energy is considered or no in the Eq. (4b). Our estimations predict also that $InN_{0.037}As_{0.59}P_{0.373}$ sample is inside the unstable region when $u_E = 0$ in (4b). Such sample is in the stable region if $u_E \neq 0$.

On the other hand, a small amount of nitrogen can has dramatic effects on physical properties: bandgap narrowing, change in the conduction band offset, and even change of the band structute from indirect to direct as in GaNP/GaP. When N-containing material is in quantum well, the conduction band offset is increased, resulting in a deeper quantum well and better electron confinement, as in InNAsP/InP and GaInNAs/GaAs [19]. The self-diffusion coefficients for the III-V compounds at room temperature are very small [20], but perhaps it is possible to use annealing at 500°C.

4. Conclusion

The spinodal decomposition ranges of $InN_xAs_yP_{1-x-y}$ alloys lattice matched to InP(001) substrate with and without the elastic energy are presented. The estimations show that elastic energy prevents spinodal decomposition.

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