Unstable states of $In_xAl_yGa_{1-x-y}N$ quaternary alloys

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Regions of unstable states characterized by the spinodal decomposition of high-Al-content $In_xAl_yGa_{1-x-y}N$ quaternary alloys lattices matched to the GaN (001) substrate are described. The alloy are represented as strictly regular solutions. In the analysis we take into account the internal deformation and elastic strain energies. The regions of unstable states or ranges of spinodal decomposition considering the compositions $0.06 \leq x \leq 0.18$ and $0 \leq y \leq 0.95$ with and without elastic energy are demonstrated up to 580°C. We conclude that high concentrations of aluminum dramatically increased the phase separation temperature.

Keywords: Quaternary alloys; spinodal decomposition.

Se describen las regiones de los estados inestables caracterizados por la descomposición espinodal de las aleaciones cuaternarias $In_xAl_yGa_{1-x-y}N$ con altos contenidos de Al crecidas sobre el substrato de GaN (001). Las aleaciones son representadas como soluciones estrictamente regulares. En el análisis tomamos en cuenta las energías de deformación interna y elástica. Se muestran las regiones de los estados inestables o los rangos de la descomposición espinodal considerando las composiciones de $0.06 \leq x \leq 0.18$ y $0 \leq y \leq 0.95$ con y sin la energía elástica hasta 580°C. Concluimos que altas concentraciones de aluminio incrementa dramáticamente la temperatura de separación de fase.

Descriptores: Aleación cuaternaria; descomposición espinodal.

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1. Introduction

Mixed group-V nitride alloy semiconductors, for example GaNP, GaNAs and GaInNAs, are novel semiconductor materials developed in the 1990s. They are very promising because they can be used to make devices with superior performance due to their uncommon physical properties, such as huge band bowing. Compared with GaN, InGaN and AlGaN, InGaAlN quaternary alloys have attracted much research interest because these semiconductors should allow almost independent control of the lattice constant and bandgap [1,2]. Enhanced luminescence in InGaN multiple quantum wells with quaternary InAlGaN barriers was demonstrated by decreasing the piezoelectric polarization [3]. Ultraviolet (UV) LEDs with AlGaN QWs as an active layer have very low efficiency. However, by introducing indium into AlGaN, a similar effect to that obtained in InGaN QWs is expected for InAlGaN quaternary alloys [4]. Device applications depend strongly on the constancy of alloy characteristics. As it was shown in Ref. 5, As-rich $In_xGa_{1-x}N_yAs_{1-y}$ alloys are inside the spinodal decomposition range at growth or thermal annealing temperatures. Therefore, an analysis of the spinodal decomposition of these materials is especially valuable because they enable us to find the region of the unstable states of an alloy. Indeed, negligibly small phase separation fluctuations are developed if an alloy is inside the spinodal decomposition range. Thus, in previous works [6-8], the spinodal decomposition ranges of the quaternary alloys based on group –III nitrides were described in this article, we estimate the spinodal decomposition range of high-Al-content $In_xAl_yGa_{1-x-y}N$ alloys lattice-matched to the GaN (001) substrate with and without the elastic strain energy.

Let us begin by saying that $In_xAl_yGa_{1-x-y}N$ alloys belong to the $A_xB_yC_{1-x-y}D$ - type quaternary alloys. The crystal structure of this type of alloys consists of one mixed cation sublattice formed of (In, Al and Ga) atoms, where they are surrounded by only one-type anions (N). As a result, $A_xB_yC_{1-x-y}D$ have three types of chemical bonds: $A-D$, $B-D$ and $C-D$. Consequently, the bond concentrations describe the chemical composition of the alloys. However, the bond concentration and elemental composition are connected by three equations: $x_{AD} = x$, $x_{BD} = y$, $x_{CD} = 1-x-y$.

Concentrations of the bonds in the quaternary alloys of three binary compounds are also independent on the arrangement of the atoms in the mixed sublattice. The distinction in the lattice constants of the binary compounds constituting the $In_xAl_yGa_{1-x-y}N$ alloys gives rise to the internal deformation energy. This energy provides the tendency to phase separation that can lead to the thermodynamically unstable states with respect to spinodal decomposition or formation of the long-period concentration waves [9]. Such states may be produced as the transformation of a homogeneous alloy into a two-phase system [9]. At the same time, this kind of decomposition leads to an occurrence of the coherency strain energy due to the stress between both formed regions with different compositions and these regions and the other part of an alloy [9]. Therefore, we have two origins controlling spinodal decomposition in the $In_xAl_yGa_{1-x-y}N$ alloys.

2. Model

The spinodal decomposition range will be described as a region where the phase separation fluctuations are negligibly small in degree but spread a large distance, decreasing the al-

loy free energy [9]. The phase separation in the vicinity of the spinodal decomposition boundary of cubic crystals should appear in the planes, ensuring a minimum of elastic strain energy [10]. The self-diffusion transfers of the atoms at the initial stage of spinodal decomposition are of the order of a lattice parameter. Thus, the initial stage in the vicinity of the spinodal decomposition boundary of $In_xAl_yGa_{1-x-y}N$ alloys grown on GaN (001) is considered to be the appearance of a set of very thin two-phase layers. Composition of the layers formed in the initial stage can be considered constant values due to their small thickness. As decomposition develops, the atom transfers and the thicknesses of the layers become larger as well as the composition of the layers, which varies with distance. Afterwards, the difference in the mean concentrations of the phases increases continuously.

The initial stage of spinodal decomposition of the $In_xAl_yGa_{1-x-y}N$ alloys results in the change x, y, or both of them in two phases after the phase separation. An alloy reaches the spinodal decomposition range when the variation in its free energy becomes equal to zero: $\delta f = 0$ [11]. This condition is fulfilled if one of two expressions

$$\frac{\partial^2 f}{\partial x^2}, \quad \frac{\partial^2 f}{\partial x^2} \times \frac{\partial^2 f}{\partial y^2} - \left(\frac{\partial^2 f}{\partial x \partial y}\right)^2. \tag{1}$$

becomes equal to zero [12]. The Helmholtz free energy of the $In_xAl_yGa_{1-x-y}N$ homogeneous alloy in the strictly regular approximation is given by [8]

$$\begin{aligned} f = & xy\alpha_{InN-AlN} + x\,(1-x-y)\,\alpha_{InN-GaN} \\ & + y\,(1-x-y)\,\alpha_{\mathrm{AlN-GaN}} + u_E \\ & + RT\,[x\ln x + y\ln y + (1-x-y)\ln(1-x-y)]\,. \end{aligned} \tag{2}$$

where $\alpha_{\mathrm{InN-AlN}}$ is the interaction parameter between binary compounds InN and AlN, R and T are the universal gaseous constant and absolute temperature. The molar elastic energy of a lattice-mismatched layer on the substrate with orientation (001) as given as [10]

$$u_E = \sum_{i=1}^{2} \gamma_i V_i Y_i \left(\frac{\Delta a_i}{a_i}\right)^2. \tag{3}$$

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. 7. Finally, a_i is the lattice parameter expressed by $a_i = xa_{\mathrm{InN}} + ya_{\mathrm{AlN}} + (1-x-y)\,a_{GaN}$.

The minimum value of the deformation energy (3) is achieved at the condition $\gamma_1{=}\gamma_2$. Conditions (1) for $In_xAl_yGa_{1-x-y}N$ alloys taking into account (2-3) can be rewritten, respectively, as

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

$$\begin{aligned} & \left[-2\alpha_{\mathrm{InN-GaN}} + \frac{RT\,(1-y)}{x\,(1-x-y)} + \frac{1}{2}YN_{\mathrm{Av}}\left(a_{\mathrm{InN}} - a_{\mathrm{GaN}}\right)^2 a\right] \\ & \times \left[-2\alpha_{\mathrm{AlN-GaN}} + \frac{RT\,(1-x)}{y\,(1-x-y)} + \frac{1}{2}YN_{\mathrm{Av}}\left(a_{\mathrm{AlN}} - a_{\mathrm{GaN}}\right)^2 a\right] \\ & - \left[\alpha_{\mathrm{InN-AlN}} - \alpha_{\mathrm{InN-GaN}} - \alpha_{\mathrm{AlN-GaN}} + \frac{RT}{1-x-y} + \frac{1}{2}YN_{\mathrm{Av}}\left(a_{\mathrm{InN}} - a_{\mathrm{GaN}}\right)\left(a_{\mathrm{AlN}} - a_{\mathrm{GaN}}\right) a\right]^2 = 0. \end{aligned} \tag{4b}$$

3. Results and discussion

The $In_xAl_yGa_{1-x-y}N$ quaternary alloys were grown on the GaN layers at 580°C [13]. Precisely, we consider this temperature to describe the spinodal decomposition ranges of these semiconductors ($0 \leq y \leq 0.9$, x = 0.06, 0.07, 0.09, 0.1, 0.12, 0.14, 0.16,0.18) with and without elastic energy. Our results are demonstrated in Fig. 1. The regions of the unstable states limited by the dotted lines is more extensive than the regions limited by the solid lines; this can be explained in the following way: the elastic energy emerging in the disintegrated alloy substantially decreases the temperature of spinodal decomposition. At the same time, Al dramatically raises the temperature of the decomposition. However, such temperatures do not mean an increase in the alloy disintegration probability, because the formation of long-period concentration waves requires permutations of atoms on macroscopic distances. The curves are determined by the second condition (4b) because it is fulfilled at a higher temperature than the first condition (4a). The spinodal decomposition temperature was estimated as a function of x and y, which were used as given values. Furthermore the self-diffusion coefficients for the III-V compounds at room temperature are very small [14], but perhaps it is possible to use annealing at 500°C. The segregation may be verified by TEM measurements. The interaction parameters between the compounds:

$$\alpha_{\mathrm{InN-AlN}} = 9.231 \times 10^4 \mathrm{J/mol},$$

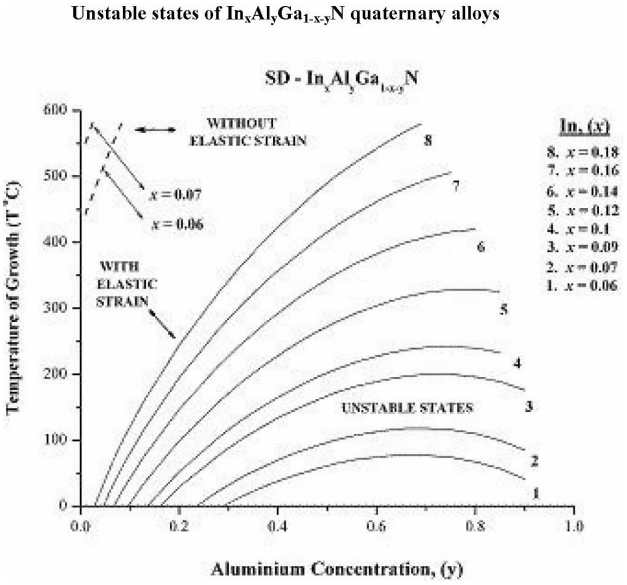

FIGURE 1. Spinodal decomposition ranges of the $In_xAl_yGa_{1-x-y}N$ alloys. Solid lines indicate the ranges estimated considering the elastic energy. Dotted lines demonstrate the ranges without the elastic strain.

$$\alpha_{\text{InN}-\text{GaN}} = 5.113 \times 10^4 \text{J/mol},$$

$$\alpha_{\text{AlN}-\text{GaN}} = 3.875 \times 10^4 \text{J/mol}$$

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].

4. Conclusions

The spinodal decomposition ranges of high-Al-content $In_xAl_yGa_{1-x-y}N$ alloys grown on GaN(001) due to the strain and elastic strain energies are presented. In the proposed model the Helmholtz free energy is described by using the strictly regular approximation.

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