

## Phase Separation in wurtzite $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$

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The wurtzite structure  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  quaternary system is studied with respect to the unstable region in mixing. The composition in the unstable region is calculated from the free energy of mixing by using the strictly regular solution model. The interaction parameter used in this calculation is obtained by using the delta-lattice-parameter method. Here, the proportionality constant connecting the lattice constants and the band-gap energy is determined by fitting the calculation to the composition data obtained experimentally from InGaN grown by metallorganic vapor phase epitaxy. From this calculation, the ternary alloys of InAlN, InGaN and GaAlN are predicted to always, sometimes, and hardly ever, respectively, have an unstable mixing region. The essential mismatch in thermal equilibrium between the strictly regular solution approximation and the growth conditions in MOVPE is removed by using a fitting calculation and experimental data. Also, the mismatch between the zinc-blende structure and the wurtzite structure is corrected. As a result, this prediction of the phase separation in  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  becomes more reliable.

### 1 Introduction

The development of wurtzite  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  for high performance [1], progressed significantly, as it is a wide-bandgap material with a direct optical transition. To improve device quality and provide new applications,  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  must be of higher quality and have a wider composition range. To grow materials with high quality, a high growth temperature is usually used. For materials in which the phase separation occurs easily, this high temperature is also effective at making the single phase composition region wider. Indeed, this is very important in InGaN for quantum-well layers in laser diodes and light emitting diodes in the region of blue and violet light. In addition, in multiterinary materials, the miscible composition region limits the device structure. From these viewpoints, it is important to clarify the unstable and stable-mixing composition regions of the material system. The author has already reported the observation of phase separation in  $\text{In}_{1-x}\text{Ga}_x\text{N}$  using X-ray diffraction and analytical transmission electron microscopy (ATEM) [2]. On the other hand, from theory, the calculation of the unstable- and stable-mixing-regions in  $\text{In}_{1-x}\text{Ga}_x\text{N}$  was done using a modified valence-force-field-model. [3] This calculation used parameters obtained by extrapolation from experimental values of zinc-blende structure III-V semiconductors.

The author also calculated the spinodal isotherms of  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  systematically on the basis of a strictly regular solution approximation [4] which simplified the calculation [5]. The strain in the film grown on a sapphire substrate was not considered because the films in devices are so much thicker than the critical thickness that the strain is relaxed.

In this paper, we review the relationship between the experimental data and the simulation of the phase separation. The phase separation in the  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  system is then systematically predicted on the basis of a strictly regular solution approximation. The parameter used for this calculation is determined by fitting a calculated phase diagram to experimental data.

### 2 Calculation Method and InGaN Growth

The  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  system can be regarded as a pseudoternary system because mixing of In, Ga and Al atoms occurs on one of the sublattices. The miscibility gap in a ternary mixture was theoretically treated by Meijering [6] on the basis of the strictly regular solution approximation, in which pair-wise interactions among nearest-neighbor atoms and random mixing of the constituent atoms in a single phase were assumed. In this calculation, the strictly regular solution model is used for calculating the free-energy of materials. The spin-

odal isotherm, which is the boundary between unstable and metastable regions, is calculated from the free energy of mixing. This isotherm can be calculated as the inflection points in the Helmholtz free-energy surface in the whole composition range. The binodal isotherm, which is the boundary between metastable and stable regions, can also be calculated as a set of tangential points on a double-tangential plane to the free energy surface. In these calculations, the pseudobinary interaction parameters (which connects the product of each two pseudobinary compositions with the enthalpy of mixing) are needed. Until now, no experimental data about interaction parameters in  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  has been presented. The interaction parameters were therefore determined from the calculation utilizing the delta-lattice-parameter model (DLP) of Stringfellow [7]. This method was developed for analyzing zinc-blende structure crystals and the pseudobinary interaction parameter  $\alpha_{i-j}$  is calculated from only the lattice constants  $a_i$  and  $a_j$  as a parameter: that is,

$$\alpha_{i-j} = 4.375K \frac{(a_i - a_j)^2}{\left(\frac{a_i + a_j}{2}\right)^{4.5}} \quad (1)$$

In this method, the wurtzite structure must be transformed to the zinc-blende structure. The (0001) plane in the wurtzite structure corresponds to the (111) plane in the zinc-blende structure. The set of lattice constants in the wurtzite structure,  $\mathbf{a}$  and  $\mathbf{c}$ , are transformed to an equivalent lattice constant,  $\mathbf{a}_{\text{eq}}$ , in the zinc-blende structure. Here, this  $\mathbf{a}_{\text{eq}}$  is expressed as  $(3^{1/2}\mathbf{a}^2\mathbf{c})^{1/3}$ .  $\mathbf{a}_{\text{eq}}$  becomes  $2^{1/2}\mathbf{a}$  for the ideal wurtzite structure; that is,  $\mathbf{c}/\mathbf{a}=(8/3)^{1/2}$  because the (0001) plane in the wurtzite structure corresponds to the (111) plane in the zinc-blende structure.  $K$  in equation (1) is the constant in the relationship between the enthalpy of atomization and the lattice constant, which was found empirically by Philips [8]. The value of  $K$  is unknown for the present case, and it must be determined for calculation of the miscibility gap of  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$ .  $K$  is determined by fitting the calculated phase diagrams to the experimental data with respect to the phase separation of  $\text{In}_{1-x}\text{Ga}_x\text{N}$ . To determine the value of  $K$ ,  $\text{In}_{1-x}\text{Ga}_x\text{N}$  of various compositions was directly grown without a buffer layer using metallorganic vapor phase epitaxy (MOVPE) on (0001) sapphire substrates at 500, 700, and 800°C [9]. The reactor pressure was held at 76 Torr. The surfaces of the sapphire substrates were nitrided by annealing at 1150°C in an ammonia atmosphere just before growth in a reactor. The source gases were triethylgallium, tri-

ethylindium, and ammonia. The carrier and bubbling gases were nitrogen. The flow rate ratio of ammonia to the group III sources was varied from 2,000 to 20,000. The composition of grown  $\text{In}_{1-x}\text{Ga}_x\text{N}$  was measured by X-ray diffraction from the (0002) plane. When determining the composition, the strain included in films and the so-called pulling effect (the composition variation from the substrate to the surface of a grown film [10]) were neglected.

### 3 Results and Discussion

In this section, the validity of the interaction parameter calculated from the DLP model is verified by comparing each spinodal isotherm calculated using the experimentally determined interaction parameters and the interaction parameters calculated using the DLP model with respect to  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{As}$ . To decide whether to use the binodal or the the spinodal isotherms to predict the miscibility gap, the experimental data is considered for the case of  $\text{InAs}_{1-x-y}\text{Sb}_x\text{P}_y$ . On the basis on these discussions, the phase separations in  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  are predicted.

First, the experimentally determined interaction parameters and those calculated using the DLP model are compared. For this purpose,  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{As}$  is used because its interaction parameters have been experimentally measured and it is a III-V semiconductor which includes only one kind of group-five element, just like  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$ . The calculated interaction parameters of  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{As}$  are compared with experimental data in Table 1. There is a difference of more than 10% between the experimental and calculated values of the interaction parameter of AlAs-InAs, while for InAs-GaAs and GaAs-AlAs, the calculated values are almost equal to the experimental data. The spinodal isotherms calculated using experimentally measured interaction parameters and calculated ones are also shown in Figure 1. The spinodal isotherms calculated using interaction parameters from the DLP model shows unstable mixing regions wider than the ones calculated using experimental interaction parameters. At low temperature, both curves overlap, while at high temperature, the difference between both isotherms becomes large. This tendency is enhanced near  $\text{In}_{1-y}\text{Al}_y\text{As}$  because of the large difference in lattice constants between AlAs and InAs. From this discussion, the interaction parameter calculated from the DLP model can be used to approximately express the spinodal isotherm.

Next, we estimate the miscibility gap. Theoretically, the miscibility gap should be explained in terms of binodal isotherms. The immiscibility under near-thermal-equilibrium conditions, such as in the solution growth of a bulk crystal and liquid phase epitaxy will be governed

by binodal points, while in the thermal annealing of a solid solution, the spinodal point will be a criterion for immiscibility. Therefore, it is important to compare experimental data with the results of calculation with respect to  $\text{InAs}_{1-x-y}\text{Sb}_x\text{P}_y$  of which the mixing compositions were experimentally investigated under liquid phase epitaxy as shown in Figure 2 [11]. The experimental data are distributed near the spinodal isotherm. This figure shows that the spinodal isotherm inside the binodal isotherm sometimes corresponds to the boundary of the miscible region and the immiscible one. Spinodal isotherms are therefore approximately sufficient for prediction of the miscibility gap in  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$ . At present,  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  is grown by MOVPE or molecular beam epitaxy (MBE), which is a non-equilibrium growth method thermally different from solution growth. This suggests that the miscibility gap becomes wider for thermally non-equilibrium growth than for the solution growth. Therefore, with respect to  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  grown by MOVPE and MBE, the spinodal isotherms are preferable for prediction of the miscibility gap. In addition, the spinodal isotherm can be calculated more easily than the binodal isotherm. That is, the spinodal isotherm is calculated as a solution of a quadratic equation in  $x$  for  $y$  given as explicitly shown in Ref. [5]. On the other hand, the binodal isotherm is calculated as the solutions of three-element simultaneous equations including nonlinear functions as follows.

$$2\alpha_{\text{In-Ga}}(x_2-x_1) + (\alpha_{\text{In-Ga}} + \alpha_{\text{In-Al}} - \alpha_{\text{Ga-Al}})(y_2-y_1) - RT \ln \frac{x_2(1-x_1-y_1)}{x_1(1-x_2-y_2)} = 0 \quad (2)$$

$$2\alpha_{\text{In-Al}}(y_2-y_1) + (\alpha_{\text{In-Ga}} + \alpha_{\text{In-Al}} - \alpha_{\text{Ga-Al}})(x_2-x_1) - RT \ln \frac{y_2(1-x_1-y_1)}{y_1(1-x_2-y_2)} = 0 \quad (3)$$

$$\alpha_{\text{In-Ga}}(x_2^2-x_1^2) + \alpha_{\text{In-Al}}(y_2^2-y_1^2) + (\alpha_{\text{In-Ga}} + \alpha_{\text{In-Al}} - \alpha_{\text{Ga-Al}})(x_2y_2-x_1y_1) + RT \ln \frac{1-x_2-y_2}{1-x_1-y_1} = 0 \quad (4)$$

Here,  $\alpha_{i-j}$  is the pseudobinary interaction parameter,  $T$  is the absolute temperature, and  $R$  is the gas constant.

The spinodal isotherms are calculated using the results of the above discussion of simulating the miscibility gap in  $\text{InAs}_{1-x-y}\text{Sb}_x\text{P}_y$ . In the course of the calculation, we have one problem even using the DLP model to calculate the interaction parameters for  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$ .

That is, the proportionality constant  $K$  between the  $a$  lattice constant and the pseudobinary interaction parameter as shown in Equation (1) is not fixed. In conventional III-V materials, the  $K$  value is determined from the measured interaction parameter, and its value is  $1.15 \times 10^7$  cal/mol  $\text{\AA}^{2.5}$ . The spinodal isotherms strongly depend on  $K$  as already reported by the author [5]. Therefore,  $K$  is determined by fitting the spinodal isotherms to the experimental data with respect to  $\text{In}_{1-x}\text{Ga}_x\text{N}$  epitaxially grown by MOVPE as shown in Figure 3. Figure 3(a) and figure 3(b) show calculated spinodal isotherms as a parameter of  $K$  and experimental phase-separated data at 700°C and 800°C, respectively.  $K$  (cal/mol  $\cdot \text{\AA}^{2.5}$ ) is 6 to  $8 \times 10^6$ . At this temperature,  $K$  of 6 or  $7 \times 10^6$  and 7 or  $8 \times 10^6$  fit the experimental data at 700°C and 800°C, respectively. According to these fits,  $7 \times 10^6$  which was estimated as the common value in both temperatures was adopted as the  $K$  value. However, this value is smaller than the value obtained from the experimentally obtained interaction parameter of  $1.15 \times 10^7$  in commonly used III-V materials such as InP, GaAs, and so on [7]. The difference of  $K$  values between commonly used III-V materials and  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  is considered to be due to the degree of thermal equilibrium in the growth conditions of the measured films, that is, more common III-V materials were grown by liquid phase epitaxy (LPE) and  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  was grown by MOVPE which uses more non-equilibrium growth conditions than those of LPE. Therefore, mixing of materials occurs easily, or in other words, the interaction parameter and thus the  $K$  value becomes small.

The spinodal isotherms calculated using the  $K$  value obtained above for  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  at 600°C to 1000°C are shown in Figure 4. The calculated interaction parameters of InN-GaN, GaN-AlN and AlN-InN are 6,559, 672, and 11,366 cal/mole, respectively. The transformed lattice constants of binary alloys are also expressed in this figure. The region surrounded by the InN-AlN line, the InN-GaN line, and the isotherms shows the unstable composition of  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$ . As an example, the hatched region indicates the unstable composition at a temperature of 1000°C. The ternary alloy in InAlN always has an unstable region at the growth temperature lower than 1000°C. GaAlN may be grown at all compositions because the isotherms are parallel to the GaN-AlN line. In InGaN, the unstable composition appears to be dependent on temperature. The tendency to instability in InAlN, GaAlN and InGaN is determined by the value of each interaction parameter, or the difference in lattice constants between binary alloys. By using the  $K$  value determined experimen-

tally, the essential mismatch between the strictly regular solution approximation and non-equilibrium in MOVPE, and between zinc-blende structure and wurtzite structure was removed. As a result, the prediction performed here for  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  became more reliable.

Spinodal isotherms are compared with the binodal isotherms, which define a thermodynamic miscibility gap, in Figure 4. In this figure, the tie lines, which connect sets of binodal points, are also shown. The binodal isotherm at a temperature of only 800°C is drawn to simplify the figure. Its detail will be reported elsewhere. For this calculation, Equation (2), Equation (3), and Equation (4) were used. The immiscible region shown with binodal curves becomes much wider than the one with the spinodal curves. The composition region with high indium content is especially restricted very near  $\text{InN}$ .

#### 4 Conclusion

The immiscible region of  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  was predicted by using a strictly regular solution approximation without any strain energy in solids. From fitting the spinodal isotherms calculated by using the delta-lattice-parameter method to the experimental data of  $\text{In}_{1-x}\text{Ga}_x\text{N}$  epitaxially grown by MOVPE, the proportionality constant  $K$  between the  $a$  lattice constant and the pseudobinary interaction parameter was determined to be  $7 \times 10^6 \text{ cal/mol}\cdot\text{\AA}^{2.5}$ . By using this  $K$  value, we calculated the spinodal and the binodal isotherms for the  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  quaternary system. We found that the ternary alloy of  $\text{InAlN}$  always has an unstable region;  $\text{GaAlN}$  may be grown at all compositions because the isotherms are parallel to the  $\text{GaN-AlN}$  line; and the unstable composition for  $\text{InGaN}$  appears to be dependent on the temperature.

The essential mismatch in thermal equilibrium between the strictly regular solution approximation and the growth conditions in MOVPE was removed by using fitting calculation and experimental data. Also the mismatch between the zinc-blende structure and the wurtzite structure was corrected. As a result, this prediction of the phase separation in  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  became more reliable.

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#### FIGURES

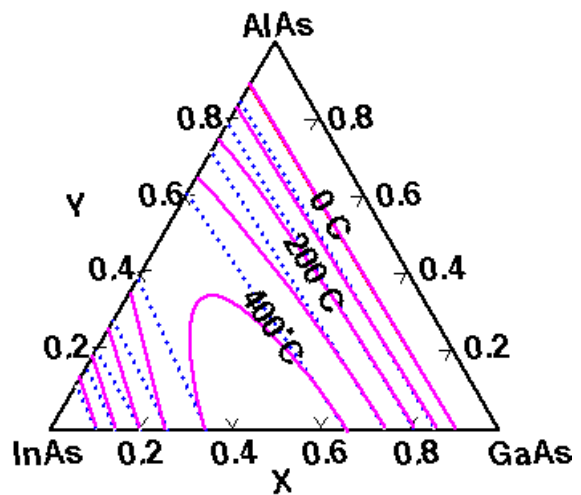


Figure 1. Comparison of spinodal isotherms in  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{As}$ . The solid and dashed lines show the spinodal isotherms calculated by using experimental data and those from the DLP model as interaction parameters, respectively.

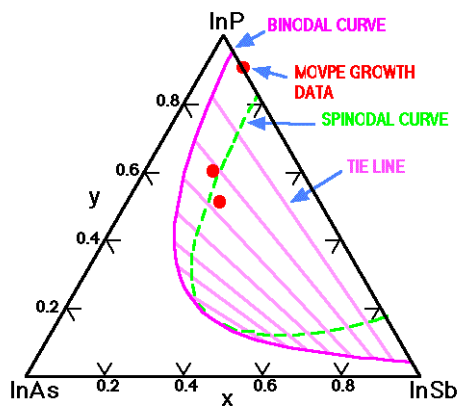


Figure 2. Comparison between binodal isotherms (solid curves), spinodal isotherms (dashed curves) for  $\text{InAs}_{1-x-y}\text{Sb}_x\text{P}_y$ , and experimental data from  $\text{InAs}_{1-x-y}\text{Sb}_x\text{P}_y$  grown by MOVPE at  $600^\circ\text{C}$ . This figure also shows tie lines (solid lines) after [11].

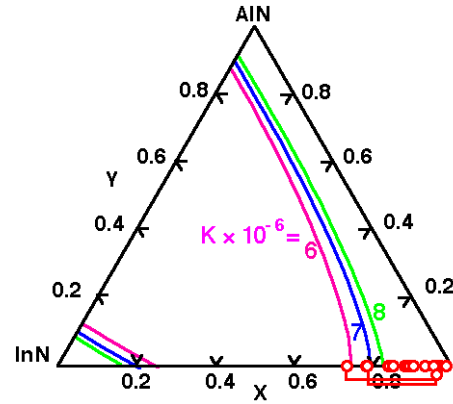


Figure 3b. Fitting spinodal isotherms of  $\text{In}_{1-x}\text{Ga}_x\text{N}$  calculated as a parameter of  $K$  to the composition of  $\text{In}_{1-x}\text{Ga}_x\text{N}$  grown at  $800^\circ\text{C}$ .

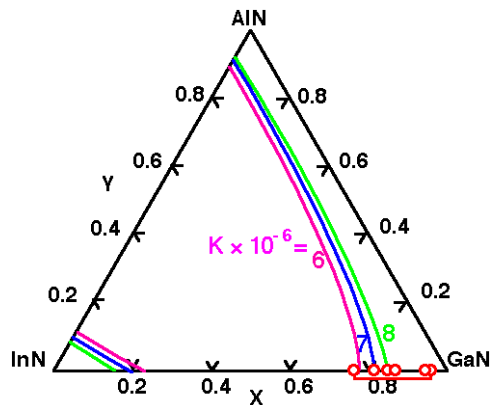


Figure 3a. Fitting spinodal isotherms of  $\text{In}_{1-x}\text{Ga}_x\text{N}$  calculated as a parameter of  $K$  to the composition of  $\text{In}_{1-x}\text{Ga}_x\text{N}$  grown at  $700^\circ\text{C}$ .

**Transformed Lattice Constant**

InN = 4.990  
GaN = 4.503  
AlN = 4.370

**Interaction Parameter**

InN - GaN = 6559  
GaN - AlN = 672  
AlN - InN = 11366

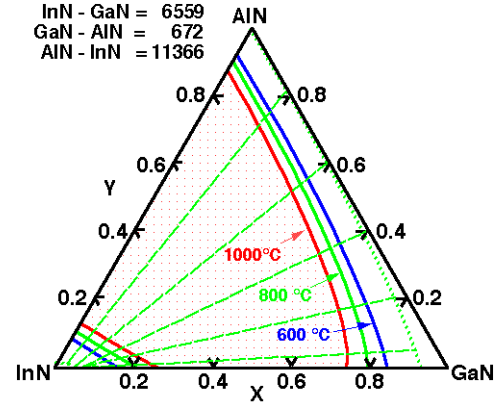


Figure 4. Calculated spinodal and isotherms for  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{N}$  for a constant  $K$  of  $7 \times 10^6 \text{ cal/mol}\cdot\text{\AA}^{2.5}$ . The spinodal isotherms at a temperature of 600, 800, and  $1000^\circ\text{C}$  are shown with solid curves. The hatched region shows the miscibility gap at  $800^\circ\text{C}$  predicted from the spinodal isotherm. The binodal isotherm at a temperature of  $800^\circ\text{C}$  and its tie lines are shown with dotted curves and dashed lines, respectively. The transformed lattice constants of binary alloys from a wurtzite structure to a zinc-blende structure and the interaction parameter of three pseudobinary alloys are also expressed.

**TABLES**

Table 1. Interaction parameters experimentally determined (EX) and those calculated by using the DLP model (DLP) in  $\text{In}_{1-x-y}\text{Ga}_x\text{Al}_y\text{As}$ .

	EX (cal/mole)	DLP (cal/mole)
InAs-GaAs	3000	2959
GaAs-AlAs	0	2
AlAs-InAs	2500	2805