# Atomic structure and phase stability of $In_xGa_{1-x}N$ random alloys calculated using a valence-force-field method

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We have calculated the atomic structure and strain energy of the  $In_xGa_{1-x}N$  random alloy ( $0 \le x \le 1$ ) based on 592~13 240-atom models. A valence-force-field method with the Keating potential is used for the strain energy calculation. We analyzed the bond-length and bond-angle distribution in the alloy due to the random fluctuation of the atom positions. The change in the average Ga–N and In–N bond lengths is calculated as a function of the composition *x*. The calculated result is in good agreement with the recent experimental data of the extended x-ray-absorption fine-structure method. The calculated enthalpy of mixing  $\Delta H_m$ , i.e., the strain energy, versus the composition *x* is expressed in the regular-solution model;  $\Delta H_m = \Omega x(1-x)$  using the *x-dependent* interaction parameter  $\Omega = -2.11x+7.41$  (kcal/mole). This  $\Omega$  value is the most reliable among those so far calculated. The calculated phase diagram shows a broad and asymmetric miscibility gap, e.g.,  $0.04 \le x \le 0.88$  at 800 °C. The critical temperature for phase separation is 1417 °C. [S0163-1829(99)05427-2]

### I. INTRODUCTION

The  $In_xGa_{1-x}N$  alloy system has recently become a leading material for the blue/green-wavelength optoelectronic devices. For example, using the  $In_xGa_{1-x}N$  alloy, the quantum well laser structures were realized by Nakamura *et al.*<sup>1</sup> More recently, the growth of  $In_xGa_{1-x}N$  quantum dots (QD's) has been carried out by Tachibana *et al.*<sup>2</sup> and Hirayama *et al.*<sup>3</sup> for the fabrication of the QD lasers.

The  $\ln_x Ga_{1-x}N$  alloy is a random alloy having the wurtzite structure. The cation sites are randomly occupied by In and Ga atoms with the compositions x and 1-x, respectively, and all the anion sites by N atoms. Due to the large difference (10.8%) between the Ga–N and In–N bond lengths, the atom positions are considered to fluctuate from the perfect lattice sites, leaving the bond-length and bondangle distortions in the alloy. Such disordered atomic structures were well studied theoretically for the III-V ternary alloys having the zinc-blende structure, e.g.,  $\ln_x Ga_{1-x}As$ ,<sup>4,5</sup> and  $\ln_x Ga_{1-x}P$ ,<sup>6</sup> while no studies were reported for the  $\ln_x Ga_{1-x}N$  alloys.

Theoretical analysis of the atomic structure of the  $In_xGa_{1-x}N$  random alloy is indispensable to understanding the phase stability of the alloy, because the enthalpy of mixing,  $\Delta H_m$ , is equal to the strain energy due to the bondlength and bond-angle distortions.<sup>4,7</sup> Recently, the phase separation of the  $In_xGa_{1-x}N$  alloy has been observed in various experiments<sup>8–11</sup> and considered a crucial issue for the optical properties of the layers. An accurate calculation of the phase diagram based on an appropriate model of the atomic structure is required in order to discuss the phase separation phenomena.

Information of the atomic structure including the alloy randomness is also important for calculating the electronic structure using an atomic-scale method, e.g., a tight-binding method. Such a calculation gives a more accurate result than the virtual crystal approximation (VCA) in which an alloy is represented by a perfect lattice with atoms having an average property of the pure semiconductors.

In this paper, we calculate the atomic structure and strain energy of the  $In_rGa_{1-r}N$  random alloy based on 592  $\sim$  13 240-atom models in order to analyze the atomic structure and phase stability. We use a valence-force-field (VFF) method with the Keating potential<sup>12</sup> for the strain energy calculation. The method of calculation is described in Sec. II. We analyze the atomic structure of the alloy in Sec. III. We show the bond-length and bond-angle distribution due to the alloy randomness. The change in the average Ga-N and In-N bond lengths is calculated as a function of the composition x. The result is compared with the recent experimental data by Jeffs et al.<sup>13</sup> measured using the extended x-ray absorption fine-structure (EXAFS) method. In Sec. IV, the enthalpy of mixing  $\Delta H_m$ , i.e., the strain energy, is calculated as a function of x. The x-dependent interaction parameter,  $\Omega$ , in a regular-solution model is obtained from the result of  $\Delta H_m$  versus x. Using this  $\Omega$  value, the phase diagram of the alloy is calculated very accurately. The conclusions are summarized in Sec. V.

## **II. METHOD OF STRAIN ENERGY CALCULATION**

We calculated the atom positions in the wurtzite  $In_xGa_{1-x}N$  random alloy having  $592\sim 13\,240$  atoms assembled in a hexagonal prism. The side length of the (0001) hexagonal base is  $\approx 9 \sim 31$  Å, the height of the prism  $\approx 18 \sim 49$  Å. To model the random alloy, we place In and Ga atoms randomly on the cation sites with the compositions *x* and 1-x, respectively, using random numbers, and place N atoms on the anion sites. All the atoms are placed on the perfect lattice sites at this stage.

To calculate the energy-minimized atom positions, we use

1701

the Keating potential<sup>12</sup> in which the strain energy  $E_{\text{strain}}$  is expressed in terms of the changes in the bond lengths and bond angles as

$$E_{\text{strain}} = \frac{1}{2} \sum_{i(j)} \frac{3\alpha_{i-j}}{8d_{0,i-j}^2} (|\mathbf{x}_i - \mathbf{x}_j|^2 - d_{0,i-j}^2)^2 + \sum_{i(j,k)} \frac{3\beta_{j-i-k}}{8d_{0,i-j}d_{0,i-k}} \bigg[ (\mathbf{x}_i - \mathbf{x}_j) \cdot (\mathbf{x}_i - \mathbf{x}_k) + \frac{1}{3}d_{0,i-j}d_{0,i-k} \bigg]^2.$$
(1)

Here the first sum is over all atoms *i* and their four neighbors *j*; the second sum is over all atoms *i* and all pairs of their neighbors *j* and *k*; and  $x_i$  is the atomic position of *i*th atom.  $d_{0,i-j}$  is the strain-free bond length of the *i*-*j* bond,  $\alpha_{i-j}$  is the bond-stretching force constant of the *i*-*j* bond, and  $\beta_{j-i-k}$  is the bond-bending force constant of the *j*-*i*-*k* bond angle.

We use  $d_{0,\text{Ga-N}}=1.94$  Å and  $d_{0,\text{In-N}}=2.15$  Å, where the values are taken from the tabulated ones by Harrison.<sup>14</sup> For the force constants, we use  $\alpha_{\text{Ga-N}}=96.3$  N/m,  $\beta_{\text{Ga-N-Ga}}=\beta_{\text{N-Ga-N}}=14.8$  N/m; and  $\alpha_{\text{In-N}}=79.2$  N/m,  $\beta_{\text{In-N-In}}=\beta_{\text{N-In-N}}=7.1$  N/m. The above  $\alpha$  and  $\beta$  values are taken from the corresponding bulk values calculated theoretically by Kim *et al.*<sup>15</sup> using a first-principles full-potential linear muffin-tin orbital method. As for  $\beta_{\text{In-N-Ga}}$  in the alloy, we adopt the average value of  $\beta_{\text{Ga-N-Ga}}$  and  $\beta_{\text{In-N-In}}$  as

$$\beta_{\text{In-N-Ga}} = \sqrt{\beta_{\text{Ga-N-Ga}} \beta_{\text{In-N-In}}}.$$
 (2)

In order to minimize the strain energy, each atom is moved in turn along the direction of the force on it,  $F_i$  $= -\nabla_i (E_{\text{strain}})$ , and the movement of atoms is iterated until the forces vanish.<sup>16</sup> After the energy minimization process, the atom positions fluctuate from the perfect lattice sites as shown in Sec. III.

In the analyses of the atomic structure (concerning the bond lengths and bond angles) and strain energy, we exclude the surface atoms which have dangling bonds, because we intend to obtain bulk properties of the alloy in this study.

#### **III. ATOMIC STRUCTURE**

In this section, firstly, we show the atomic structure of the  $In_{0.2}Ga_{0.8}N$  alloy with 592 atoms in order to illustrate how the structure is disorded by alloying. Next, we calculate the strain energy of the  $In_{0.2}Ga_{0.8}N$  alloy versus the number of atoms (592~13 240 atoms). We find that the strain energy reaches a bulk value above 9756 atoms. Lastly, for the 9756-atom model of the  $In_xGa_{1-x}N$  alloy, we analyze the average Ga–N and In–N bond lengths versus *x* and compare the result with the EXAFS measurement.<sup>13</sup>

Figure 1 shows the calculated atom positions in the  $In_{0.2}Ga_{0.8}N$  alloy with 592 atoms. The random mixing of In and Ga atoms on the cation sites is visible in this figure. Moreover, the atom positions fluctuate randomly from the perfect wurtzite lattice sites. The atom rows indicated by the arrows in the figure are clear examples; they run in a zigzag in the alloy, while they run straight in the perfect lattice. This



FIG. 1. Perspective view of the atom positions in the  $In_{0.2}Ga_{0.8}N$  alloy with 592 atoms; In (black), Ga (white), and N (gray) atoms. The atom rows, indicated by the arrows, show a significant fluctuation from the perfect lattice sites.

is a structural disorder caused by the random alloying, i.e., "alloy disorder."

Figure 2 shows the In–N and Ga–N bond-length distribution in the above  $In_{0.2}Ga_{0.8}N$  alloy with 592 atoms. The average Ga–N and In–N bond lengths, av.(Ga–N) and av.(In– N), become 0.25% longer and 1.31% shorter, respectively, than the corresponding bulk values indicated by the vertical dashed lines.

Figure 3(a) shows the bond-angle distribution in the alloy. As a whole, the bond angles,  $\theta$ 's, are distributed in the range



FIG. 2. Bond-length distribution in the  $In_{0.2}Ga_{0.8}N$  alloy with 592 atoms. av.(Ga–N) and av.(In–N) indicate the average Ga–N and In–N bond lengths, respectively, and av.(alloy) the average bond length in the whole  $In_{0.2}Ga_{0.8}N$  alloy.



FIG. 3. (a) Bond-angle distribution in the  $In_{0.2}Ga_{0.8}N$  alloy with 592 atoms. The bond angles are categorized into the N–In–N, N–Ga–N, In–N–In, In–N–Ga, and Ga–N–Ga bond angles. The vertical arrow indicates an average bond angle for each category. (b) Simplified model of the changes in bond angles around a single In atom (the closed circle) which is substituted for a Ga atom in the pure GaN lattice. The arrows indicate displacement of the nearest neighbor N atoms.  $\theta_0$  denotes the perfect tetrahedral angle.  $\theta_1$  and  $\theta_2$  are In–N–Ga and Ga–N–Ga bond angles, respectively, after the N atom displacement. This model roughly explains the changes in the average bond angles in (a).

109.47 (tetrahedral angle,  $\theta_0$ )  $\pm$  10 degree. The N–In–N and N-Ga-N angles (vertex; cation) are distributed almost symmetrically about  $\theta = \theta_0$ . On the other hand, the In–N–In, In-N-Ga, and Ga-N-Ga angles (vertex; N) are distributed less symmetrically. An average bond angle is smaller than  $\theta_0$ for the In–N–In and In–N–Ga angles, and larger than  $\theta_0$  for the Ga-N-Ga angles. This result concerning the average bond angles is roughly explained by the simplified model shown in Fig. 3(b). By substituting an In atom (the closed circles) for a Ga atom in the pure GaN lattice in order to make the alloy, the four nearest neighbor N atoms are displaced outward to make the In-N bonds longer than the Ga-N bonds. Due to the displacement of the N atoms, the In–N–Ga angle ( $\theta_1$ ) becomes smaller than  $\theta_0$ , and the Ga– N–Ga angle ( $\theta_2$ ) larger than  $\theta_0$ . When the N atom happens to bond to two In atoms, that N atom is displaced more largely, and the In–N–In angle becomes even smaller. On the other hand, the In atom is not displaced because it bonds to the four equivalent N atoms, hence the N-In-N angles are



FIG. 4. Enthalpy of mixing,  $\Delta H_m$ , versus the number of atoms in a model of the In<sub>0.2</sub>Ga<sub>0.8</sub>N random alloy (the number of atoms = 592, 1098, 4732, 9756, and 13 240).

kept  $\theta_0$ . The changes in the bond angles in this model (a dilute limit of the alloy) correspond to those in the *average* bond angles in Fig. 3(a) (x=0.2), where the bond angles in the latter case are distributed due to the overlap of the strain fields around the randomly substituted In atoms.

The bond-length and bond-angle distribution causes the strain energy,  $E_{\text{strain}}$ , which is a sum of bond-stretching and bond-bending strain energies [Eq. (1)]. The strain energy of semiconductor alloys is equal to the enthalpy of mixing,  $\Delta H_m$ , as shown by Martins and Zunger,<sup>7</sup> and Fukui.<sup>4</sup> Hereafter the calculated strain energy is shown as  $\Delta H_m$ .

Figure 4 shows  $\Delta H_m$  of the In<sub>0.2</sub>Ga<sub>0.8</sub>N random alloy versus the number of atoms in a model, here the number of atoms = 592, 1098, 4732, 9756, and 13 240. As shown in the figure, the calculated  $\Delta H_m$  takes a constant value when the number of atoms is larger than 9756, while  $\Delta H_m$  decreases gradually with decreasing the number of atoms. In the 592atom model,  $\Delta H_m$  is 16.2% smaller than that of the 9756atom model. This decrease in  $\Delta H_m$  is caused by the nearsurface atoms which have lower strain energy than the inside atoms of the models. Hereafter in this paper, we use the 9756-atom model in order to deduce accurately the bulk properties concerning the average bond lengths (the next paragraph) and phase stability (Sec. IV).

Figure 5 shows the average Ga–N and In–N bond lengths, av.(Ga–N) and av.(In–N), respectively, as a function of the composition x in the  $In_xGa_{1-x}N$  alloy with 9756 atoms (indicated by the closed circles). Starting from the pure GaN (x=0), the average Ga–N bond length becomes longer almost linearly with increasing the composition x. Similarly, the average In–N bond length becomes shorter starting from the pure InN (x=1). The changes in the average Ga–N and In–N bond lengths are much smaller than that calculated using the VCA,

$$(\text{VCA bond length}) = xd_{0,\text{In-N}} + (1-x)d_{0,\text{Ga-N}}, \qquad (3)$$

as shown in Fig. 5. This indicates limitations of the VCA for electronic structure calculations of the alloy. The above result for the average bond lengths versus x is qualitatively similar to those in zinc-blende alloys such as  $\ln_x \text{Ga}_{1-x} \text{As.}^{4,7}$ 

The almost linear changes in the average bond lengths in Fig. 5 are consistent with the general theory of bond lengths



FIG. 5. Average Ga–N and In–N bond lengths, av.(Ga–N) and av.(In–N), respectively, as a function of the composition x in the In<sub>x</sub>Ga<sub>1-x</sub>N alloy. The closed circles indicate the result of the present VFF calculation for the 9756-atom model. The open squares indicate the result of the EXAFS measurement by Jeffs *et al.* (Ref. 13). The dashed line "VCA" shows an average bond length in the whole alloy calculated using the virtual crystal approximation.

in random semiconductor alloys constructed by Cai and Thorpe.<sup>17,18</sup> They proved analytically that the average bond lengths in the pseudobinary alloys  $(A_{1-x}B_x)C$  are perfectly linear in the composition *x* if the force constants ( $\alpha$  and  $\beta$ ) for the two pure materials are the same.<sup>17</sup> The variations in the force constants have a minor effect,<sup>18</sup> and hence the VFF result in Fig. 5 is quite reasonable.

In Fig. 5, we compare the average Ga-N and In-N bond lengths obtained by the present VFF calculation with those obtained using the EXAFS experiment by Jeffs et al.<sup>13</sup> In their experiment,<sup>13</sup> the  $In_xGa_{1-x}N$  films ( $\approx 1 \ \mu m$  thick) were grown using a modified molecular-beam-epitaxy technique. The growth temperatures were low ( $\approx 400$  °C) to avoid phase separation. To measure the bond lengths, the total electron yield EXAFS technique for the Ga and In edges was employed.<sup>13</sup> As shown in the figure, the calculated result is in very good agreement with the EXAFS result in the whole range of the composition x. The agreement is better for the average Ga–N bond length than for the In–N case. Since the atomic structures calculated in the present study reproduce the measured structural data concerning the bond lengths, they are very adequate for the studies of phase stability and electronic structures.

#### **IV. PHASE STABILITY**

In order to study the phase stability of the  $In_xGa_{1-x}N$  random alloys, we calculate the phase diagram based on the regular-solution model.<sup>19</sup> The material-dependent parameter in the regular-solution model, i.e., the interaction parameter, is obtained from the VFF calculation.

In the regular-solution model,<sup>19</sup> the Gibbs free energy of mixing,  $\Delta G_m$ , for the  $\ln_x \text{Ga}_{1-x}$ N alloys is expressed as

$$\Delta G_m = \Delta H_m - T \Delta S_m, \qquad (4)$$



FIG. 6. Enthalpy of mixing,  $\Delta H_m$ , as a function of the composition *x* in the  $\ln_x \operatorname{Ga}_{1-x}$ N random alloy. The closed circles indicate the present VFF result for the 9756-atom model. The solid and dashed curves are calculated using the regular-solution model with the *x-dependent* and *x-independent* interaction parameters  $\Omega$ 's, respectively.

$$\Delta H_m = \Omega x (1 - x), \tag{5}$$

$$\Delta S_m = -R[x \ln x + (1 - x) \ln(1 - x)].$$
(6)

 $\Delta H_m$  and  $\Delta S_m$  are the enthalpy and entropy of mixing, respectively.  $\Omega$  is the interaction parameter, *R* is the gas constant, and *T* is the absolute temperature. Only the interaction parameter,  $\Omega$ , depends on material.

 $\Omega$  is assumed to be *x-independent* in usual phenomenological calculations of  $\Omega$  such as the delta-lattice-parameter (DLP) model.<sup>20</sup> On the other hand,  $\Omega$  is found to be weakly *x-dependent* in the present study due to the use of the atomicscale VFF calculation, as shown below. For III-V zincblende semiconductor alloys, *x* dependence of  $\Omega$  was calculated in detail using a first-principles calculation by Wei *et al.*<sup>21</sup>

First, we calculate  $\Omega$  as a function of x, from  $\Delta H_m$  calculated using the VFF method. In Fig. 6, we show  $\Delta H_m$  of the In<sub>x</sub>Ga<sub>1-x</sub>N random alloy with 9756 atoms for the composition x=0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1 calculated using the VFF method, as indicated by the closed circles.  $\Delta H_m$  has a maximum near x=0.5.

By rewriting Eq. (5) as

$$\Omega = \Delta H_m / x (1 - x), \tag{7}$$

we can calculate, for each x, a value of  $\Omega$  from the above VFF value of  $\Delta H_m$ . Figure 7 shows  $\Omega$  versus x calculated in this manner, as indicated by the closed circles.  $\Omega$  decreases almost linearly with increasing x. From a linear fit to the  $\Omega$  values, we obtain

$$\Omega = -2.11x + 7.41 \text{ (kcal/mole)}. \tag{8}$$

Next, we calculate  $\Delta H_m$  expressed by  $\Delta H_m = \Omega x(1-x)$ [Eq. (5)] with  $\Omega = -2.11x + 7.41$  (kcal/mole) [Eq. (8)], as drawn by the solid curve in Fig. 6. The VFF result of  $\Delta H_m$ (the closed circles) is accurately reproduced by the above  $\Delta H_m$  curve.



FIG. 7. Interaction parameter,  $\Omega$ , as a function of the composition x in the  $In_xGa_{1-x}N$  random alloy obtained from the present VFF result of  $\Delta H_m$  in Fig. 6, indicated by the closed circles. From a linear fit to the  $\Omega$  values, we obtain  $\Omega = -2.11x + 7.41$  (kcal/mole) as indicated by the dashed line.

The average value of the *x*-dependent  $\Omega$  in the range 0  $\leq x \leq 1$  is obtained as  $\Omega = -2.11 \times 0.5 + 7.41$ = 6.36 (kcal/mole).  $\Delta H_m$  expressed by  $\Delta H_m = \Omega x (1-x)$ [Eq. (5)], using  $\Omega = 6.36$  (kcal/mole) independent of *x*, is drawn in Fig. 6 by the dashed curve. This  $\Delta H_m$  curve is symmetric about x = 0.5, while that with the *x*-dependent  $\Omega$ (the solid curve) is asymmetric showing a deviation toward the lower *x* side. The effect of this asymmetry of  $\Delta H_m$  appears in the phase diagram as shown later.

Now, we can calculate accurately the free energy of mixing,  $\Delta G_m$  [Eq. (4) with Eqs. (5) and (6)], for the  $\ln_x Ga_{1-x}N$ random alloy using  $\Omega = -2.11x + 7.41$  (kcal/mole) [Eq. (8)] obtained from the present VFF result.

From  $\Delta G_m$  as a function of *x*, we calculate the temperature (T)-composition (x) phase diagram which shows the stable, metastable, and unstable mixing regions of the alloy following the standard theory.<sup>19</sup> At a temperature lower than the critical temperature  $T_c$ , the two binodal points are determined as those points at which the common tangent line touches the  $\Delta G_m$  curve. The two spinodal points are determined as those points at which the second derivative of  $\Delta G_m$  is zero;  $\partial^2(\Delta G_m)/\partial x^2 = 0$ .

Figure 8 shows the calculated phase diagram for the  $In_xGa_{1-x}N$  random alloy. It has a broad miscibility gap (or an immiscible region) surrounded by the binodal line. For example, at a typical growth temperature of 800 °C, the alloy is immiscible in the range  $0.04 \le x \le 0.88$ ; the alloy in this range is subject to phase separation into the  $In_{0.04}Ga_{0.96}N$  and



FIG. 8. Phase diagram for the  $\ln_x \operatorname{Ga}_{1-x} N$  random alloy calculated from the regular-solution model using  $\Omega = -2.11x + 7.41$  kcal/mole. The binodal and spinodal curves are shown by the solid and dashed lines, respectively.

In<sub>0.88</sub>Ga<sub>0.12</sub>N regions in thermal equilibrium. The miscibility gap is significantly asymmetric about x=0.5 due to the asymmetry of the  $\Delta H_m$  curve in Fig. 6. With increasing the temperature, the miscibility gap disappears just at  $T_c$ = 1417 °C and  $x_c=0.39$  (the critical composition).<sup>22</sup> In experiments, the phase separation was observed by several researchers in thick films<sup>8,9</sup> and multiple quantum wells<sup>10,11</sup> of the In<sub>x</sub>Ga<sub>1-x</sub>N alloys.

Another possible phase change, which can occur in the random alloys, is the atom *ordering*. Some experimental observations of the long-range atom ordering in the  $In_xGa_{1-x}N$  alloys have been reported recently.<sup>9,23</sup> Further calculation is required for studying the ordering phenomena theoretically, although the strain energy calculation in the ordered alloys can be done readily using the present computer code.

The phase diagram calculated in the present study (Fig. 8) is qualitatively very similar to those calculated previously by Ho and Stringfellow<sup>24</sup> and Matsuoka<sup>25</sup> concerning the presence of the miscibility gap. (The parameters of the phase diagram are summarized in Table I.) However, the present one is quantitatively much more reliable than the previous ones due to the following reasons. Ho and Stringfellow<sup>24</sup> calculated the phase diagram using a modified VFF method, but they used (i) the empirically extrapolated values for the force constants  $\alpha$  and  $\beta$ , (ii) the zinc-blende lattice for the strain energy calculation, and (iii) the *x*-independent  $\Omega$ , i.e., the average value of  $\Omega(x \rightarrow 0)$  and  $\Omega(x \rightarrow 1)$ . Their phase diagram is symmetric about x=0.5. On the other hand, in the

TABLE I. Parameters of the phase diagram for the  $In_xGa_{1-x}N$  random alloy calculated by various methods.

	VFF (present study)	VFF (Ho and Stringfellow) <sup>a</sup>	DLP (Matsuoka) <sup>b</sup>
$\Omega$ (kcal/mole)	-2.11x + 7.41	5.98	10.68
$T_c(^{\circ}\mathrm{C})$	1417	1250	2416
<i>x</i> <sub>c</sub>	0.39	0.5	0.5
miscibility gap	asymmetric	symmetric	symmetric

<sup>a</sup>Reference 24.

<sup>b</sup>Reference 25.

present study, we used (i) the values of  $\alpha$  and  $\beta$  from the first-principles calculation,<sup>15</sup> (ii) the wurtzite lattice, and (iii) the *x-dependent*  $\Omega$  [Eq. (8)], and obtained the asymmetric phase diagram. Matsuoka<sup>25</sup> calculated the phase diagram using the DLP model which uses the phenomenological and empirical parameters defined for the zinc-blende lattice. *Consequently, our phase diagram is the most reliable among those so far reported.* 

The  $In_xGa_{1-x}N$  random alloys with  $592 \sim 13\,240$  atoms are considered freestanding  $In_xGa_{1-x}N$  QD's. We can calculate the electronic structure of the QD's using, e.g., a tightbinding method<sup>16</sup> for the atom positions obtained in this study. The result will be published elsewhere.

# **V. CONCLUSIONS**

We have calculated the atomic structure and strain energy of the  $In_xGa_{1-x}N$  random alloy ( $0 \le x \le 1$ ) based on 592 ~13 240-atom models. The VFF method with the Keating potential<sup>12</sup> is used for the strain energy calculation. We find the bond length and bond angle distribution in the alloy due to the random fluctuation of the atom positions. The change

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in the average Ga–N and In–N bond lengths calculated as a function of the composition *x* is in good agreement with the experimental data of EXAFS by Jeffs *et al.*<sup>13</sup> The enthalpy of mixing,  $\Delta H_m$ , is calculated in the whole composition range  $0 \le x \le 1$ . The calculated  $\Delta H_m$  is expressed within the regular-solution model;  $\Delta H_m = \Omega x(1-x)$  using the *x*-dependent interaction parameter  $\Omega = -2.11x + 7.41$  (kcal/mole). This  $\Omega$  value is the most reliable among those so far calculated. The calculated phase diagram shows a broad and asymmetric miscibility gap, e.g.,  $0.04 \le x \le 0.88$  at 800 °C. The critical temperature for phase separation,  $T_c$ , is 1417 °C.

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