

# Evolution of structural properties and formation of N-N split interstitials in GaAs<sub>1-x</sub>N<sub>x</sub> alloys

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 (Received 9 December 2004; published 27 April 2005)

Using first-principles total energy calculations, we have studied the structural properties of the large lattice mismatched GaAs<sub>1-x</sub>N<sub>x</sub> alloys. We first discuss the validity of Vegard's law, which assumes a linear variation of the alloy concentration with both the lattice constant and the volume. In the dilute-N limit, the calculated lattice constant coincides with Vegard's law for the lattice constant, but not for the volume variation. This deviation implies that using Vegard's law for the volume variation overestimates the N concentration. In the dilute-As limit, the calculated lattice constant is larger than that suggested by the Vegard's law for both the volume and the lattice constant, implying that using Vegard's law overestimates the As concentration. The calculated bulk moduli for GaAs<sub>1-x</sub>N<sub>x</sub>, however, show almost linear behavior in the two region, increase monotonically with N concentration. We have also studied the effect of the split interstitial defect (N-N)<sub>spl</sub> on the electronic and structural properties of the alloy. We find that the split interstitial is an amphoteric defect with (+/0) transition at 0.2 eV and (0/-) transition at 0.3 eV above the valence band maximum. The concentration of the split nitrogen interstitial [N-N] is relatively small compared to the substitutional nitrogen [N], but it would be large if the system could be grown at the As-rich limit and the sample were doped *n*-type.

DOI: 10.1103/PhysRevB.71.165212

PACS number(s): 71.55.-i, 61.72.Vv

## I. INTRODUCTION

The large mismatch in electronegativity and size between N and As causes many unusual physical properties for GaAs<sub>1-x</sub>N<sub>x</sub> alloys.<sup>1</sup> For example, unlike other III-V semiconductor alloys that change their physical properties smoothly as a function of alloy concentration, a small amount of N in GaAs can drastically reduce the band gap,<sup>2,3</sup> with a bowing coefficient as large as 20 eV. This has led to extensive studies of GaAs<sub>1-x</sub>N<sub>x</sub> and related materials for optoelectronic device applications such as long-wavelength light emitters<sup>4</sup> and high-efficiency solar cells.<sup>5</sup> However, the application of this material has been limited by the perceived poor materials quality, partly due to the poor understanding of its materials and defect properties. For example, it is not clear how N is incorporated into GaAs, whether it is mixed as an isovalent constituent forming a substitutional GaAs<sub>1-x</sub>N<sub>x</sub> alloy or as dopants that form defects such as the (N-N) split interstitial in GaAs.<sup>6,7</sup> It is also not clear whether "Vegard's law,"<sup>8</sup> which assumes linear interpolation of the structural parameters, such as lattice constant, volume, and bulk modulus, still holds for this system with large lattice mismatch<sup>9</sup> between the constituents (5.6526 Å for GaAs and 4.5000 Å for GaN).<sup>10</sup> There is some experimental evidence that Vegard's law is not obeyed in this system.<sup>11-13</sup> Because the volume is proportional to the cube of the lattice constant, for systems with large lattice mismatch, Vegard's law cannot be satisfied *simultaneously* for the lattice constant and for the volume. Despite these considerations, it is often assumed experimentally that Vegard's law holds for the lattice constant and, in fact, it is often used to derive the N concentration of the alloy.<sup>14,15</sup>

In this paper, using first-principles total-energy calculations, we study the structural properties of GaAs<sub>1-x</sub>N<sub>x</sub> alloys to investigate the validity of Vegard's law for the lattice constant and bulk modulus. We find that in the dilute-N limit, the calculated volumes are smaller than those expected from Ve-

gard's law, implying that using Vegard's law for the volume overestimates the N concentration. Fortunately, Vegard's law applied to the lattice constant is close to the calculated results. On the other hand, in the dilute-As limit, the calculated lattice constants are larger than Vegard's law prediction for both volumes and lattice constants, implying that using Vegard's law overestimates the As concentration. The calculated bulk moduli for GaAs<sub>1-x</sub>N<sub>x</sub>, show a small positive bowing, i.e., the bulk modulus increases almost linearly with the N concentration.

We also report the effects of the (N-N)<sub>spl</sub> split interstitial defect on the electronic and structural properties of the alloy. We find that the split interstitial is an amphoteric defect with the (+/0) transition at about 0.2 eV and the (0/-) transition at about 0.3 eV above the valence band maximum (VBM). The concentration ratio between the split nitrogen interstitial [N-N] and the substitutional nitrogen [N] is usually very small, but it could be significantly larger if the system is grown under As-rich conditions, has high total N concentration, or if the sample is *n*-type, causing the (N-N)<sub>spl</sub> to be negatively charged.

## II. METHOD OF CALCULATIONS

Our calculations are performed within the local density approximation<sup>16</sup> (LDA) as implemented in the VASP code<sup>17,18</sup> and using the projector-augmented-waves (PAW) method.<sup>19,20</sup> The dilute alloys are modeled using supercells containing 32, 64, 128, and 256 atoms. Atomic and volume relaxations are performed for each supercell. The energy cut-off is 350 eV. Ga *d* electrons are treated as part of the core. **k** points, which are equivalent to the 10 special *k* points in the zinc-blende structure, are used for the Brillouin zone integration.<sup>21</sup> The lattice constants and bulk moduli of the system are obtained by fitting the calculated total energy as a function of the volume to Teter's equation of state.<sup>22</sup> The

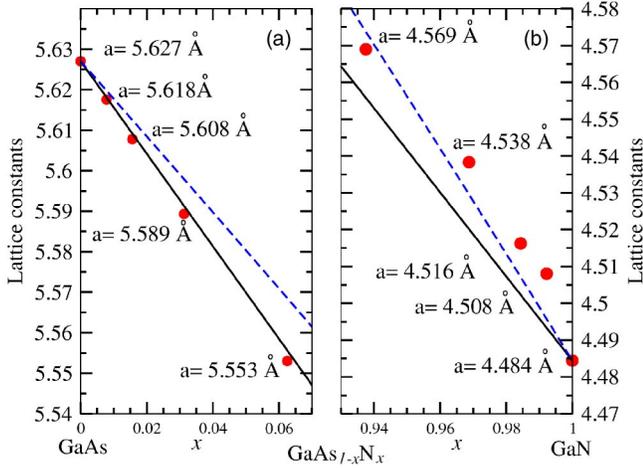


FIG. 1. (Color online) Comparison between Vegard's law and LDA calculated lattice constants of  $\text{GaAs}_{1-x}\text{N}_x$  alloy. The graph on the left corresponds to dilute-N ( $x \sim 0$ ), whereas the graph on the right corresponds to dilute-As ( $x \sim 1$ ). Solid lines assume linear interpolation of the lattice constant, whereas dashed lines assume linearity with cell volume.

calculated lattice constants and bulk moduli are 5.627 Å and 75.3 GPa for GaAs, and 4.484 Å and 213.0 GPa for GaN, in good agreement with experimental values of 5.653 Å and 75.3 GPa for GaAs and 4.500 Å and 210 GPa for GaN.<sup>10</sup> Our calculations are done for zinc-blende alloys, and we assume similar behavior will exist in the As-dilute alloys where wurtzite structure can be more stable.

The defect formation energy for the split N-N interstitial defect is given by

$$H_f^q(\text{N-N}) = E_t^q(\text{GaAs:N-N}) - E_t^0(\text{GaAs}) - 2\mu_{\text{N}} + \mu_{\text{As}} + q(\epsilon_F), \quad (1)$$

where  $E_t^q(\text{GaAs:N-N})$  is the total energy of the supercell with  $(\text{N-N})_{\text{spl}}$  at charge state  $q$ , and  $E_t^0(\text{GaAs})$  is the total energy of the same cell without the defect. Both of them are calculated at the host lattice constant, i.e., that of GaAs.  $\mu_{\text{N}}$  and  $\mu_{\text{As}}$  are the chemical potentials of N (referenced to the  $\text{N}_2$  molecule) and As (referenced to bulk As), and  $\epsilon_F$  is the Fermi energy (referenced to the VBM). The transition energy level ( $q/q'$ ) is the Fermi energy at which the formation energies of the defect with different charge states  $q$  and  $q'$  are the same. For the N substitutional defect, the expression for the formation energy takes the form

$$H_f^0(\text{N}_{\text{As}}) = E_t^0(\text{GaAs:N}_{\text{As}}) - E_t^0(\text{GaAs}) - \mu_{\text{N}} + \mu_{\text{As}}. \quad (2)$$

More detailed descriptions of the defect calculation can be found elsewhere.<sup>7,23</sup>

### III. STRUCTURAL PARAMETERS OF THE ALLOYS

Figure 1 plots the calculated lattice constant (solid dots) as a function of nitrogen concentration  $x$  together with Vegard's law predictions assuming linearity either with lattice constant (solid line) or volume (dashed line). Figure 1 shows that (i) for systems with large size mismatch, assuming lin-

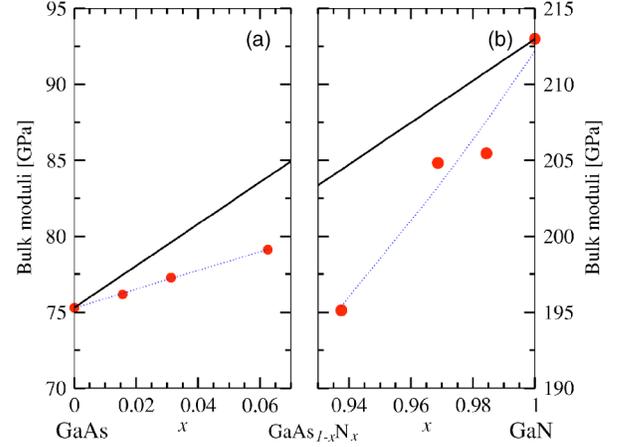


FIG. 2. (Color online) Comparison between Vegard's law (solid line) and LDA-calculated bulk moduli (dots) of  $\text{GaAs}_{1-x}\text{N}_x$  alloys. The graph on the left corresponds to dilute-N ( $x \sim 0$ ), whereas the graph on the right corresponds to dilute-As ( $x \sim 1$ ). The dotted line indicates the fit to a quadratic equation.

earity with volume gives a larger lattice constant than assuming linearity with lattice constant. The difference is about 0.1% at  $x=0.03$ . (ii) In the dilute-N region [Fig. 1(a)], the calculated LDA lattice constant is smaller than that predicted by the Vegard's law. The agreement is better if one assumes linearity with the lattice constant. This negative deviation from Vegard's law indicates that the Ga-N bond embedded in the GaAs network is still stronger than the Ga-As bond. (iii) In the dilute-As regime [Fig. 1(b)], the calculated lattice constant is larger than that predicted by the Vegard's law, but is closer if one assumes linearity with volume. The positive deviation from Vegard's law indicates that the Ga-As bond embedded inside the GaN network is more difficult to compress. The S-shaped deviation from the Vegard's law is also predicted by Denton *et al.*<sup>9</sup> for alloy systems with large size-mismatched constituents. This deviation from Vegard's law affects the determination of the N concentration in  $\text{GaAs}_{1-x}\text{N}_x$  alloys from their lattice constants, and consequently the analysis of experimental results (e.g., the corresponding band gap). Using Vegard's law for the lattice constant gives slightly overestimated concentrations. However, using Vegard's law for the volume, the error is larger and the estimated N concentration for a sample with a calculated lattice constant of 5.589 Å becomes 3.32% instead of the true N concentration, which is 3.125%.

Figure 2 shows the evolution of the bulk modulus as a function of concentration obtained by fitting to Teter's<sup>22</sup> equation of states from the calculated total energy as a function of volume. We find that the calculated bulk moduli show small positive bowing. The bulk modulus increases almost linearly with the increase of the nitrogen concentration, consistent with the general rule that the bulk modulus increases when the volume decreases<sup>24</sup> with an increase of the nitrogen concentration. The relatively small variation of the bulk modulus near the end point compounds suggests that the elastic constant in bulk  $\text{GaAs}_{1-x}\text{N}_x$  alloys should not change drastically, as reported for  $\text{GaAs}_{1-x}\text{N}_x$  thin film alloys' measurements.<sup>13</sup>

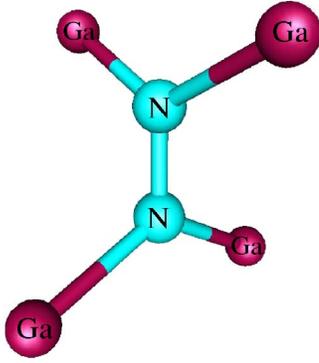


FIG. 3. (Color online) Geometry of the N-N split interstitial defect and surrounding atoms. The perturbation affects up to the *fifth* neighbors, compared to bulk GaAs bond structure.

#### IV. PROPERTIES OF THE (N-N) SPLIT INTERSTITIALS

In the above discussion, we have assumed that when N is incorporated into GaAs, N always goes to the substitutional site. However, recent theoretical<sup>7</sup> and experimental studies<sup>6</sup> suggest that when the N concentration is high, N may form the (N-N)<sub>spl</sub> where two nitrogen atoms replace a single As atom in the GaAs. To estimate the concentration of the split interstitial (N-N)<sub>spl</sub> and understand the effect of (N-N)<sub>spl</sub> on the electronic and structural properties of the alloy, we have calculated the defect formation energies and transition energy levels of (N-N)<sub>spl</sub> using Eq. (1) and compared them with the substitutional defect N<sub>As</sub> [Eq. (2)]. The (N-N)<sub>spl</sub> can be considered as an N<sub>2</sub> molecule that replaces an As atom.<sup>25</sup> Based on molecular orbital theory, N<sub>2</sub> has fully occupied *ppπ* and *ppσ* bonding orbitals and fully unoccupied *ppπ\** antibonding orbitals. On the other hand, the vacant arsenic site, V<sub>As</sub>, has a high-lying singly occupied *t*<sub>2</sub> defect level.<sup>23</sup> Thus, at neutral charge state, the electron at the *t*<sub>2</sub> state will transfer to the *ppπ\** state, so the (N-N)<sub>spl</sub> will have a singly occupied defect level inside the band gap with the *ppπ\** character.<sup>7</sup> The defect can also exist in either (1+) or (1-) charge states. Figure 3 shows the geometry of the neutral (N-N)<sub>spl</sub> in GaAs. The N-N bond distance is 1.35 Å, larger than the bond length of an isolated N<sub>2</sub> molecule, partly because of the occupation of the *ppπ\** state. The N-Ga bond distance is 1.95 Å. For the positively charged state, the N-N defect constricts with the N-N bond length reduced to 1.33 Å, due to the depopulation of the *ppπ\** level. On the other hand, for the negatively charged state, the N-N defect elongates with the N-N bond length increasing to 1.38 Å, due to the further population of the *ppπ\** level.

Figure 4 shows the calculated formation energies for the (N-N)<sub>spl</sub> and N<sub>As</sub> as a function of Fermi energy. We find that the formation energy of the neutral (N-N)<sub>spl</sub> defect is much higher than that of substitutional N<sub>As</sub> at μ<sub>N</sub>=0 and μ<sub>As</sub>=0. However, because the formation energy of (N-N)<sub>spl</sub> decreases twice as fast as that of N<sub>As</sub> when the chemical potential of N increases [see Eqs. (1) and (2)], at higher<sup>7</sup> μ<sub>N</sub> the formation energy difference between (N-N)<sub>spl</sub> and N<sub>As</sub> will be smaller (see Ref. 7). Moreover, if the Fermi energy shifts toward the conduction band minimum (CBM), then

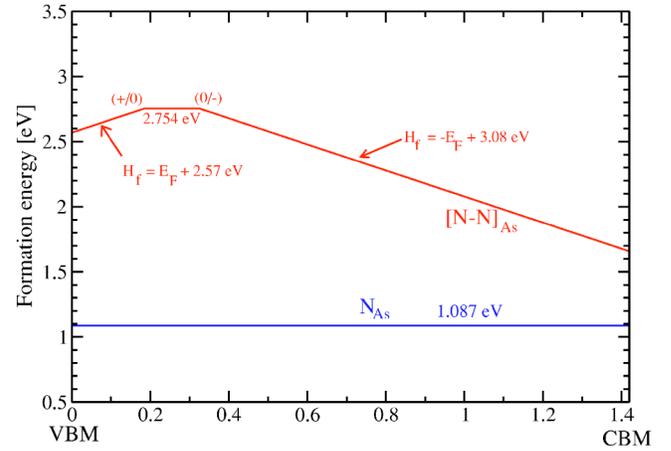


FIG. 4. (Color online) Formation energy of N substitutional and N-N split interstitial defects calculated at μ<sub>N</sub>=0 and μ<sub>As</sub>=0. The slope of the curve indicates the charge state of the defect.

(N-N)<sub>spl</sub> is negatively charged, and the formation energy difference will also be much smaller.

To evaluate quantitatively the ratio between the concentration of the split interstitial, [(N-N)], and the concentration of the substitutional N, [N<sub>As</sub>], we assumed that there is no special correlation between the defects, i.e.,

$$[(N-N)^q] = 3e^{-[H_f^q(N-N)]/kT} \quad (3)$$

and

$$[N_{As}] = e^{-[H_f^0(N)]/kT}. \quad (4)$$

Here,  $H_f$  are the formation energies defined in Eqs. (1) and (2). The coefficient 3 in Eq. (3) stands for the three possible directions for the (N-N)<sub>spl</sub>. Combining Eqs. (3) and (4), we obtain the detailed balance formula

$$\frac{[(N-N)^q]}{[N_{As}^0]^2} = 3e^{-[H_f^q(N-N) - 2H_f^0(N)]/kT}. \quad (5)$$

Substituting Eqs. (1) and (2) above and taking into account the different charge states  $q$  of (N-N)<sub>spl</sub> (see Fig. 4), we obtain a set of equations:

$$\frac{[(N-N)_{As}^+]}{[N_{As}^0]^2} = 3e^{-[(E_F + 2.57 \text{ eV}) - 2 \times 1.087 \text{ eV} - \mu_{As}]/kT},$$

$$\frac{[(N-N)_{As}^0]}{[N_{As}^0]^2} = 3e^{-[(2.754 \text{ eV}) - 2 \times 1.087 \text{ eV} - \mu_{As}]/kT},$$

$$\frac{[(N-N)_{As}^{-1}]}{[N_{As}^0]^2} = 3e^{-[(-E_F + 3.08 \text{ eV}) - 2 \times 1.087 \text{ eV} - \mu_{As}]/kT},$$

$$y = [N_{As}^0] + 2 \sum_{q=-1}^{+1} [(N-N)_{As}^q], \quad (6)$$

which can be solved numerically to give the ratio between the split N-N interstitial and N substitutional defects as a function of the total nitrogen concentration  $y$ , temperature,

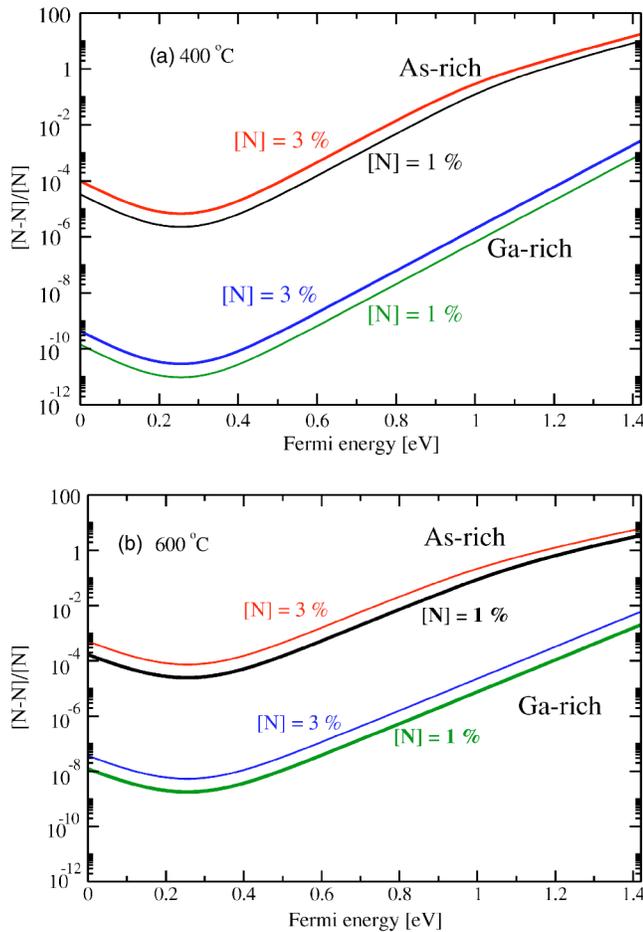


FIG. 5. (Color online) Ratio between N-N split interstitial and N substitutional defect concentrations as a function of Fermi level at (a) 400 °C and (b) 600 °C, and at As-rich limit and Ga-rich limit. We see that the ratio increases as the temperature increases.

and Fermi energy. Figure 5 shows the results at temperature of 400 °C and 600 °C at the arsenic-rich ( $\mu_{\text{As}}=0$ ) and gallium-rich [ $\mu_{\text{As}}=\Delta H(\text{GaAs})=-0.74$  eV] limits, for two nitrogen concentrations: 1% and 3%. Here,  $\Delta H(\text{GaAs})$  is the calculated formation energy of GaAs. The actual experimental situation is in between the two limiting cases. We find that (i) at fixed concentration  $y$ , which in most cases indicates fixed chemical potential difference ( $\mu_{\text{N}}-\mu_{\text{As}}$ ), the ratio is larger for the As-rich limit than for the As-poor (Ga-rich)

limit; this is because, for  $(\text{N-N})_{\text{spl}}$ , two N replace only one As, whereas in  $\text{N}_{\text{As}}$ , two N replace two As. Therefore, the binding energy to form  $(\text{N-N})_{\text{spl}}$  from two individual  $\text{N}_{\text{As}}$  is larger if the As chemical potential increases. (ii) The ratio also increases when total N concentration  $y$  is higher, because high N concentration means high N chemical potential. (iii) The ratio is much higher for an  $n$ -type sample, for which  $(\text{N-N})_{\text{spl}}$  is negatively charged. This indicates that when the sample is  $n$ -type, the probability of finding  $(\text{N-N})_{\text{spl}}$  increases. However, the negatively charged  $(\text{N-N})_{\text{spl}}$  defect acts as an acceptor, compensating the  $n$ -type material. Then at high N concentration, the  $(\text{N-N})_{\text{spl}}$  defect can pin the Fermi energy around the  $(0/-)$  transition energy level at  $\text{VBM}+0.3$  eV, at which the probability of finding the split interstitial is small. Our analysis, thus, suggests that under normal growth conditions, the probability of finding  $(\text{N-N})_{\text{spl}}$  is several orders of magnitude smaller than finding  $\text{N}_{\text{As}}$  and its effect on the structural parameters should also be small.<sup>6</sup>

## V. SUMMARY

In conclusion, we have shown that Vegard's law cannot be applied simultaneously to the lattice constants and the volume. We have found that due to the large size mismatch between N and As, the lattice constant of  $\text{GaAs}_{1-x}\text{N}_x$  significantly deviates from Vegard's empirical law, which has an important effect on the analysis of the experimental data (e.g., for the determination of the bowing coefficient). We have also determined that the bulk modulus increases monotonically with increased nitrogen concentration. We found that the split interstitial is an amphoteric defect with  $(+/-)$  transition at 0.2 eV and  $(0/-)$  transition at 0.3 eV above the valence band maximum. The ratio between the concentration of the split nitrogen interstitial  $(\text{N-N})_{\text{spl}}$  and the substitutional nitrogen  $\text{N}_{\text{As}}$  increases when the sample is grown under As-rich conditions, at a Fermi energy close to CBM, or for high total N concentration.

## ACKNOWLEDGMENTS

We thank R. S. Goldman for many helpful discussions and for providing us Ref. 13 before its publication. This work was funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, under Contract No. DE-AC36-99GO10337.

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