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The role of nitrogen-nitrogen pairs in the deviation of the GaAsN lattice parameter from Vegard’s law

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We propose several physical mechanisms that may account for the difference between the nitrogen composition in GaAsN materials measured by secondary ion mass spectroscopy and x-ray diffraction. A simplified model proposed here proves that Vegard’s law remains valid as long as all nitrogen atoms in the GaAsN alloys are located substitutionally at the arsenic sites. The theoretical results based on N-N pair defects are in good agreement with the experimental data, suggesting that the N-N pairs are the predominant nitrogen-related defects that cause deviation from the GaAsN lattice constant predicted by Vegard’s law. © 2004 American Institute of Physics.

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I. INTRODUCTION

The attractiveness of employing InGaAsN materials grown on GaAs substrates for the fabrication of long-wavelength optoelectronic devices has generated a large amount of interest in GaAs-based nitride materials in the past 7 years.1 Since the demonstration of an InGaAsN laser diode emitting at the wavelength of 1.1 μm in 1996,2 devices for both 1.31 and 1.55 μm communication systems have been achieved by such types of laser diode.3,4 InGaAsN, which has been used to fabricate the long-wavelength laser diodes, benefits from the large energy gap bowing coefficient of GaAsN. GaAsN has been reported to have the largest energy gap bowing coefficient, up to 20 eV per mole percentage, as compared with other ternary semiconductor compounds.5,6 Thus, a small nitrogen composition can significantly reduce its energy gap. The high sensitivity of the energy gap to the nitrogen concentration necessitates precise determination of the nitrogen content in the GaAsN material. Furthermore, the material quality of GaAsN is also highly sensitive to the nitrogen concentration, as significant deterioration occurs with increasing nitrogen composition. A previous report7 has shown that a nitrogen composition of 5% or more has the effect of completely quenching the photoluminescence of the GaAsN materials. The accurate determination of nitrogen composition in this material is therefore important not only for the energy band tailoring but also for the material quality control.

X-ray diffraction (XRD) is probably the most convenient nondestructive method routinely used to examine the nitrogen composition in GaAsN and related materials. Alternatively, secondary ion mass spectroscopy (SIMS) is sometimes employed to calibrate and verify the nitrogen composition. However, the nitrogen composition results obtained by these methods are not always in agreement with each other, especially when the nitrogen composition in GaAsN ternary exceeds 3%. Spruytte et al.8 have reported that the nitrogen composition results deduced from the SIMS measurements are higher than those obtained from the XRD measurements. The reverse has been reported by Li et al.9

By comparing the nitrogen contents deduced from the XRD and SIMS measurements, this paper provides a physical insight into the origins of the above contradiction between Spruytte’s results and Li’s data, using a batch of GaAsN samples specially grown by a solid source molecular beam epitaxy (SSMBE) system. A theoretical model is proposed to relate the nitrogen compositions obtained from the XRD and SIMS measurements. The analysis reveals that the nitrogen-related point defects have a significant influence on the determination of nitrogen composition of GaAsN material, and N-N pairs and present as predominant nitrogen-related defects in GaAsN, especially, with high nitrogen composition.

II. EXPERIMENTAL PROCEDURE

The GaAsN samples were grown in a SSMBE system, equipped with standard effusion cells for the group III elements and cracker cells for the group V elements. The purity of all the sources is 99.9999%. The nitrogen radicals are generated using a radio-frequency (RF) plasma-assisted nitrogen source, and supplied to the substrate in a dispersive mode.10 All samples were grown on the (001)-oriented semi-insulating GaAs substrates prepared using the standard preparation procedures. Prior to growth, the surface oxide desorption, was carried out under the As2 flux pressure. The beam equivalent pressure of Ga is 4.5 × 10−7 torr, resulting in a growth rate of ~1.0 μm/h verified by the time resolved reflection high-energy electron diffraction measurements. The As/Ga flux ratio is fixed at 14. The nitrogen plasma source operates under a nitrogen background pressure of

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The accuracy of determining the nitrogen composition is considerably significant to verify the validity of Vegard’s law. In an ideal GaAs crystal, the distance RGa-As between two neighboring gallium and arsenic atoms can be written as

\[ R_{\text{Ga-As}} = r_{\text{Ga}} + r_{\text{As}}, \]

where \( r_{\text{Ga}} \) and \( r_{\text{As}} \) are Pauling covalent radii of gallium atom and arsenic atom, respectively. \( R_{\text{Ga-As}} \) is oriented along the \( \langle 111 \rangle \) direction of the crystal unit cell.

Assuming a variation in \( R_{\text{Ga-As}} \) due to some causes, the elastic strain \( \varepsilon \) along \( \langle 111 \rangle \) direction will be

\[ \varepsilon = \frac{\Delta R_{\text{Ga-As}}}{R_{\text{Ga-As}}}. \]

When projected along the three axis directions \( \langle 100 \rangle \), \( \langle 010 \rangle \), and \( \langle 001 \rangle \), the components \( \varepsilon_x \), \( \varepsilon_y \), and \( \varepsilon_z \) along the three axes are the same as \( \varepsilon \).

\[ \varepsilon_x = \varepsilon_y = \varepsilon_z = \varepsilon. \]

Therefore, the stress along the \( \langle 001 \rangle \) direction (i.e., \( z \) axis) due to the variation in \( R_{\text{Ga-As}} \) will be

\[ f_z = C_{11} \varepsilon_z + C_{12} (\varepsilon_x + \varepsilon_y) = (C_{11} + 2C_{12}) \varepsilon. \]

The strain along the \( \langle 001 \rangle \) direction \( \Delta d_{\langle 110 \rangle}/d_{\langle 110 \rangle} \) will then take the following form:

\[ \frac{\Delta d_{\langle 110 \rangle}}{d_{\langle 110 \rangle}} = f_z C_{11} = \left( \frac{C_{11} + 2C_{12}}{C_{11}} \right) \varepsilon. \]

In an ideal GaAsN solid solution, it is reasonable to assume that every incorporated nitrogen atom occupies a substitutional arsenic site. Therefore, based on Eq. (1) and (2), the strain \( \varepsilon \) along the \( \langle 111 \rangle \) direction due to the nitrogen atom incorporation becomes

\[ \varepsilon = \frac{\Delta R_{\text{Ga-As}}}{R_{\text{Ga-As}}} = \left( \frac{R_{N} - R_{\text{As}}}{R_{\text{Ga}} + R_{\text{As}}} \right) x. \]

Hence, the lattice constant variation due to the nitrogen atom incorporation becomes

\[ \Delta d_{\langle 110 \rangle} = d_{\langle 110 \rangle} \cdot \left( \frac{C_{11} + 2C_{12}}{C_{11}} \right) \left( \frac{R_{N} - R_{\text{As}}}{R_{\text{Ga}} + R_{\text{As}}} \right) x. \]
~2.6%. By taking into account the extremely large lattice mismatch of ~20% between GaAs and cubic GaN, the data deduced from this simplified model is generally consistent with that from Vegard’s law. Neugebauer et al. have reported that the atomic relaxation in such a large lattice-mismatch material system is of great significance to the lattice property. When the atomic relaxation is taken into consideration, the data obtained from the total-energy calculation is consistently in agreement with that from Vegard’s law (dots on solid line). But the theoretical results from the total-energy calculations are in good agreement with our simplified model for the cases where the internal relaxation is not allowed (dots on dashed line). This suggests that the 2.6% discrepancy between our simplified model and Vegard’s law comes from the atomic relaxation. Therefore, Vegard’s law remains valid provided that the GaAsN material is an ideal alloy, and the XRD remains an effective method for the nitrogen composition determination in the ideal III-As-N nitrides.

B. Deviation from Vegard’s law

Figure 3 shows a nitrogen concentration profile obtained from the SIMS measurement of a GaAsN sample with 1.65% nitrogen composition. Due to the fluctuation of the nitrogen composition in the GaAsN epilayer, the average nitrogen composition is indicated with the dashed line. The nitrogen composition within the first 5 nm from the sample surface is high, probably caused by the surface adsorption effect. If this is the case, a GaAs cap layer would be needed to minimize the nitrogen surface adsorption effect. A 10 nm-thick nitrogen diffused region is observed on both sides of the GaAsN layer, indicating that a 10 nm-thick GaAs blocking layer is required to minimize the nitrogen diffusion effect.

Unlike the XRD measurement, where only the nitrogen atoms that have effects on the GaAsN’s lattice constant can be detected, the SIMS measurement can detect all the nitrogen atoms within the GaAsN alloy regardless of where their occupational sites are. Therefore, intuitively, the nitrogen composition value deduced from the SIMS measurement should never be lower than that from the XRD measurement. Hence,

\[ N_{\text{SIMS}} \geq N_{\text{XRD}} \]  

(8)

It is worthy to note that the condition \( N_{\text{SIMS}} = N_{\text{XRD}} \) applies only for the above-mentioned ideal GaAsN alloy, i.e., every incorporated nitrogen atom occupies a substitutional site. Figure 4 shows a comparison of the nitrogen compositions obtained by the SIMS and XRD measurements. The horizontal axis denotes the XRD-measured nitrogen composition, while the vertical axis denotes the SIMS-measured nitrogen composition. The solid diagonal line indicates the equalities of the XRD-measured nitrogen composition and the SIMS-measured nitrogen composition. Both methods give the same composition results for the GaAsN samples where the nitrogen composition is less than ~3%. However, the nitrogen composition deduced from the SIMS measurement becomes larger than that from the XRD measurement when the nitrogen composition in the GaAsN sample is higher than 3%. Equation (8) is therefore approximately validated by these experimental results. Our experimental results are in agreement with the condition of the ideal GaAsN alloy, where every incorporated nitrogen atom occupies a substitutional site.
agreement with those of Spruytte et al., but different from those reported by Li et al. where their explanations were somewhat ambiguous and insufficient.

### C. Models for deviation from Vegard’s law

In the ideal GaAs$_{1-x_0}$N$_{x_0}$ alloy where every nitrogen atom occupies the substitutional arsenic site, the SIMS-measured nitrogen composition ($x_{\text{SIMS}}$) is equal to the XRD-measured nitrogen composition ($x_{\text{XRD}}$)

$$x_{\text{SIMS}} = x_{\text{XRD}} = x_0.$$

However, Fig. 4 shows that the XRD-measured nitrogen composition values are smaller than the SIMS-measured nitrogen composition values, when the nitrogen composition in GaAsN is higher than 3%. This implies that some nitrogen atoms in GaAsN are not detectable by the XRD measurement. According to the Bragg’s equation, this is true because only those nitrogen atoms that affect the lattice constant of GaAsN can vary the diffraction angle of the x-ray, and therefore be detected. Nitrogen atoms that do not affect the lattice constant of GaAsN are not detected by the XRD measurements. For example, there are one and a half hollow tetrahedrons and six hollow octahedrons per unit cell as well in GaAs besides four arsenic atoms and four gallium atoms. While the nitrogen atom’s covalent radius (0.075 nm) is much smaller than that of the gallium atom (0.126 nm) and the arsenic atom (0.12 nm) as is shown in Table I. This implies the presence of sufficient spaces for the interstitial nitrogen atoms. If there is a nitrogen atom filling in the center of such a hollow tetrahedron, the distance ($R_{N-A}$) between this interstitial nitrogen atom (N$_i$) and its nearest neighbors (A) is,

$$R_{N-A} = r_{N_i} + r_A$$

where, A denotes Ga for the gallium hollow tetrahedron, or As for the arsenic hollow tetrahedron. Because the GaAsN lattice constant is decided by Eq. (1), the lattice constant can be changed only when $R_{N-A}$ is larger than $R_{\text{Ga-As}}$. According to Ref. 14, if the following conditions as $r_{N_i} + r_A (\text{GaAs}) \leq r_{\text{Ga}} + r_{\text{As}}$ for tetrahedron hollows and $r_{N} \leq (\sqrt{13}/3 - 1)(r_{\text{Ga}} + r_{\text{As}})/2$ for octahedron hollows can be met, the effect of nitrogen interstitials in such hollows on the lattice constants will be negligible. Due to the very small volume of nitrogen atom, our calculations (not shown here) found that the above conditions can always be met, therefore the single nitrogen atoms in both types of hollows would not affect the lattice constant of GaAsN, and in turn the XRD-measured nitrogen composition remains unchanged. Suppose there are $\delta x_{0}$ single nitrogen atoms in such hollows, then the SIMS-measured nitrogen composition ($x_{\text{SIMS}}$) increases by $\delta x_{0}$. The possibility of finding a nitrogen atom in hollows is proportional to the amount of nitrogen present in the GaAsN lattice. Therefore, the number of single nitrogen atoms in hollows could be reasonably assumed to be proportional to the nitrogen composition in the ideal GaAs$_{1-x_0}$N$_{x_0}$ alloy

$$\delta x_{0} = k x_{0}$$

and

$$x_{\text{SIMS}} = x_0 + \delta x_{0}$$ for nitrogen interstitials.

Besides interstitial N atoms, other nitrogen-related factors such as As-N pairs, Ga-N pairs, and N-N pairs might occur in an actual GaAsN alloy that would increase $x_{\text{SIMS}}$ and reduce $x_{\text{XRD}}$. Similar deduction can get the amount of nitrogen-arsenic (As-N) pair, nitrogen-gallium (Ga-N) pair, and nitrogen-nitrogen (N-N) pair as

$$\delta x_{0} = k x_{0} (1 - x_0)$$

and

$$x_{\text{SIMS}} = x_0 + \delta x_{0}$$ for As-N pairs,

$$\delta x_{0} = k x_{0}$$

and

$$x_{\text{SIMS}} = x_0 + \delta x_{0}$$ for Ga-N pairs,

$$\delta x_{0} = k x_{0}^2$$

and

$$x_{\text{SIMS}} = x_0 + 2 \delta x_{0}$$ for N-N pairs.

In Eq. (14), the amount of nitrogen-nitrogen (N-N) pair ($\delta x_{0}$) has a square dependence on the nitrogen content ($x_0$) in GaAs$_{1-x_0}$N$_{x_0}$ alloy. This is because that the amount of nitrogen-nitrogen (N-N) pair ($\delta x_{0}$) is proportional to the possibility of finding a nitrogen atom and the possibility of finding another nitrogen in the GaAs$_{1-x_0}$N$_{x_0}$ lattice. How $x_{\text{XRD}}$ is affected by the presence of these nitrogen-related defects could be calculated using Eqs. (1)–(7). The theoretical relationship between the calculated SIMS nitrogen compositions and the calculated XRD nitrogen compositions is indicated in Fig. 4 by the dashed, dotted, dashed-dotted, and solid curves individually for each case. This theoretical consideration indicates that the presence of the nitrogen interstitials, As-N pairs and Ga-N pairs authentically causes the deviation of the GaAsN lattice constant from Vegard’s law. However, when compared with the experimental data, these theoretical results show merely a linear dependence, which deviates from the nonlinear experimental behavior. This suggests that such nitrogen interstitials, As-N pairs and Ga-N pairs are not dominant defects in real GaAsN materials. As for nitrogen-nitrogen pairs, they not only cause deviation of the GaAsN lattice that Vegard’s law predicts but also the theoretical result based on such defects shows good agreement with the experimental data when $k = 1.5$, indicating that N-N pairs are the dominant defects in GaAsN materials grown by molecular beam epitaxy.

| TABLE I. Parameters of GaAs and GaN for the Vegard’s law verification [Ref. 12]. |
|------------------|---------------|---------------|---------------|---------------|
| D (nm) | C$_{11}$ (GPa) | C$_{12}$ (GPa) | r (nm)$^*$ | |
| GaAs | 0.565 325 | 1221 | 566 | Ga:0.126; As:0.12 |
| GaN | 0.45 | 293 | 159 | N:0.075 |

$^*$Data adopted from the periodical table compiled by Sargent-Welch scientific company.
Spruytte et al.\(^8\) suggested that the N\(_2\) molecules could be a type of nitrogen-related defect due to their small volume. Li et al.\(^9\) proposed the N-As and N-N pairs (even N-clusters) as energetically favored defects. In both cases, the theoretical models failed to match the experimental results. In one of our papers,\(^1\) we have assumed that the nitrogen-related defect concentration is proportional to the square of the substitutional nitrogen composition [N], but no theoretical foundation of the square dependence was given. Here, we have proved that our simplified but effective model can explain the basis for the nonlinear relationship between the SIMS-measured nitrogen composition and the XRD-measured nitrogen composition, and verified that N-N pairs are the dominating defects in the GaAsN materials. This is analogous to the case of the low-temperature (for example, \(\sim 250^\circ\text{C} \)) grown GaAs, where the As-As pairs at the substitutional arsenic sites are the dominant defects.\(^1\) The GaAs growth requires the interaction between the gallium and arsenic species on the heated substrate surface (\(\sim 250^\circ\text{C} \)), where the As\(_4\) or As\(_2\) molecules (\(\sim 500^\circ\text{C} \)) and the gallium atoms (\(\sim 900^\circ\text{C} \)) are supplied. Since the substrate temperature (\(\sim 250^\circ\text{C} \)) is not high enough to ensure the complete interaction of the arsenic and gallium species, some arsenic dimers would remain in the GaAs epilayers. In a nitrogen plasma source,\(^1\) the nitrogen species include neutral nitrogen atom N, metastable activated nitrogen atom N\(_2^*\), metastable activated nitrogen molecule N\(_2^*\), nitrogen ion N\(_{i+}\)\((i=1,2,\ldots)\), and nitrogen molecule ion N\(_2\)\(_{i+}\)\((i=1,2,\ldots)\). The excited nitrogen molecule species, such as N\(_2^*\) and N\(_2\)\(_{i+}\)\((i=1,2,\ldots)\), are effectively reactive species. Due to the difficulty in breaking the extremely strong N-N chemical bonds at the low substrate temperature (\(\sim 460^\circ\text{C} \)) in the MBE growth, these molecule species are readily incorporated into the GaAsN material to form the N-N pair defects. Therefore, there should be two nitrogen states in GaAsN, i.e., the nitrogen atom and the N-N pairs, both present in the substitutional arsenic sublattice sites. In accordance with the x-ray photoelectron spectroscopy results of GaAs\(_{0.94}\)N\(_{0.06}\) in Ref. 8, the binding energy between the gallium and nitrogen atoms should be different from that between the gallium atom and the N-N pairs. The intensity of the Ga-NN bond is much lower than that of the Ga-N bond, because according to our model, the N-N pairs comprises only 9% of the substitutional nitrogen atoms.

IV. CONCLUSIONS

In summary, this paper reported the difference between the SIMS nitrogen composition and the XRD nitrogen composition of the GaAsN materials. A simplified model proved that Vegard’s law remained valid so long as all the nitrogen atoms in the GaAsN alloys were located at the substitutional arsenic sites. Theoretical results based on the N-N pair defects were in good agreement with the experimental data, suggesting that the N-N pair was the dominant nitrogen-related defect causing deviation of the GaAsN lattice from that predicted by Vegard’s law.

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