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Comparison of nitrogen compositions in the as-grown $\text{GaN}_x\text{As}_{1-x}$ on GaAs measured by high-resolution x-ray diffraction and secondary-ion mass spectroscopy

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High-resolution x-ray diffraction (HRXRD) and secondary-ion mass spectroscopy were used to measure the N compositions of a series of as-grown GaNAs samples grown by solid-source molecular-beam epitaxy. We found that N compositions measured by the two methods agree well at lower N compositions ($x < 3\%$), and deviate at larger N compositions ($x > 3\%$). The HRXRD measurement by using Vegard's law to extract the lattice constant of GaNAs, underestimates N composition at larger N compositions. We found that the underestimation is up to 14.3% at the $x = 4.2\%$. In order to explain the deviation, a model for analyzing the correlation between lattice parameters and point defects in the epilayer was carried out. © 2002 American Institute of Physics. [DOI: 10.1063/1.1483913]

Recently, group III–N–As alloys have attracted considerable attention due to their unusual physical properties and their potential application in 1.3 and 1.55 μm telecommunication optoelectronic devices grown on GaAs substrate.^{1–8} It is known that the very small N content can greatly reduce the band gap due to the very large bowing factor of this material (as large as 10–20 eV)^{1,2} and, the quality of III–N–As decreases rapidly with increasing N composition.³ So, it is important to exactly determine the N composition for controlling the band gap and quality of the $\text{GaN}_x\text{As}_{1-x}$ material. Usually high-resolution x-ray diffraction (HRXRD) and secondary ion mass spectroscopy (SIMS) techniques are used to determine the N composition. Recently, Li *et al.*⁹ and Spruytte *et al.*¹⁰ have reported the N compositions in the $\text{GaN}_x\text{As}_{1-x}$ epilayers grown on GaAs measured by the two methods. However, the results from the two groups are contradictory. Li *et al.* reported that the HRXRD method overestimated the N compositions; and the Spruytte *et al.* results indicated that the HRXRD method underestimated the N compositions for the N compositions above 2.9%. In order to clarify this confusion, a series of GaNAs samples were grown by molecular beam epitaxy (MBE), and characterized by HRXRD and SIMS and a model was carried out to analyze the correlation between lattice parameters and the N-related point defects in the epilayer.

All our samples were grown by a RIBER-32P solid-source molecular beam epitaxy (SSMBE) with nominal structures of 20 nm GaAs/100 nm GaNAs/300 nm GaAs buffer layer on semi-insulating GaAs (100) substrates using elemental sources of gallium (7N), arsenic (6N), and a nitrogen radio frequency (rf) plasma source, except the samples with the N compositions above 3% with nominal structures

of 10 nm GaAs cap/50 nm GaNAs/300 nm GaAs buffer layer. The GaNAs layer thickness was reduced to prevent strain relaxation. The As/Ga flux ratio was fixed at about 20 and the growth rate of GaAs at 1 $\mu\text{m}/\text{h}$. Since only a small amount of nitrogen is incorporated into the nitride layer, we expect no significant change in the GaNAs growth rate under the same Ga flux. The GaNAs layers were grown between 460 and 500 °C to avoid phase segregation and clear streaky RHEED patterns were observed for all samples, which indicate the samples were grown coherently. GaNAs samples with different nitrogen compositions were prepared by varying the rf power from 80 to 350 W and the N_2 background pressure from 3.4E-6 to 2E-5 Torr.

HRXRD measurements were performed using a Phillips x-ray diffractometer with a conventional x-ray generator with a copper target ($K\alpha_1 = 0.154\,06\text{ nm}$) as the radiation source. For all samples presented in this letter, XRD rocking curves were recorded in the symmetrical (004) reflection. Figure 1 shows the experimental HRXRD (004) rocking curves of GaNAs samples with N compositions of 1.3% and 3.4%. All samples have clear Pendellosung fringes which indicate that the films have high epitaxial quality. All samples were verified by the asymmetric (115) XRD mapping measurements to show no strain relaxation in the nitride layers. The N composition, x is estimated from a_0 assuming Vegard's law:

$$a_0 = xa_{\text{GaN}} + (1-x)a_{\text{GaAs}}, \quad (1)$$

where a_0 , a_{GaN} , and a_{GaAs} are the lattice constants of the unstrained cubic GaNAs, GaN, and GaAs, respectively. a_0 is determined from the lattice constant in growth direction of GaNAs epilayer, $a_{\perp}$:

$$a_{\perp} = a_{\parallel} + (a_0 - a_{\parallel})(C_{11} + 2C_{12})/C_{11}, \quad (2)$$

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FIG. 1. HRXRD (004) experimental rocking curves and simulation curves of GaNAs samples indicating the N compositions of 1.3% and 3.4%.

where $a_{\parallel}$ is the in-plane lattice constant of strained GaNAs epilayer, which is equal to $a_{\text{GaAs}} \cdot C_{11}$ and C_{12} are the elastic constants for GaNAs. All the band parameters used are from Ref. 6.

Figure 2 shows the SIMS N concentration profiles of the GaNAs samples with N compositions of 1.3% and 3.7%. Because of the N fluctuation, the average N concentration in GaNAs layer was used to determine the N composition. The nitrogen concentration was measured with SIMS after calibration with known GaNAs standards. The Cs^+ ions were used as primary ions and the primary ion energy used was 10 keV. The nitrogen concentration was extracted from the SIMS profile based on the intensity ratio of $^{202}\text{CsN}^+ / ^{208}\text{CsGa}^+$. The details on this SIMS technique were reported in Ref. 11.

Figure 3 shows the comparison of nitrogen compositions measured by the SIMS and HRXRD. The solid line indicates that the SIMS N compositions are equal to the HRXRD N compositions. The two methods give the almost same results for the N compositions below about 3%. However, the N compositions measured with HRXRD are underestimated by

FIG. 2. SIMS nitrogen concentration profiles of GaNAs samples with the N compositions of 1.3% and 3.7%.

FIG. 3. Comparison of the N compositions measured by SIMS and HRXRD.

using Vegard's law for the N composition above about 3%. For example, at the N composition of 4.2% (SIMS result), the underestimation is about 14.3%. Our results are different with the report in Ref. 9 where the HRXRD method overestimated the N composition. However, our results agree well with the Spruytte *et al.* results where the HRXRD method underestimated the N compositions for the N compositions above 2.9%.

The possible nitrogen configurations in the epilayer grown by MBE are (i) substitutional N_{As} , (ii) interstitial N–As complex, (iii) interstitial N–N complex, and (iv) interstitial isolated N.^{9,10} A model can be used to analyze the correlation between lattice parameters and the N-related point defects in the GaAs epilayer.¹² The lattice strain $\Delta a/a$ caused by the substitutional N_{As} is given by¹²

$$\frac{\Delta a}{a} = \frac{C_{11} + 2C_{12}}{C_{11}} \frac{r_{\text{N}} - r_{\text{As}}}{r_{\text{Ga}} + r_{\text{As}}} \frac{x}{2}, \quad (3)$$

where r_{N} , r_{Ga} , and r_{As} are the covalent radii of N, Ga, and As, respectively. The lattice strain caused by the interstitial N–As complex is given by¹²

$$\frac{\Delta a}{a} = \frac{C_{11} + 2C_{12}}{C_{11}} \frac{d_b - r_{\text{Ga}} - r_{\text{As}}}{r_{\text{Ga}} + r_{\text{As}}} x \quad (4)$$

where $d_b = \sqrt{3}r_{\text{eff}}/3 + \sqrt{(r_{\text{eff}} + r_{\text{Ga}})^2 - 2r_{\text{eff}}^2}/3$ is the distance of the N–As complex from its nearest neighbors. $r_{\text{eff}} = (r_{\text{N}} + r_{\text{As}})/2$ is the effective bond radius. According to the above model, the effects of interstitial N–N complex and interstitial isolated N on the lattice strain can be neglected. Using Eqs. (2)–(4), we can estimate the effects of the substitutional N_{As} and interstitial N–As complex on the GaAs lattice constant in growth direction. Figure 4 shows the dependence of lattice constant in growth direction on the N composition caused by the substitutional N_{As} (the dashed line), and the interstitial N–As complex (the dotted line). The dot-dashed line is the result by using Vegard's law. The squares are experimental data, the lattice constants in growth direction were measured by HRXRD, the N compositions were measured by SIMS. The solid line is the fitting curve. For the ideal case, all N substitute of As, the calculated dependence of lattice constant in growth direction on the nitrogen composition caused by such substitutional N_{As} agrees well with Vegard's law (the dot-dashed line). However, the dependence becomes quite

FIG. 4. Dependence of the as-grown GaNAs lattice constant in growth direction on N composition caused by substitutional N_{As} (dashed line), interstitial As–N complex (dotted line). The dot–dashed line is the result by using Vegard's law. The squares are experimental data. The solid line is the fitting curve assuming the concentration ratio of $[N-As]/[N_{As}]=30[N]^2$.

different when the nitrogen is interstitial N–As complex. Unlike N_{As} , the interstitial N–As complex expands the lattice constant in growth direction. This may be the reason why the critical thickness of the GaNAs epilayer was much larger than that predicted by Matthew and Blakeslee's model.¹³ Li *et al.*'s calculation shows that the formation of interstitial isolated N in GaNAs is unlikely due to their high formation energy in the lattice,⁹ so, the amount of the interstitial isolated N should be very small and can be neglected. The GaNAs photoluminescence (PL) and annealing experiments of ours and other groups' show that the PL intensity decreases rapidly with N composition, the PL intensity is improved after annealing.^{3,7} This is mainly due to the N related defects increase rapidly with the N composition and disappear after annealing. So, we can roughly assume the concentration ratio of $[N^*]/[N_{As}]=C[N]^2$. Where $[N^*]$ is the concentration of the N related interstitial defect, $[N_{As}]$ is the concentration of substitutional N_{As} , $[N]$ is the total N composition (which can be measured by SIMS), C is the fitting parameter. First, we consider the interstitials are N–N complex only. We found the fitting curve agrees well with the experiment data when $C=60$, i.e., $[N-N]/[N_{As}]=60[N]^2$. Based on the above assumption, we found that 10.8% of the nitrogen is interstitial for $GaN_{0.03}As_{0.97}$. However, recent nuclear reaction analysis (NRA) shows that $(2.5 \pm 0.2)\%$ of the N is in an interstitial lattice site for the as-grown sample GaNAs with N composition of 3.02%. (The experiment did not identify the nitrogen interstitials.¹⁴) Similarly, we con-

sider the interstitials are the N–As complex only. We found the C is around 30 to fit the experimental data well, i.e., $[N-As]/[N_{As}]=30[N]^2$. This indicates that 2.7% of N is interstitial for GaNAs with N composition of 3%. This agrees well with the NRA's result of $(2.5 \pm 0.2)\%$. Based on the above analysis, the most N interstitials should be the N–As complex, the amount of interstitial N–N complex is very small. Those N–As complexes and the small amount of N–N complex result in the underestimation of N composition measured by HRXRD. In order to obtain more accurate theoretical curve of the dependence of lattice constant in growth direction on N composition, the further work will be necessary: (i) the experiments to identify the N-related interstitials, (ii) the experiments to determine the dependence of the percentage of the N-related interstitials over the substitutional N_{As} on N composition.

In conclusion, both HRXRD and SIMS methods were used to measure the N compositions of a series of as-grown GaNAs samples grown by SSMBE. Our data show that N compositions measured by the two methods agree well at the lower N compositions ($x < 3\%$), deviate at larger N compositions ($x > 3\%$). The HRXRD measurement by using Vegard's law to extract the lattice constant of GaNAs underestimates N composition at larger N compositions. At $x=4.2\%$, the underestimation is up to 14.3%. The model analysis show that the most N interstitials are the N–As complex, the amount of N–N complex is very small. Those N–As complex and a small amount of N–N complex result in the underestimation of N composition measured by HRXRD.

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