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Effect of In and N incorporation on the properties of lattice-matched GaInNAs/GaAs grown by radio frequency plasma-assisted solid-source molecular beam epitaxy

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We present the effect of nitrogen (N) and indium (In) incorporation on the structural and optical properties of $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$ with low lattice mismatch to GaAs grown by solid-source molecular beam epitaxy using a radio frequency (rf) nitrogen plasma source. The results show that excessive introduction of nitrogen during the growth of GaInNAs may lead to greater incorporation of interstitial nitrogen and degradation in crystal quality. This effect is more significant in GaInNAs compared to GaNAs. A drastic $6\times$ increase in x-ray diffraction full width at half maximum (XRD-FWHM) was observed in GaInNAs compared to $1.5\times$ increase of the same in GaNAs when reactive nitrogen is introduced into the material. The more significant degradation in GaInNAs quality is believed to be due to greater incorporation of interstitial nitrogen in the presence of indium during growth. By changing the In content and fixing the N incorporation rate, a sample of $\text{Ga}_{0.924}\text{In}_{0.076}\text{N}_{0.026}\text{As}_{0.974}$ /GaAs with relatively low lattice mismatch of -896 ppm (or $\sim 8.96 \times 10^{-4}$) was grown. Low temperature (4 K) photoluminescence emission at 1518 nm was observed and XRD-FWHM of 118.2 arcsec was measured. © 2002 American Vacuum Society.
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I. INTRODUCTION

Recently, group III–N–As has attracted considerable attention due to potential applications in 1.3 and 1.55 μm optoelectronic devices grown on GaAs substrate. However, it has been observed that the optical and structural quality of GaNAs degrades following increase in nitrogen composition.¹ In GaInNAs, the degradation in crystal quality seems to worsen in the presence of indium incorporation. So far, the effect of indium and/or nitrogen incorporation and their mechanism of interaction at the growth surface is relatively unclear. Such effects have given rise to problems such as: (i) limited incorporation of nitrogen into the material containing indium² and (ii) poorer GaInNAs crystal quality compared to GaNAs.³ In this article, the effect of In and N incorporation on changes in structural and optical properties of GaInNAs is investigated under close lattice-matched condition to GaAs and photoluminescence (PL) emission from 1.3–1.55 μm at 4 K. A comparison to GaNAs will be made.

II. EXPERIMENTAL PROCEDURE

All samples were grown by solid-source molecular beam epitaxy (SSMBE) on SI-GaAs (001) oriented substrates under As-rich growth conditions (As/III flux ratio of ~ 35) at 460 °C. A radio frequency (rf) nitrogen plasma source was used to generate the reactive nitrogen radicals from ultrapure nitrogen gas. To allow time for establishing stable plasma conditions, a growth interruption of 3 min was introduced after the growth of the 300-nm-thick GaAs buffer layer and prior to the GaInNAs layer. A further 1 min of growth inter-

ruption was introduced after the GaInNAs layer growth to terminate the plasma. Diffused and streaky (2×1) surface reconstruction pattern was observed by reflection high-energy electron diffraction (RHEED) throughout the growth of the GaInNAs layer.

Structures of nominal thickness 20 nm GaAs/200 nm GaInNAs/300 nm GaAs buffer were grown to investigate the effect of In and N incorporation on the optical and structural properties of the GaInNAs layer. The range of In and N composition investigated are 6.2%–11.3% and 2.7%–3.1%, respectively. For comparison to GaInNAs, structures of nominal thickness 20 nm GaAs/100 nm GaNAs/300 nm GaAs buffer were grown under the same growth condition as GaInNAs except that the indium flux was removed and rf power of the nitrogen source varied to adjust the amount of N incorporation in the GaNAs layer from 1.6%–3.6%. All samples were characterized by high-resolution x-ray diffraction (XRD) and low-temperature (4 K) PL. The indium composition in the $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$ is assumed to be the same as that in GaInAs grown under identical growth conditions, i.e., the nitrogen incorporation into the material will not affect the indium composition.⁴ Under such an assumption, the nitrogen composition (as in the y value) of $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$ was deduced through fitting of the XRD rocking curve data by varying the y value while fixing the x value (indium composition) in the simulation parameters.⁵ Since we have been able to grow GaInNAs with thickness of up to 200 nm due to its low lattice mismatch, strong x-ray intensity of the GaInNAs peak can be obtained, thereby making the curve fitting process easily achievable. The following section describes the measurement results from our as-grown (i.e., without annealing) GaNAs and GaInNAs samples.

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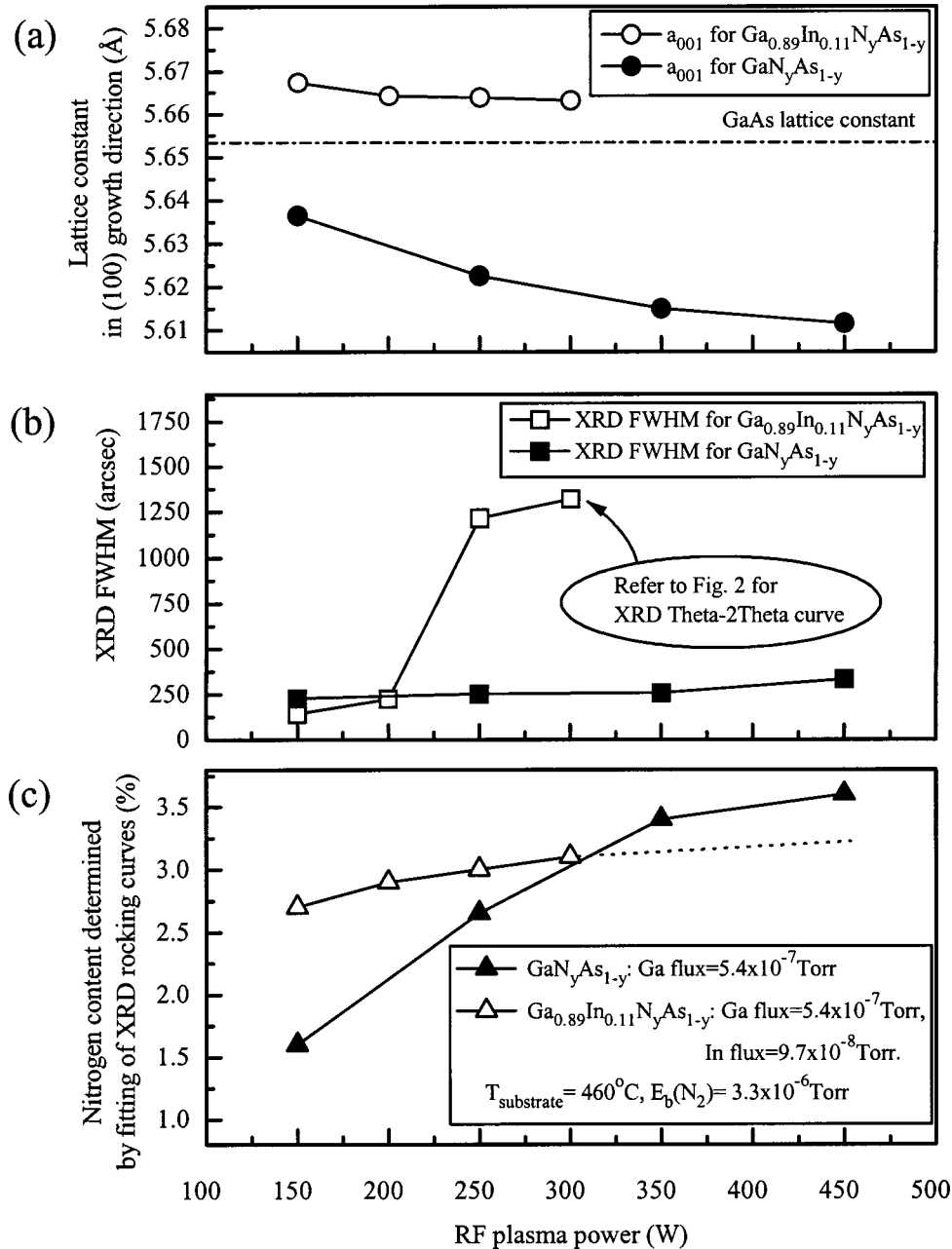


FIG. 1. Plot of (a) lattice constant in the (100) growth direction, (b) XRD-FWHM, and (c) nitrogen content in GaInNAs layer grown at different rf plasma power.

III. RESULTS AND DISCUSSION

Figure 1 shows the plot for GaInNAs and GaNAs samples of: (a) lattice constant in the growth direction, (b) x-ray diffraction full width at half maximum (XRD-FWHM), and (c) nitrogen content. The GaInNAs samples have the same indium composition of 11% (by fixing the In/Ga flux ratio at 0.18) but grown at a different rf power of the nitrogen plasma source (150–300 W). For the GaNAs samples, the rf power was varied from 150 to 450 W.

As expected, at increasing rf power of the nitrogen plasma source, more nitrogen is incorporated into the GaInNAs layer. This is evident from the gradual decrease in the lattice constant for rf power increasing from 150 to 200 W, as

shown in Fig. 1(a). This change is associated with a $1.8\times$ increase in the XRD-FWHM of the GaInNAs layer [from 120.0 to 222.4 arcsec in Fig. 1(b)], indicating degradation in the crystal quality of the material. Further increase in the rf power from 200 to 300 W causes more reactive nitrogen to be incorporated into the GaInNAs layer. As shown in Fig. 1(b), this gave rise to a $6\times$ increase in the XRD-FWHM of the GaInNAs layer (from 222.4 to 1320.3 arcsec), indicating significant degradation in crystal quality. Had the lattice mismatch between the GaInNAs/GaAs been the reason for degradation in the GaInNAs quality, bringing the GaInNAs lattice constant towards that of GaAs would have seen an improvement. Contrary to this, our experiment

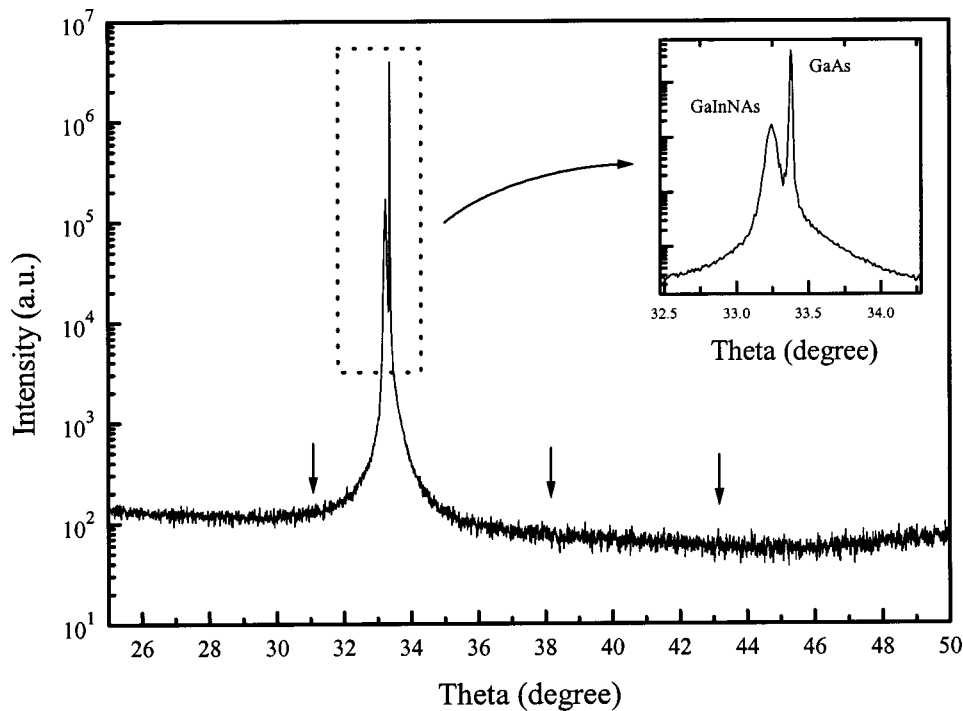


FIG. 2. X-ray θ - 2θ curve of GaInNAs grown at 460 °C using In/Ga of ~ 0.18 (In=0.11) and rf plasma power of 300 W (N background pressure= 3.3×10^{-6} Torr). The three downward arrows indicate the calculated cubic InAs (30.56), InN (38.22), and GaN (43.21) Bragg angle (004) reflections.

has shown that as more reactive nitrogen is introduced, the XRD-FWHM increased gradually followed by more drastic changes as seen in Fig. 1(a).

The increase in XRD-FWHM of the GaInNAs from 150 to 200 W could be due to the incorporation of N atoms into interstitial sites, in addition to them substituting the sublattice of As (which is one of the mechanisms thought responsible for its band-gap reduction). It is possible that such interstitial N incorporation, which was also found in GaNAs,⁶ be responsible for the degradation in the GaInNAs crystal quality. Previous work by Fan *et al.*⁷ has shown that for GaNAs, $\sim 12\%$ higher N content was detected by secondary ion mass spectroscopy (SIMS) compared to XRD measurement for materials grown at rf power exceeding 350 W at N background pressure of 3.3×10^{-6} Torr. Cross-hatched lines, which are indications of misfit dislocations, were not observed at the surface of our GaNAs samples even for nitrogen composition of up to 3.6%. However, this cannot totally rule out the presence of misfit dislocations at the interface. It is possible that some of the interstitial N can be gettered at such misfit dislocations, but this would require further investigation for confirmation.

Figure 1(b) shows an increase of $1.5\times$ in the GaNAs XRD-FWHM when the rf power was increased from 150 to 450 W. Such degradation in the XRD-FWHM, which is relatively smaller compared to that of GaInNAs in our case, has been attributed to (i) presence of crystal imperfections or point defects caused by high concentration of interstitial N incorporation,^{6,8} and (ii) a large difference in the lattice parameter between GaAs and GaN ($\sim 20\%$) which can lead to spontaneous ordering or even phase separation.³ In our case, however, it is believed that the former reason is more plausible, since the N composition is relatively small (1.0%–

4.0%) and the increase in XRD-FWHM is only $1.5\times$. Under such low N composition in the material, phase separation is thought to be unlikely.

The more significant and abrupt increase in the GaInNAs XRD-FWHM ($6\times$) seen in Fig. 1(b), as the rf power was increased from 200 to 300 W could possibly be the result of spontaneous ordering (deviation from the random alloy approximation) or phase separation³ in the GaInNAs. However, the XRD θ - 2θ curve of this sample shown in Fig. 2 did not show any evidence of phase separation. A similar method was used by Bi and Tu (Ref. 9) to detect phase separation in GaNAs materials grown by gas source molecular beam epitaxy (GSMBE). A further attempt was made to grow GaInNAs at rf power exceeding 300 W, but the RHEED pattern deteriorated and became spotty at ~ 200 nm. Hence, further work is necessary to investigate the reason for the rapid degradation in the GaInNAs XRD-FWHM at increasing rf power.

Friedman *et al.*¹⁰ proposed that the presence of indium adatoms on the growth surface could change its surface reconstruction. This decreases the surface N solubility and has a nonlinear effect on the nitrogen incorporation into the material. In our experiment, a similar effect of N incorporation was observed when the rf power was varied under the same In/Ga flux ratio. This is shown in Fig. 1(a) for both GaInNAs and GaNAs, in which the N incorporation into substitutional sites, as exhibited by the change in lattice constant, did not decrease linearly following the increase in rf power. In addition, the increase in N content as shown in Fig. 1(c), also showed a nonlinear dependence on the increase in rf power. Such a trend could only be caused by the presence of indium in the GaInNAs, since the rest of the growth conditions were identical. In the absence of experimental data, a dotted line

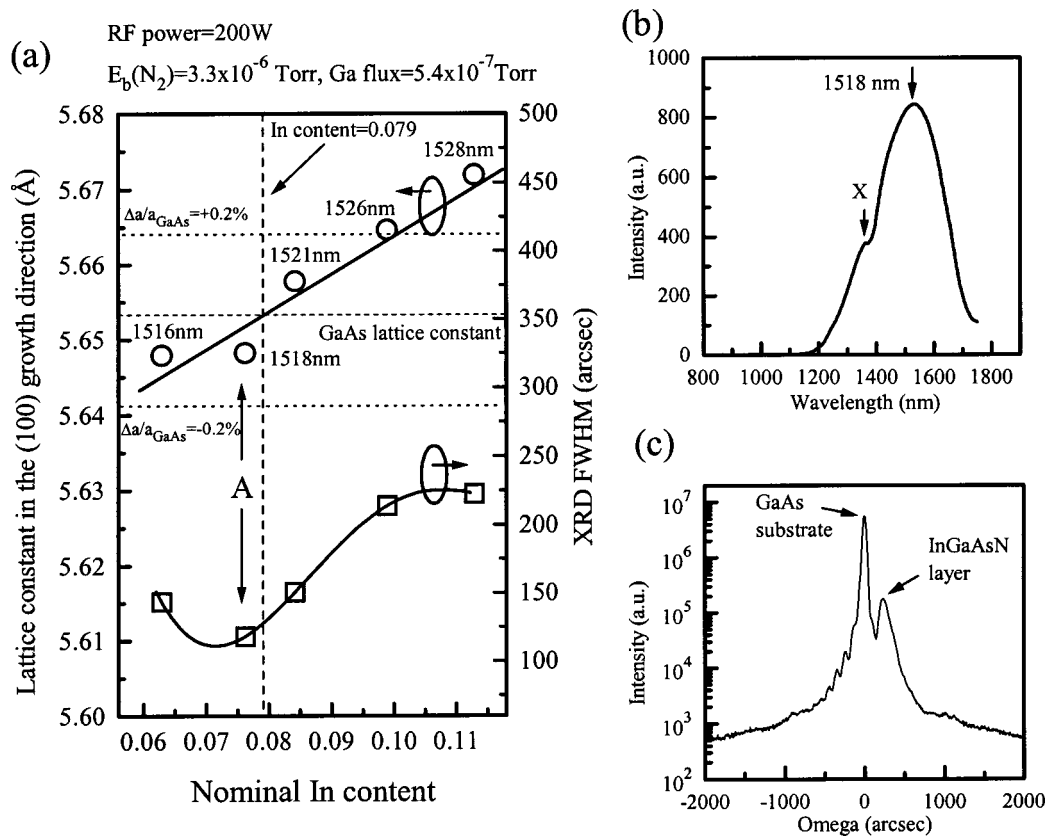


Fig. 3. Plot of (a) lattice constant and XRD-FWHM of GaInNAs with different nominal In content (b) low-temperature PL spectrum, and (c) XRD spectrum of sample A (20 nm GaAs/200 nm Ga_{0.924}In_{0.076}N_{0.026}As_{0.974}/300 nm GaAs).

was drawn to extrapolate the N content in GaInNAs beyond 300 W of rf power [Fig. 1(c)]. Thereafter, it can be seen that for rf power beyond 300 W, the N content in the GaInNAs is apparently lower compared to that in GaNAs, implying the presence of a maximum N level that can be incorporated into the GaInNAs given a certain indium composition in the material. Such suppression of N incorporation caused by the presence of indium was also observed in InN_xP_{1-x} material grown by MBE with a nitrogen source similar to ours.² Furthermore, a drastic degradation in the crystal quality is seen, as shown by the increase in the XRD-FWHM in Fig. 1(b). This implies a situation similar to GaNAs, in which a greater tendency exists for the reactive N to be incorporated into interstitial sites. In fact, this tendency is even greater in GaInNAs compared to GaNAs.

However, within the rf power range of 150–300 W in Fig. 1(c), a higher N content was found in GaInNAs compared to GaNAs. This result contradicts the reason given earlier of lower N solubility caused by the presence of indium adatoms on the growth surface. A possible reason for the observed behavior is the decrease in nitrogen surface mobility caused by the presence of indium surface adatoms. This could reduce the recombination kinetics of nitrogen radicals at the growth surface by forming N₂ and thereby increasing the nitrogen composition.

As indicated by our experimental results, it appears that given a certain indium composition, the growth of GaInNAs

is affected by two different mechanisms depending on the rf plasma power: (i) at low rf power, the presence of indium enhances the incorporation of N into substitutional sites (as shown by XRD measurement). From the slight reduction in XRD-FWHM (150–200 W) of GaInNAs compared to GaNAs [Fig. 1(b)], the presence of indium could also suppress the incorporation of N into interstitial sites, (ii) at high rf power, the presence of indium enhances the incorporation of N into interstitial sites, but at the same time suppresses the incorporation of N into substitutional sites.

Figure 3(a) shows the plot of GaInNAs lattice constant [in the (100) growth direction] and XRD-FWHM of samples with different In composition from 6.2%–11.3% (by changing the In/Ga flux ratio). These samples were grown using the same rf power of 200 W and N background pressure of 3.3×10^{-6} Torr (which would give a N composition of 2.1% in GaNAs). Their respective low-temperature PL peak wavelengths (1516–1528 nm) are labeled on the lattice constant curve of Fig. 3(a). It is seen that by changing the In content and fixing the rf power at a level which minimizes the incorporation of N into interstitial sites (i.e., 150–250 W), relatively good lattice matching of GaInNAs to GaAs can be obtained without severely degrading its crystal quality. The N composition in these samples was found to be relatively constant at ~2.6% by fitting of the XRD rocking curves. Hence, the effect of nitrogen composition reduction caused by the increase in growth rate (following the increase in

group-III flux) is not evident in our experiment. Therefore, the increase in the PL peak wavelength at low temperature appears to be due mainly to the increase in indium composition. From the straight line fitted to the lattice constant data in Fig. 3(a), the nominal GaInNAs composition for a lattice-matched condition to GaAs is estimated to be $\text{Ga}_{0.921}\text{In}_{0.079}\text{N}_{0.026}\text{As}_{0.974}$ as indicated by the vertical dashed line. This yields an x/y ratio of ~ 3.04 , which is in good agreement with $x/y=3$ for the lattice-matched condition of $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$ to GaAs.¹¹ This point is also close to the minimum value of the XRD-FWHM curve as seen in Fig. 3(a), roughly following the expected trend of increase in the XRD-FWHM (hence worsening of the crystal quality) as the mismatch to GaAs increases. Hence the results show an apparent linear dependence of the lattice constant (in the growth direction) on the In content. As indicated by the vertical arrows, sample A of composition $\text{Ga}_{0.924}\text{In}_{0.076}\text{N}_{0.026}\text{As}_{0.974}$ has a lattice mismatch of -896 ppm (or $\sim 8.96 \times 10^{-4}$) and the smallest XRD-FWHM of 118.2 arcsec compared to other samples. Its corresponding 4 K PL spectrum with peak energy at 1518 nm and XRD rocking curve are shown in Figs. 3(b) and 3(c), respectively. The slight shoulder signal at 1389 nm (marked "X" on the spectrum) in Fig. 3(b) is the result of an optical attenuation effect caused by the PL instrument.

IV. CONCLUSION

The growth of GaInNAs with different In and N composition on GaAs substrate and its effect on XRD-FWHM and

low-temperature (4 K) PL peak wavelength is presented in this article. It is shown that when higher rf plasma power is used to grow GaInNAs with N content exceeding 2.6%, an abrupt increase in XRD-FWHM is observed. The change in XRD-FWHM is more abrupt in GaInNAs compared to GaNAs for the same increase in N content. It is believed that the rapid degradation in GaInNAs crystal quality at high rf plasma power is due to greater incorporation of N as interstitials. By changing the In content and fixing the N content, good lattice match between GaInNAs and GaAs ($\sim 8.96 \times 10^{-4}$) was achieved with PL peak wavelength at 1518 nm without degradation in crystal quality.

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