

# Nitrogen incorporation into GaInNAs lattice-matched to GaAs: The effects of growth temperature and thermal annealing

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(Received 1 July 2005; accepted 6 September 2005; published online 27 October 2005)

We have studied the effects of growth temperature and subsequent thermal annealing on nitrogen incorporation into lattice-matched dilute  $\text{Ga}_{0.942}\text{In}_{0.058}\text{NAs}$ -on-GaAs epilayers, which were grown by the molecular-beam epitaxy method. The samples were studied experimentally by means of x-ray diffraction and Raman spectroscopy and theoretically by calculations within the density-functional theory. Over the entire range of growth temperatures applied (410–470 °C), nitrogen appeared to be mainly located on substitutional sites in “short-range-order clusters” as N–Ga<sub>4</sub> and, to a lesser extent, as N–Ga<sub>3</sub>In. There were also indications of the presence of nitrogen dimers NN, as suggested by Raman spectroscopy, in qualitative agreement with the calculations. An increase in growth temperature reduced the amount of substitutional nitrogen and decreased the number of N–Ga<sub>4</sub> clusters relative to N–Ga<sub>3</sub>In. Postgrowth thermal annealing promoted the formation of In–N bonds and caused a blueshift in the optical band gap, which increased as the growth temperature was lowered. © 2005 American Institute of Physics. [DOI: 10.1063/1.2112173]

## I. INTRODUCTION

Besides the development of thin films of dilute nitride  $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}/\text{GaAs}$  quantum-well (QW) structures for 1.3  $\mu\text{m}$  laser diodes,<sup>1</sup> thick films of GaInNAs lattice-matched to GaAs are also attractive for preparing heterojunction bipolar transistors<sup>2</sup> (HBTs), high-speed resonant-cavity-enhanced photodetectors,<sup>3</sup> and the fabrication of photovoltaic cells.<sup>4</sup> Unfortunately, alloying even a small amount of N with Ga(In)As is challenging because of a low incorporation efficiency of N into the growing crystal and a large alloy miscibility gap in the phase diagram.<sup>5,6</sup> These problems are, in part, responsible for the creation of nonradiative centers and structural inhomogeneity, resulting in general in a poor luminescence efficiency of as-grown GaInNAs. The problems can be alleviated to some extent by growing Ga(In)NAs by molecular-beam epitaxy (MBE) under nonequilibrium conditions at low temperatures, which may be 50–100 °C lower than those normally used for growth of generic nitrogen-free compounds.

A useful range for  $y$  in  $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$  with large  $x > 30\%$  is, from the experimental point of view,  $y < 2\%$  (which is also a theoretical solubility limit of nitrogen in GaAs).<sup>7</sup> The band gap of such a coherently strained  $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$  alloy is remarkably reduced when compared to  $\text{Ga}_{1-x}\text{In}_x\text{As}$  at the same  $x$ , and the material quality

remains reasonably good for device applications. It is also known that for  $y < 2\%$  a change in MBE growth temperature ( $T_{\text{gr}}$ ) within an optimal range of 420–480 °C does not significantly affect the incorporation rate of nitrogen and indium at compositions  $30\% \leq x < 40\%$ .<sup>5</sup> This observation is a consequence of a nearly temperature-independent sticking coefficient of nitrogen, when  $420 < T_{\text{gr}} < 480$  °C, and the fact that incorporation of N into  $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$  is almost constant for  $10\% < x < 40\%$ .<sup>5,6</sup>

For low indium concentration ( $x < 10\%$ ),<sup>8</sup> the nitrogen mole fraction could readily exceed 2% to obtain a 1-eV band gap, while satisfying the lattice matching condition  $x \approx 2.7y$ . Here, the nitrogen incorporation is different from the case of indium-rich alloys. In the present paper we shall show that the incorporation of nitrogen into lattice-matched GaInNAs at a dilute limit ( $x \approx 5.8\%$ ,  $y \approx 2.8\%$ ) is substantially influenced by a change in growth temperature.

## II. EXPERIMENT

The samples used in our study consisted of 300-nm-thick GaInNAs layers with  $x \approx 5.8\%$  and  $y \approx 2.8\%$ , grown on GaAs (100) substrates at  $410 \leq T_{\text{gr}} \leq 470$  °C by solid-source MBE. Constant beam fluxes of the group-III and group-V elements were used for all growth temperatures. The samples were labeled S410, S430, S450, and S470, where the numbers indicate the  $T_{\text{gr}}$  applied. All samples were nominally undoped. They were capped with 10-nm-thick GaAs top lay-

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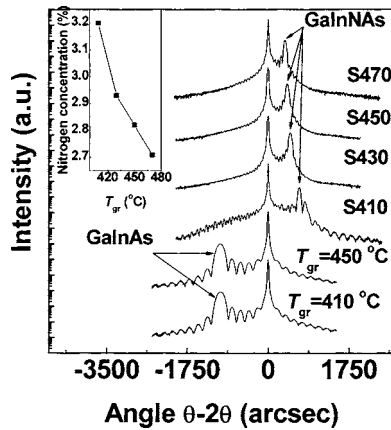


FIG. 1. X-ray diffraction rocking curves of samples S410 to S470 as well as for two GaInAs reference samples grown at a  $T_{gr}$  of 410 and 450 °C, respectively. The inset shows the dependence of the nitrogen concentration on growth temperature.

ers for surface protection. Crystallographic properties were studied by measuring double-crystal x-ray diffraction (XRD) rocking curves. Raman spectra were recorded at 77 K in backscattering from the (100) growth surface, using the 568.2 nm line of a  $Kr^+$  laser. The incident and scattered light were both polarized parallel to the (110) direction. Thermal annealing was carried *ex situ* at 800 and 900 °C for 60 s in dry N atmosphere.

### III. RESULTS AND DISCUSSION

XRD rocking curves of samples S410 to S470 are shown in Fig. 1. The presence of Pendellösung fringes is indicative of a good structural quality. The epilayers are under slight tensile strain, the size of which depends on  $T_{gr}$ ; tensile strain decreases as  $T_{gr}$  is increased. This is to say that  $y$  of the alloy decreases in spite of a constant nitrogen beam flux. Figure 1 also shows XRD profiles for two 100-nm-thick GaInAs-on-GaAs reference layers prepared at  $T_{gr}=410$  and 450 °C, respectively. As the GaInAs-related XRD peaks appear at the same angular position for both the samples, incorporation of In is independent of the  $T_{gr}$  applied for the present range of growth parameters. Therefore, we conclude that the reduction in tensile strain with increasing  $T_{gr}$  observed for the GaInNAs layers is due to a reduction in the nitrogen concentration  $y$  rather than an increased incorporation of In. Photoluminescence (PL) spectra taken at 9 K (not shown here) indicate a blueshift of the near band-edge PL with increasing  $T_{gr}$ , which provides further evidence of the reduction in nitrogen content with increased  $T_{gr}$ . This variation of incorporation of N can be attributed to a change of the sticking coefficient of N as a function of  $T_{gr}$  or variations in the amount of nitrogen surface adatoms available for incorporation. Within  $430 < T_{gr} < 470$  °C,  $y$  is approximately a linear function of  $T_{gr}$  (see the inset of Fig. 1), as inferred from the XRD data assuming that  $x$  is independent of  $T_{gr}$ . The linear relationship between  $y$  and  $T_{gr}$  allows us to control the nitrogen concentration in GaInNAs by simply varying  $T_{gr}$ .

In Fig. 2, XRD rocking curves are shown for samples S410 and S470 before and after postgrowth annealing. The rocking curves are essentially unaffected by annealing up to

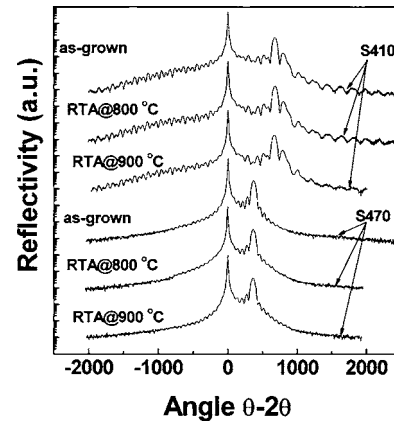


FIG. 2. X-ray diffractions rocking curves recorded before and after post-growth annealing from samples S410 and S470. Annealing temperatures are given in the figure.

at least 900 °C. Thus we may conclude that the GaInNAs layer composition remains unchanged under these annealing conditions.

Figure 3 shows Raman spectra of samples S410 to S470, normalized to the intensity of the GaAs 2LO mode.<sup>9</sup> The spectra are dominated by a peak at 473  $cm^{-1}$ , which is associated with the presence of Ga–N bonds in a local  $Ga_4-N$  configuration.<sup>9,10</sup> The 473  $cm^{-1}$  peak has “shoulders” at 460 and 492  $cm^{-1}$ . They originate from In–N bonds in a local  $Ga_3In_1-N$  configuration.<sup>9,10</sup> Also discernible are two broad peaks at 409 and 426  $cm^{-1}$ . The 409  $cm^{-1}$  one may be attributed to local vibration mode (LVM) of a nitrogen dimer (NN) on the Ga site, i.e.,  $NN_{Ga}$ .<sup>11</sup> The origin of the 426  $cm^{-1}$  feature is more difficult to decide. It could be a LVM of a NN dimer on the As site,  $NN_{As}$ ,<sup>11</sup> or it could be a Ga–N bond in an N-rich domain.<sup>12</sup> The above given assignments of the 473, 492, and 409  $cm^{-1}$  Raman lines and the interpretation of the 426  $cm^{-1}$  Raman peak as a  $NN_{As}$  mode are also supported by our density-functional theory (DFT) force-field calculations (see details below).

The shoulders at 460 and 492  $cm^{-1}$  imply that the  $Ga_3In_1-N$  clusters are already formed during growth. Their intensities relative to that of the main 473  $cm^{-1}$   $Ga_4-N$  peak increase at high  $T_{gr}$  (Fig. 4) due to the formation of

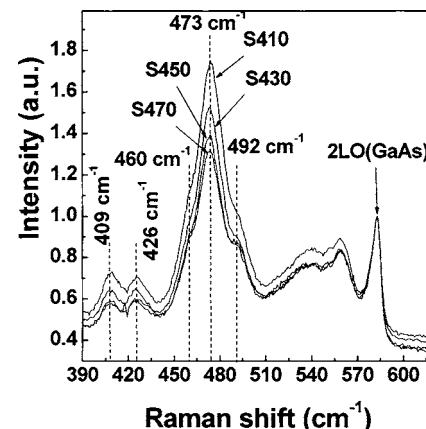


FIG. 3. Normalized Raman spectra recorded from samples S410 to S470. Signals assigned to Ga–N bonds (at 473  $cm^{-1}$ ) and In–N bonds (at 460 and 492  $cm^{-1}$ ) are resolved.

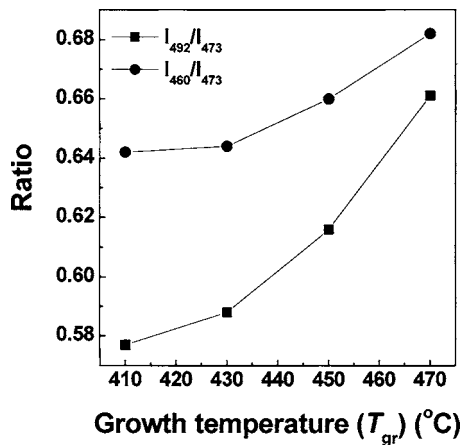


FIG. 4. Growth-temperature dependence of (a) the intensity ratio of the Raman shoulder 460  $\text{cm}^{-1}$  ( $I_{460}$ ) to the main Raman peak at 473  $\text{cm}^{-1}$  ( $I_{473}$ ); (b) the intensity ratio of the Raman shoulder at 492  $\text{cm}^{-1}$  ( $I_{492}$ ) to the 473  $\text{cm}^{-1}$  peak ( $I_{473}$ ).

$\text{Ga}_3\text{In}_1\text{-N}$  clusters at the expense of  $\text{Ga}_4\text{-N}$  bonds, in qualitative agreement with theory.<sup>13</sup> We should also note that as  $T_{gr}$  is increased the integrated intensities of the  $\text{Ga}_4\text{-N}$  and  $\text{Ga}_3\text{In}_1\text{-N}$  related Raman peaks decrease, which is a consequence of a reduced incorporation rate of nitrogen at high  $T_{gr}$ .

Relative strengths of the 460 and 492  $\text{cm}^{-1}$  shoulders increases upon annealing (Fig. 5). In sharp contrast to this, strength of the  $\text{Ga-N}$  473  $\text{cm}^{-1}$  peak decreases. These phenomena together indicate a considerable redistribution in group-III-nitrogen nearest-neighbor bonds towards In-N bonding. This interpretation is consistent with the noticeable blueshift of the alloy band gap,<sup>14</sup> as inferred from the 9 K PL data, which increased with annealing temperature. As detailed in Ref. 13, a redistribution of group-III-nitrogen bonds towards In-nitrogen bonding causes an increase in band-gap energy even if the overall alloy composition remained unchanged.

Intensity of the 409- $\text{cm}^{-1}$  band also decreases upon post-growth annealing at 800 °C and vanishes after annealing at 900 °C (Fig. 5). Strength of the peak at 426  $\text{cm}^{-1}$  also diminished upon annealing at 800 °C, but annealing up to 900 °C does not further affect it. Interestingly, a new peak

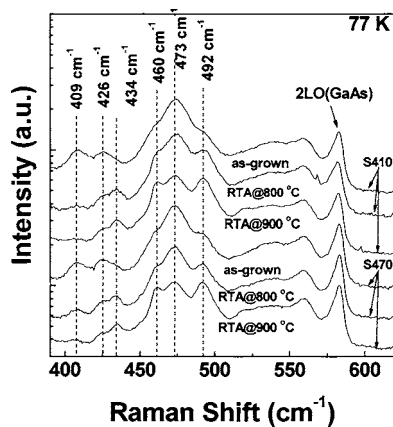


FIG. 5. Normalized Raman spectra recorded before and after annealing from samples S410 and S470.

appears at 434  $\text{cm}^{-1}$  after annealing. Because the 434  $\text{cm}^{-1}$  peak is not observed in postgrowth-annealed GaNAs,<sup>10</sup> it must be related to the presence of indium in the alloy. The exact origin of the 434  $\text{cm}^{-1}$  peak is unknown, but it could stem from a complex composed of In and  $\text{NN}_{\text{As}}$  dimers, whose formation is promoted by annealing through a mechanism resembling the annealing-induced formation of  $\text{Ga}_{4-i}\text{In}_i\text{-N}$  complexes in GaInNAs.

First-principles density-functional theory (DFT) total energy calculations were carried out for the harmonic force field (or Morse potential) of N and NN impurities in several different bonding configurations. With these calculations at hand, we are able to predict local vibrational modes and defect stabilities and lend partial support to several of the above-suggested interpretations of Raman frequencies. We did not attempt to extract Raman selection rules or mode intensities from the force-field approach. For our calculations, a state-of-the-art plane-wave pseudopotential method and the VASP code<sup>15,16</sup> with the projector-augmented wave extension and local-density approximation were chosen. The adopted model consisted of 64 or 65 atoms in  $2 \times 2 \times 2$  periodic supercell of the relevant GaInNAs compound for the substitutional N and NN impurities, respectively. The initially relaxed N-N bond length was kept fixed in force-field evaluation, but different metastable orientations are considered, although the (001) orientation was found to be most stable as it has been also suggested before.<sup>17</sup> To describe a dilute limit of N we chose to use the supercell lattice constant of GaAs properly relaxed for the bulk lattice. Within the supercell, however, full N-induced local relaxation is allowed. The plane-wave cutoff energy of 400 eV and eight Monkhorst-Pack  $k$  points were found sufficient for convergence in total energy.

The reduced mass of vibration, due to the recule motion of the lattice, cannot be easily evaluated from our “static” model. This vibration effect together with the first-principles nature of our approach can be expected to cause an overall shift of the calculated mode frequencies. Shifting the calculated mode frequencies to higher energies by 35  $\text{cm}^{-1}$  yielded an excellent match to the measured frequencies for most of the Raman lines. With this shift, the observed 473, 409, and 492  $\text{cm}^{-1}$  Raman lines closely matched the calculated frequencies of 472 (for N- $\text{Ga}_4$ ), 411 (for NN- $\text{As}_4$ ), and 495  $\text{cm}^{-1}$  (for N- $\text{Ga}_3\text{In}$ , the vibration takes place in a plane perpendicular to the In-N bond) within 1–3  $\text{cm}^{-1}$ . Furthermore, the assignment of the broad 426  $\text{cm}^{-1}$  structure to NN- $\text{Ga}_4$  gets support from the calculated 431  $\text{cm}^{-1}$  NN dimer vibration along the (010) axis, though even slightly better match was obtained with our calculations on NN- $\text{Ga}_3\text{In}$  mode frequencies.

As suggested above, the observed 434  $\text{cm}^{-1}$  line is obviously related to In neighboring nitrogen, as we find two mode frequencies also from our calculations, which lie within 2  $\text{cm}^{-1}$ , for  $\text{NN}_{\text{As}}$  dimers with one or two In neighbors. However, the calculated total energies favor In to be located on next nearest-neighbor sites of the  $\text{NN}_{\text{As}}$  dimer rather than the formation of  $\text{NN-Ga}_{4-i}\text{In}_i$  ( $0 \leq i \leq 4$ ) cluster (the former configuration is energetically favored by about 50 meV per In). In other words, the lower the number of In

nearest neighbors, the higher the stability of the complex. As a matter of fact, one of the lower NN–Ga<sub>3</sub>In frequencies of 427 cm<sup>-1</sup> raises to around 434 cm<sup>-1</sup> as In moves further away to the next nearest site of NN<sub>As</sub>. This effect could naturally explain the increase of the 434 cm<sup>-1</sup> peak strength upon annealing.

#### IV. CONCLUSIONS

Effects of growth temperature and subsequent thermal annealing on nitrogen incorporation into dilute Ga<sub>0.942</sub>In<sub>0.058</sub>NAs epitaxial layers lattice matched to GaAs have been investigated, in the case where the epilayers were grown by molecular-beam epitaxy under constant beam fluxes. It was found that, over the entire range of growth temperature investigated, 410–470 °C, nitrogen was incorporated as isolated atoms on substitutional sites N<sub>As</sub> and as substitutional NN dimers on gallium and arsenic sites, as inferred from Raman spectroscopy and DFT calculations. Isolated substitutional nitrogen is present in the form of N–Ga<sub>4</sub> complexes and, to a lesser extent, as N–Ga<sub>3</sub>In complexes. An increased in growth temperature reduced the amount of substitutional nitrogen and decreased the intensity ratio between N–Ga<sub>4</sub> and N–Ga<sub>3</sub>In complex-related Raman signals, i.e., the In–N bonding becomes more favorable at higher growth temperatures. At the same time, the alloy band gap increased. The amount of nitrogen dimers also decreases with increasing growth temperature. Postgrowth thermal annealing was found to promote the formation of In–N bonds, to diminish the amount of NN dimers and to lead to the appearance of a new peak at 434 cm<sup>-1</sup> in the Raman spectrum. This new peak was related to the presence of indium in the lattice and was tentatively attributed, as suggested by the

DFT calculations, to the local vibrational mode of a complex composed of a NN<sub>As</sub> dimer and a second-nearest-neighbor In atom.

#### ACKNOWLEDGMENTS

This work was supported by the Academy of Finland within the TULE QUEST Project. The computing facilities were provided by the Centre for Scientific Computing in Finland (CSC Project No. tkk2008).

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