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Nitrogen lattice location in MOVPE grown $Ga_{1-x}In_xN_yAs_{1-y}$ films using ion beam channeling

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Abstract

We have investigated the nitrogen lattice location in MOVPE grown $Ga_{1-x}In_xN_yAs_{1-y}$ with x = 0.07 and y = 0.025 by means of ion beam channeling technique. In this system, the lattice constant of the $Ga_{1-x}In_xN_yAs_{1-y}$ film is equal to GaAs lattice. Therefore, we can grow apparently no strain, high quality and very thick GaInNAs film on GaAs substrate. The quality of the films as well as the lattice location of In and N were characterized by channeling Rutherford backscattering spectrometry and nuclear reaction analysis using 3.95 MeV He^{2+} beam. The fraction of substitutional nitrogen in the film was measured using the $^{14}N(\alpha,p)^{17}O$ endothermic nuclear reaction. Our results indicate that more than 90 % of In and N atoms are located in the substitutional site, however, N atoms are slightly displaced by ~0.2 Å from the lattice site. We suggest that the GaInNAs film has a local strain or point defects around the N atoms.

1. Introduction

III-V-N alloy systems have attracted a great deal of attention due to potential application for telecommunication devices and their interesting physical properties. They exhibit unusual optical and electronic properties, such as very large band-bending, a large blue-shift and intensity enhancement of photoluminescence upon post-growth annealing, and remarkable variations in local lattice strain and short range order clustering, all related to the presence of ~3 % nitrogen in the lattice [1-3]. It is important to know the characteristics of N in the epitaxial layer not only from an application point of view, but also to better understanding of the fundamental growth mechanisms.

For general Rutherford backscattering spectrometry (RBS) measurements using ~2 MeV ion beams, it is difficult to detect trace light elements such as oxygen, nitrogen, carbon etc., because of overlapping signals from heavier elements in the film. In such cases, analysis via nuclear reaction or characteristic x-rays is used. Recently, successful measurements were made by RBS combined with nuclear reaction analysis (NRA) on GaN_xAs_{1-x} and $GaAs_{1-x-y}N_xBi_y$ with nitrogen fractions of a few percents. [4,5]

In this paper, RBS in channeling mode and NRA using $^{14}N(\alpha,p)^{17}O$ endothermic nuclear reaction are applied to investigate as-grown and annealed $Ga_{1-x}In_xN_yAs_{1-y}$ epitaxial layers with x = 0.07 and y = 0.025 grown on (001) GaAs substrates by metal-organic vapor phase epitaxy (MOVPE). We also perform the so-called tri-angulation, i.e. the angular scan profile measurements about three major axes, that is useful for the lattice location determination.

2. Experimental methods

GaInNAs layers with thickness of 1 μm were grown on (001) GaAs substrate by low pressure MOVPE with horizontal reactor. Triethylgallium (TEG), trimethylindium (TMI), tertiarybutylarsine (TBA) and dimethylhydrazine (DMHy) were used as the Ga, In, As and N sources, respectively. The carrier gas was palladium-purified H_2. The total pressure in the reactor during growth was 76 Torr for all runs. The sample of GaInNAs film was thermally annealed at ~670˚C for 10 minutes in TBA ambient.

Ion beam scattering experiments were performed with the 1.7 MV tandem accelerators at Kochi University of Technology. A 3.95 MeV He^{2+} beam was used for In, Ga and As detection by RBS and N detection by NRA. For both measurements, the incident beam was collimated by a 1mm × 1mm aperture. The typical beam current was 10 nA. The samples were placed on a 2 axis remote controlled goniometer. The total collected charge for each measurement was 60 μC

in order to get sufficient statistics while keeping the beam induced damage negligible.

For RBS measurements, the scattered α particles were detected by a conventional silicon surface barrier detector located at a scattering angle of 168°. The energy resolution of the detector is about 15 keV. The random spectrum was obtained by a standard procedure, that is, while rotating the sample around a selected axis to erase any channeling effects.

Several nuclear reaction can be used to characterize nitrogen, including $^{14}N(d,\alpha)^{12}C$, $^{14}N(d,p)^{15}N$ and $^{14}N(\alpha,\gamma)^{18}F$. However, deuterium beam activation induces long time radiation background in the setup. In the present study, the N content and its lattice location was investigated using the $^{14}N(\alpha,p)^{17}O$ endothermic nuclear reaction with 3.95 MeV He^{2+} beam where the proton was detected at 135° with respect to the beam direction [6]. When the incident α particle energy is 3.95 MeV, the emerging protons have energy of about 1.4 MeV. A 19 μm Mylar foil was placed in front of the detector to stop the elastically scattered α particles. When the α particles with incident energy of 3.95 MeV are elastically scattered by 135° by In atoms, the heaviest element in GaInNAs alloy, they have energy of about 3.5 MeV. According to the stopping power data in the literature, the Mylar foil of 19 μm thick will stop α particles up to 4.0 MeV and will stop proton particles up to 1.06 MeV, therefore it can stop all elastically scattered α particles but not the proton particles emerging from N atoms [7].

The channeling spectrum was obtained by carefully aligning the ion beam incident direction to major crystalline axes of the sample. We selected three major axes, <001>, <011> and <111>, to accurately locate In and N atoms in the lattice. After the channeling measurements, the crystal orientation was scanned with respect to the ion beam direction, and the variation of scattering intensity was measured as a function of the tilt angle. This procedure provides the so-called channeling dip curve, which is sensitive to displacements of atoms.

3. Results and discussion

Figure 1 a) shows the RBS spectra of as-grown GaInNAs collected in random and <001> direction. Both the In and the GaAs signals are visible. Ga and As signals can not be separated because their masses are very close by. The N signal is invisible because it is covered with the Ga+As substrate signal. In the random spectrum, the In signal region is from 900ch to 750ch, and Ga+As signal in GaInNAs alloy rises near 830ch. Therefore, both signals overlap in 830ch ~ 750ch region to form a bump. The minimum yields, χ_{min}(In) and χ_{min}(GaAs), obtained by comparing the <001> channeling and random spectra, are both ~8%, which

demonstrates a good quality of the epitaxial layer. Figure 1 b) shows the NRA spectra from the same sample. By comparing the integrated intensity around channel 400 in Fig.1 b), χ_{min}(N) is about 12%. Taking into account that χ_{min} for GaAs is ~8 %, the fraction of substitutional nitrogen f_n can be estimated by the following equation [8]:

$$f_n = \frac{1-\chi_{\min}(NRA)}{1-\chi_{\min}(RBS)},$$

in this case 96 % of the total nitrogen is located substitutionally. Figure 2 a) shows the RBS spectra of annealed GaInNAs. Again the quality of the layer is good andχ_{min}(In) and χ_{min}(GaAs) is ~8 %. Figure 2 b) shows the NRA spectra. In this case, χ_{min} is about 15 % and the fraction of substitutional nitrogen is 92 %. In the annealed sample, nitrogen fraction on random site slightly increases compared with the as-grown sample although the χ_{min}(RBS) is same. Other direction results, <011> and <111>, were very similar to the <001> direction, therefore not shown in this paper. These results suggest that only nitrogen atoms are moved by the annealing effect in this lattice matched system. The fraction of moved nitrogen atoms is estimated to be ~4 % ± 1 %. On the other hand, the In atoms are substitutional in the as-grown sample, and they do not move by the annealing.

Figure 3 shows the angular scans of the Ga+As, In and N spectra in the <001>, <011> and <111> directions of the as-grown sample, respectively. Ga+As and In spectrum are obtained from the RBS, and N spectrum obtained from the NRA. The normalized yield is defined here as the ratio of channeling scattering yield to the random scattering yield. In Fig.3 (a), it is seen that all spectra fully overlap, which is an indication that In and N are substitutional. Since the <001> angular dip profiles are identical, there is no misfit between the substrate and film lattice constants parallel to the surface. On the other hand, a distinct narrowing of the N angular scan relative to those for the Ga+As and In is observed in Fig.3 (b) and Fig.3 (c). These results indicate that the nitrogen atoms are slightly displaced from the substitutional site. Displacements of the order of ~0.1 Å can be detected using the angular scan technique. In this case the magnitude of the displacement r_x can be estimated from the half angle of the impurity channeling scan $\psi_{1/2}$(impurity) by the same principles as used to obtain the half angle of host $\psi_{1/2}$(host) by the following equation [8,9]:

$$\frac{\psi_{1/2}(impurity)}{\psi_{1/2}(host)} = \frac{\{\ln(C\alpha / r_x)^2 + 1\}^{1/2}}{\{\ln(C\alpha / \rho)^2 + 1\}^{1/2}}.$$

C is a constant of magnitude ~1.73, α is the Thomas-Fermi screening distance, and ρ is the root mean square thermal vibration amplitude. For GaAs, α is ~0.13 Å, ρ is ~0.10 Å [7, 9]. Using the measured $\psi_{1/2}$'s of N and Ga+As, we obtain r_x ~0.17 ±

0.05 Å in the <011> direction and ~0.29 ± 0.05 Å in the <111> direction, respectively. Since the In dip curves fully overlap with those of Ga+As in all directions, this result suggests that only N atoms are displaced slightly, and subsequently the GaInNAs lattice has local strains or point defects around the nitrogen atoms.

Previous studies have reported that the nitrogen atoms in as-grown GaInNAs distribute nonuniformaly and form a short range order clustering [1, 10]. Our results indicate that after annealing at 670 ˚C, such clustering of nitrogen atoms is broken and diffuse away. However, the local strain or point defect remains around nitrogen atoms because the atom radius of nitrogen is smaller than Ga, As, and In atoms. Those diffused N atoms induce local strain and increase χ_{min}(N).

4. Conclusion

The 1μm thick lattice matched $Ga_{1-x}In_xN_yAs_{1-y}$ samples were characterized by RBS/channeling and NRA/channeling technique. The results confirm that high quality epitaxial layers were grown on the (001) GaAs substrate. Based on the RBS and NRA results on the random and channeling geometries, more than 90 % of In and N atoms in this epitaxial layer occupy substitutional sites. However, the angular scan results indicate that N atoms are slightly displaced from the substitutional site, ~0.17 ± 0.05 Å when viewed in the <011> direction and ~0.29 ± 0.05 Å when viewed in the <111> directions, respectively. These results agree with previous studies and support that the nitrogen atoms in as-grown GaInNAs nonuniformly distribute. This distribution is diffused away after annealing, however, local strains or point defects remain around the N atoms.

References

[1] T. Kitatani, K. Nakahara, M. Kondow, K. Uomi, T. Tanaka, J. Cryst. Growth 209 (2000) 345.

[2] Sylvia G. Spruytte, Christopher W. Coldren, James S. Harris, William Wampler, Peter Krispin Klaus Ploog and Michael C. Larson, J. Appl. Phys. 89, 8 (2001) 4401.

[3] G. Bisognin, D. De Salvador, C. Mattevi, M. Berti, A. V. Drigo G. Ciatto, L. Grenouillet, P. Duvaut, P. Gilet and H. Mariette, J. Appl. Phys., 95 (2004) 48

[4] P. Wei, M. Chicoine, S. Gujrathi, F. Schiettekatte, J.-N. Beaudry, R.A. Masut, and P. Desjardins, J. Vac. Sci Technol. A 22 (2004) 908

[5] P. Wei, S. Tixier, M. Chicoine, S. Francoeur, A. Mascarenhas, T. Tiedje, F. Schiettekatte , Nucl. Instr. and Meth. B219-220 (2004) 671.

[6] Z. Lin, L. C. McIntyre, Jr., J. A. Leavitt, M. D. Ashbaugh and R. P. Cox, Nucl. Instr. and Meth. B 79 (1993) 498

[7] J. R. Tesmer and M. Nastasi, *Handbook of Modern Ion Beam Materials Analysis* (Materials Research Society, Pittsburgh 1995)

[8] L. C. Feldman, J. W. Mayer and S. T. Picraux, *Materials Analysis by Ion Channeling* (Academic, New York 1982)

[9] H. Kobayashi and W. M. Gibson, Appl. Phys. Lett, 74 (1999) 2355

[10] A. Hashimoto, T. Kitano, A. K. Nguyen, A. Masuda, A. Yamamoto, S. Tanaka, M. Takahashi, A. Moto, T. Tanabe and S. Takagishi, Sol. Energy Mater. & Sol. Cells 75 (2003) 313.

Figure captions

Fig. 1. a) Random and <001> aligned RBS spectra for as-grown GaInNAs and b) Nuclear reaction analysis spectra obtained in the <001> and the random directions for as-grown GaInNAs, using $^{14}N(\alpha,p)^{17}O$ endothermic nuclear reaction.

Fig. 2. a) Random and <001> aligned RBS spectra for annealed GaInNAs and b) Nuclear reaction analysis spectra obtained in the <001> and the random directions for annealed GaInNAs, using $^{14}N(\alpha,p)^{17}O$ endothermic nuclear reaction.

Fig. 3. Channeling angular scan of the as-grown GaInNAs along the (a) <001> axial direction, (b) <011> axial direction and (c) <111> axial direction.

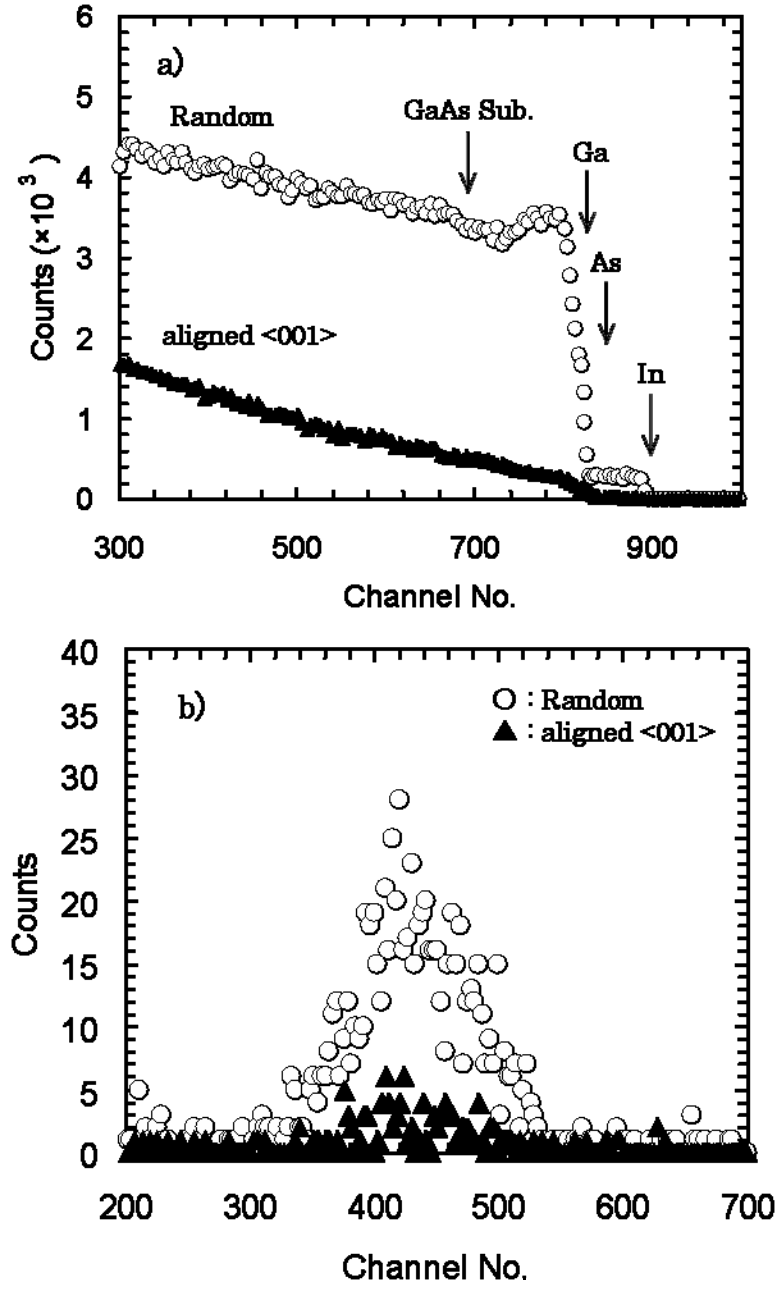
a)
Random
GaAs Sub.
Ga
As
In
aligned <001>
Counts (×10^3)
Channel No.
b)
○ : Random
▲ : aligned <001>
Counts
Channel No.

Figure 1

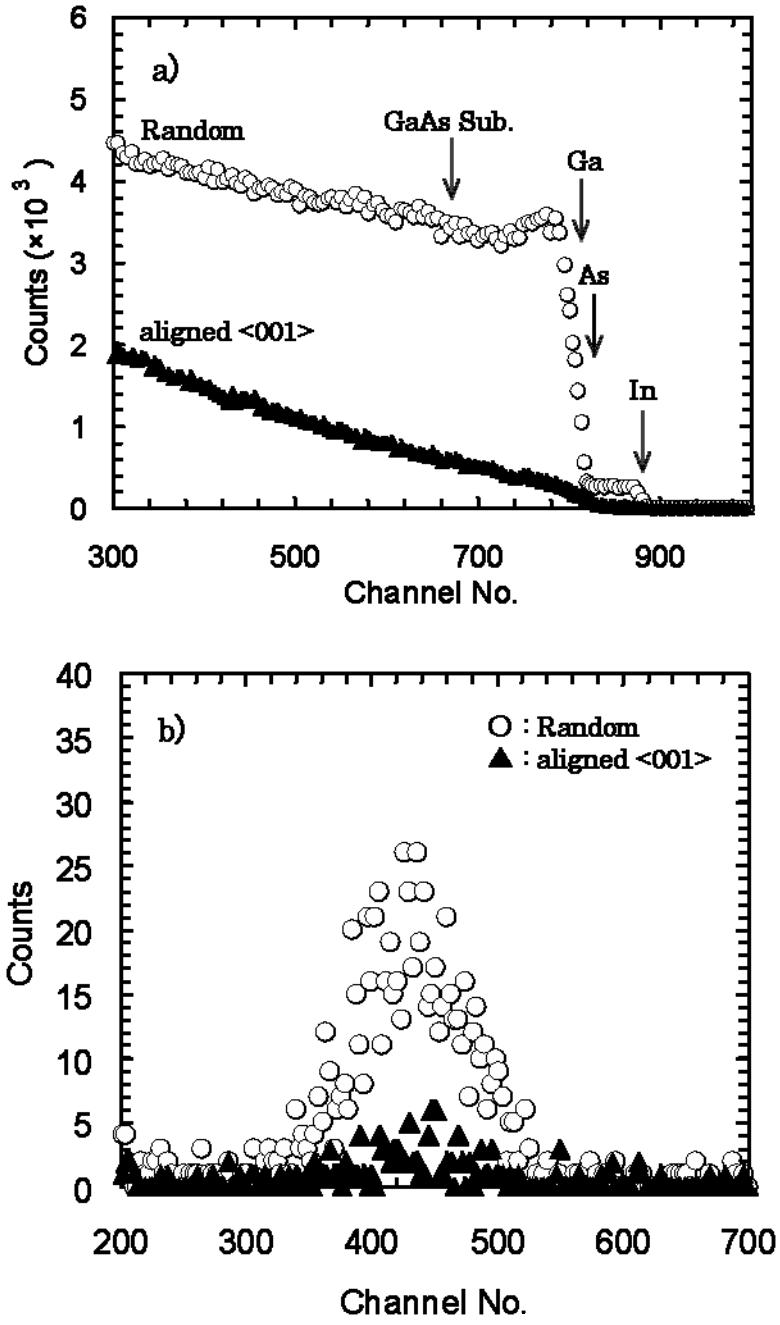
a)
Random
GaAs Sub.
Ga
As
In
aligned <001>
Counts (×10 3)
Channel No.
b)
○ : Random
▲ : aligned <001>
Counts
Channel No.

Figure 2

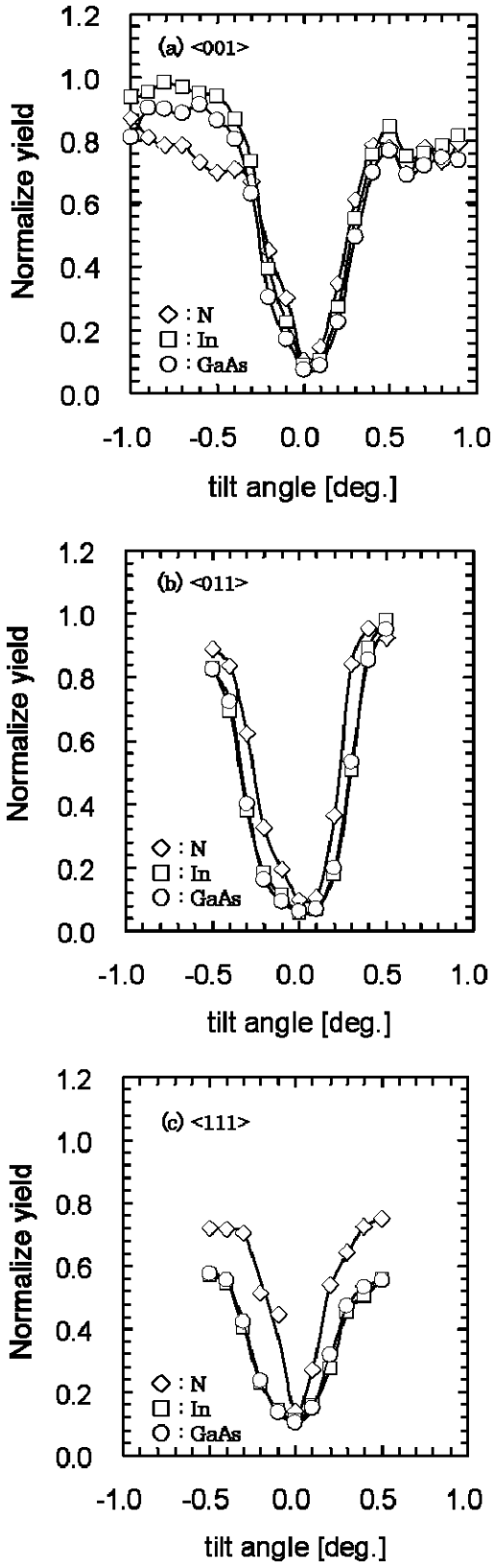
(a) <001>
Normalize yield
◇ : N
□ : In
○ : GaAs
tilt angle [deg.]
(b) <011>
Normalize yield
◇ : N
□ : In
○ : GaAs
tilt angle [deg.]
(c) <111>
Normalize yield
◇ : N
□ : In
○ : GaAs
tilt angle [deg.]

Figure 3