# Concentration of interstitial and substitutional nitrogen in GaN$_x$As$_{1-x}$

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The interstitial to substitutional nitrogen atoms as a function of concentration in GaNAs were determined by nuclear reaction analysis utilizing the $^{14}$N$(d,p)^{15}$N and $^{14}$N$(d,\alpha)^{12}$C reactions using ion channeling technique. The GaNAs films with mean nitrogen concentration between 0.3% and 3%, measured with secondary ion mass spectrometry and time-of-flight elastic recoil detection analysis, were grown using gas-source molecular-beam epitaxy. The fraction of nitrogen atoms occupying substitutional sites was observed to increase linearly with increasing nitrogen amount, while the concentration of interstitial nitrogen was nearly constant at $2 \times 10^{19}$ cm$^{-3}$ throughout the concentration region. Annealing at 750 °C decreases the concentration of interstitial nitrogen. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1465522]

The rapid development of optoelectronic devices, especially at wavelength range of 1.3–1.55 $\mu$m, has focused the research toward Ga(In)NAs alloys, where a small amount of N leads to considerable band gap reduction due to the large band gap bowing.[1] Incorporation of N into Ga(In)As, though deteriorates the crystalline quality. The origin for this has received a lot of attention in recent publications,[2–6] but still remains unclear. In the study conducted by McKay *et al.*[2] measurements of the arrangement of N atoms in GaNAs by scanning tunneling microscopy show that N atoms are randomly distributed and no clustering is observed. However, some enhancement of the number of second nearest neighbor pairs was observed. Bösker *et al.*[7] showed that N diffuses in GaAs by a kick-out mechanism involving interstitial N. From their measurements, however, it is not possible to conclude the fraction of interstitial N.

The purpose of this study is to experimentally determine the concentrations of interstitial and substitutional N as a function of mean N concentration and temperature. This information is indispensable for N diffusivity calculations where the interstitial to substitutional ratio is needed and for understanding the effects of rapid thermal annealing (RTA) on Ga(In)NAs structures.

The growth of GaN$_x$As$_{1-x}$ (100-nm-thick) samples with a 10-nm-thick GaAs cap layer and different N concentrations (0% < $x$ < 3%) was performed in a gas-source molecular-beam epitaxy system. Group-III fluxes were produced by thermal effusion cells, group-V flux was provided by thermally cracking of AsH$_3$, and reactive nitrogen was provided by a radio-frequency plasma cell. The GaNAs films were grown at 480 °C to incorporate N into the GaNAs layers.

The detailed growth conditions were reported elsewhere.[8,9] RTA was conducted with halogen lamps under N$_2$ gas flow.

The N concentration measurements were done by secondary ion mass spectrometry,[10] and time-of-flight elastic recoil detection analysis (ERDA) with the 5 MV tandem accelerator EGP-10-II of the University of Helsinki. In the ERDA measurements, a 53 MeV beam of $^{127}$I$^{10+}$ ions was used. The detector angle was 40°, and the samples were tilted relative to the beam direction by 20°. The elementary concentrations were calculated using known geometry and SRIM-96 stopping powers for energy loss calculations.[11–13]

For the $^{14}$N and GaAs channeling measurements, beams of 1.3 MeV deuterium ions and 1.8 MeV protons were used, respectively. The vacuum during measurements was kept better than $5 \times 10^{-6}$ Pa by placing a liquid nitrogen cooled, large area metal plate close to the sample. The experimental setup used standard electronics, detector, and a beam chopper system. The utilization of a beam chopper system allowed an accurate way to normalize the total collected charge for the random and aligned spectra. The scattered H from Rutherford backscattering spectrometry, and high energy H and He from nuclear reaction analysis (NRA), were detected by a silicon surface barrier detector with a thickness of 700 $\mu$m, and an effective area of 50 mm$^2$ placed 2.5 cm from the sample (solid angle 80 msr), at an angle of 135° relative to the beam direction. In the NRA measurements a 32-$\mu$m-thick mylar foil was placed in front of the detector to prevent the high counting rate from scattered D. During the experiment a neutron radiation between 30 and 50 mrem was monitored at the analyzing magnet. To identify the NRA yields from N, a pure Ta sample was implanted with $^{14}$N ions with energy 120 keV and dose $5 \times 10^{16}$ cm$^{-2}$.

Figures 1(a)–1(d) show the NRA yields from GaNAs and reference $^{14}$N implanted Ta sample as a function of outcoming particle energy from reactions $^{14}$N$(d,p)^{15}$N, $^{14}$N$(d,\alpha)^{12}$C for N, and reactions $^{16}$O$(d,p)^{17}$O and

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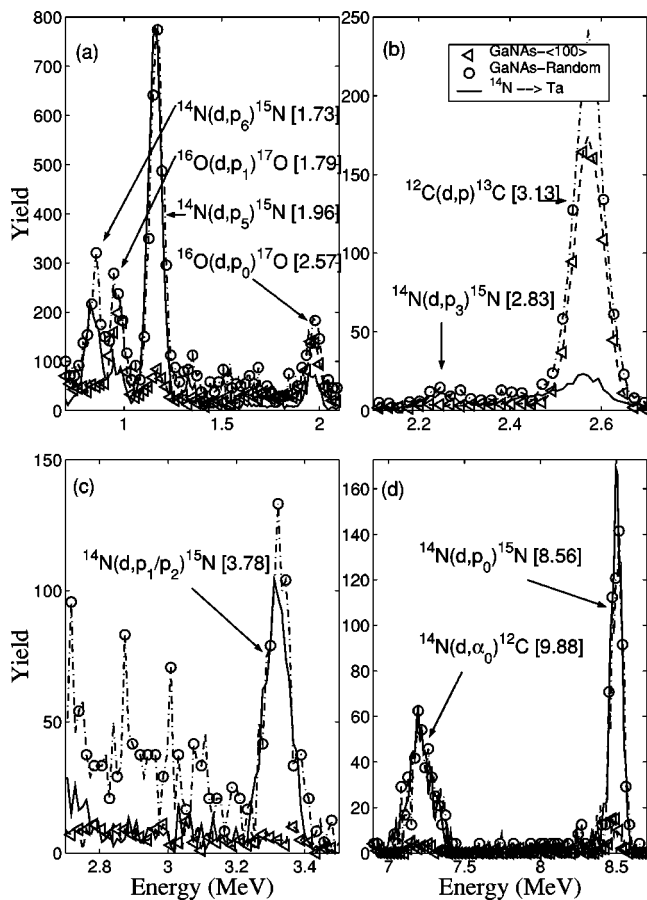[b)]Present address: ASM Microchemistry Ltd, P.O. Box 132, FIN-02631 Espoo, Finland.

FIG. 1. Experimental NRA yields from GaNAs ($\langle 100 \rangle$ and random direction) and $^{14}$N implanted Ta. Triangles and rings denote $\langle 100 \rangle$ and random yields, respectively. The values in the square brackets are the initial particle energies in mega-electron-volts before the mylar foil in front of the detector. Figures (a), (b), (c), and (d) corresponds to the reaction yield in different regions of particle energy.



FIG. 2. Normalized $\langle 100 \rangle$ channel to random yields ($\chi_{min}$) for N and GaAs as a function of mean N concentration in the samples. $\chi_{min}$ decreases for N and increases for GaAs signal as the N concentration increases. The inset shows how the RTA decreases interstitial N and increases GaAs yield.

$^{12}$C($d,p$)$^{13}$C for surface oxygen and carbon, respectively. The NRA yields for GaNAs are taken both when the D ion beam is aligned parallel to the low index crystallographic direction $\langle 100 \rangle$ and random direction, which is defined as a tilt angle of 5° off from the $\langle 100 \rangle$ channel with an 15° azimuthal angle from the [110] plane. The energies in the square brackets (see figure) are the initial particle energies in mega-electron-volts before the 32-$\mu$m-thick mylar foil in front of the detector. For the determination of interstitial and substitutional concentrations the He and proton reaction peaks in Fig. 1(d) were chosen due to the low background. From these peak areas the N minimum yield, i.e., the normalized ratio of the channeled and random yields, could be determined.

Figure 2 presents the minimum yield results obtained by NRA for N and RBS for GaAs. As can be seen, the N channel to random ratio decreases fast from about 16% to 7% when the nitrogen concentration increases from about 2 $\times 10^{20}$ to $10 \times 10^{20}$ at./cm$^3$. As the N concentration increases and because As and N atoms are isovalent, the increasing substitutional N should lead to an increase in the displaced or interstitial As amount. Indeed, as the substitutional nitrogen increases, we see a slight increase in the minimum yield originating from the GaAs lattice. In an *ab initio* study of substitutional N in GaAs by Orellana *et al.*[14] the formation
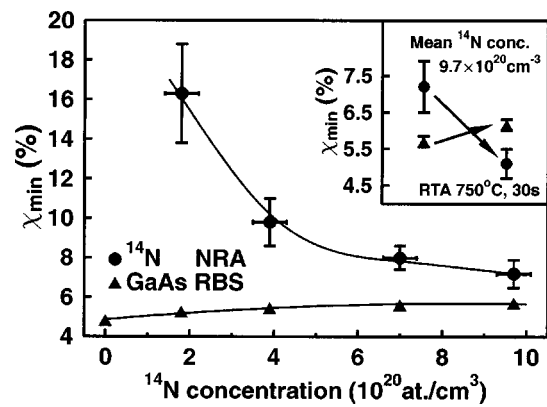
energy of substitutional N atom occupying Ga site was calculated to be much larger than for N atom occupying As site. Thus, we can assume that most of the increase in the minimum yield originating from the GaAs lattice can be attributed to an increase in the As interstitials. This is in good agreement with the N diffusion study in GaAs[7] where it has been shown that nitrogen diffuses by a kick-out mechanism involving interstitial N and As atoms. In the inset, we can further see that when the sample containing 9.7 $\times 10^{20}$ N at./cm$^3$ is subjected RTA at 750 °C for 30 s, the N channel to random ratio decreases noticeably, and at the same time the GaAs channel to random ratio increases. This clearly indicates that during annealing a large amount of interstitial N atoms takes substitutional sites.

To calculate the substitutional fraction of N atoms ($Frac.N_S$) from the minimum yield, the following equation was used

$$Frac.N_S = \frac{1 - \chi_{min}(\text{N})/100}{1 - \chi_{min}(\text{GaAsREF})/100}, \tag{1}$$

where the $\chi_{min}$(GaAsREF) and $\chi_{min}$(N) are the minimum yield for virgin GaAs (Fig. 2) and N, respectively. Equation (1) should apply if N atoms are not arranged in large clusters, which indeed is the case shown by McKay *et al.*[2] The formula can be used to calculate the concentration of interstitial and substitutional nitrogen from the known total N atomic concentration. In Fig. 3, the calculated atomic concentrations of substitutional and interstitial nitrogen are plotted. This picture shows that substitutional N increases linearly with total N content. Very interesting is that the interstitial nitrogen concentration increases very slow and stays at about $2.2 \times 10^{19}$ at./cm$^3$ at the whole region. In the inset we see that RTA at 750 °C decreases the concentration of interstitial nitrogen by a factor of about 10. In a study of the effects of RTA on GaInNAs/GaAsP quantum well structures and lasers, Li *et al.*[9] concluded that the optimum annealing temperature is about 750–800 °C. At this temperature, maximum photoluminescence intensity was observed, due to the removal of N-induced nonradiative centers from GaInNAs wells. Present results show that the majority of N interstitials are removed during RTA, hence, we suggest that these nonradiative centers could be defects involving interstitial N.
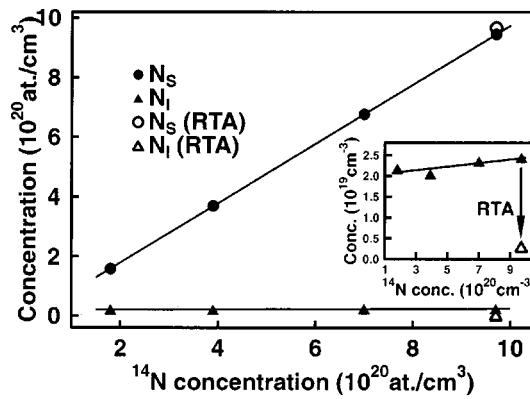
FIG. 3. The interstitial and substitutional N concentrations as a function of mean N concentration in the samples. Substitutional N ($N_S$) increases linearly, while the interstitial N ($N_I$) has almost the same concentration in the whole N concentration region. The inset shows dramatic decrease of interstitial N after RTA.

To look more closely at the process where a N interstitial moves to an As site, we write the equilibrium reaction between nitrogen and arsenic atoms as

$$N_I + As_S \leftrightarrow N_S + As_I, \tag{2}$$

where subscripts $I$ and $S$ denote interstitial and substitutional atoms, respectively. Based on this reaction we get the relation for the interstitial and substitutional concentrations, denoted by the square brackets

$$\frac{[N_S][As_I]}{[N_I][As_S]} = K, \tag{3}$$

where $K$ is the equilibrium constant which depends on temperature. Using Eq. (3) to calculate the equilibrium constants at the growth temperature 480 °C and at the 750 °C, 30 s RTA annealed samples with N concentration of $10 \times 10^{20}$ cm$^{-3}$, we obtained constants $\approx 0.36$ and $\approx 4.64$ at 480 and 750 °C, respectively. We assume here that the $As_I$, $As_S$, $N_I$, and $N_S$ species have attained local equilibrium at the RTA temperature and then frozen in during quenching. Assuming that the temperature dependence of $K$ is described by the usual equation $K = K_0 \times \exp(-E_a/kT)$, where $K_0$ and $E_a$ are the reaction constant and activation energy, respectively, $k$ is the Boltzmann's constant, and $T$ the absolute temperature, we get that $K_0 \approx 10^4$ and $E_a \approx 0.7$ eV. These values are only approximate, and more temperature points are clearly needed for their accurate determination.

We have measured the concentrations of interstitial and substitutional N in GaAs as a function of total N concentration. It was shown that substitutional N increases linearly as total N increases, but interstitial N is almost constant at about $2 \times 10^{19}$ cm$^{-3}$. RTA at 750 °C for 30 s removed almost all of the interstitial N, resulting in an estimate for the equilibrium reaction constant between N and As in GaNAs as a function of temperature.

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