Defects in nitride-based semiconductors probed by positron annihilation

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Abstract. Point defects in In$_x$Ga$_{1-x}$N grown by metal organic chemical vapor deposition were studied by a monoenergetic positron beam. Measurements of Doppler broadening spectra of the annihilation radiation as a function of incident positron energy for In$_x$Ga$_{1-x}$N ($x = 0.08$ and $0.14$) showed that vacancy-type defects were introduced with increasing InN composition. From comparisons between coincidence Doppler broadening spectra and the results calculated using the projector augmented-wave method, the major defect species was identified as the complexes between a cation vacancy and nitride vacancies. The concentration of the defects was found to be suppressed by Mg doping. An effect of Mg-doping on the positron diffusion properties in GaN and InN was also discussed. The momentum distribution of electrons at the In$_x$Ga$_{1-x}$N/GaN interface was close to that in defect-free GaN or In$_x$Ga$_{1-x}$N, which was attributed to the localization of positrons at the interface due to the electric field caused by polarizations.

1. Introduction

Growth techniques of GaN and Ga-rich In$_x$Ga$_{1-x}$N have been extensively studied for the past two decades, and this has led to the realization of present GaN-based solid state lighting technologies [1,2]. The In$_x$Ga$_{1-x}$N material system has also attracted great research interest for use as high-efficiency thin-film photovoltaic device materials [3] because of its potential in controlling the band gaps spanning from 0.65 eV to 3.43 eV, which can cover the wavelength from infrared to ultraviolet regions. The theoretical conversion efficiency of the solar cell using In$_x$Ga$_{1-x}$N has been reported to be greater than 60% [4]. The efficiency of solar cells using In$_x$Ga$_{1-x}$N/GaN multilayers, however, has been reported to be lower than the theoretical value. The origin of the degradation has been explained by low In$_x$Ga$_{1-x}$N crystal quality which mainly due to the difficulty of its epitaxial growth. This is mainly associated with large differences in the growth temperatures, equilibrium vapor pressures, and lattice constants of InN and GaN. As a result, the film growth process gives rise to unusually high strain and high defect densities. Dislocations and stacking faults, misorientations, residual strains, and phase separations of In$_x$Ga$_{1-x}$N have been studied [5], but knowledge regarding point-defects, such as monovacancies and vacancy composites, is also crucial to improve the conversion efficiency. Positron annihilation is a powerful
technique for evaluating vacancy-type defects in semiconductors [6], and the defects in group-III nitrides have been investigated using this method [7-9]. In the present study, we have used a monoenergetic positron beam to probe native vacancies in undoped and Mg-doped In$_{x}$Ga$_{1-x}$N grown by metal organic chemical vapor deposition (MOCVD).

2. Experiment
The samples investigated were In$_{x}$Ga$_{1-x}$N ($x = 0.08$ and 0.14) grown using MOCVD. The growth method and the optical properties of the samples are described elsewhere [10,11]. 1.4-$\mu$m-thick GaN films (+c-face) were grown on sapphire substrates at 1000$^\circ$C with buffer layers, and then 300-nm-thick In$_{x}$Ga$_{1-x}$N films were grown. For In$_{0.14}$Ga$_{0.86}$N, the film was deposited on Mg-doped GaN(120 nm)/GaN/sapphire substrate. The growth temperatures of the In$_{x}$Ga$_{1-x}$N layers were 790-800$^\circ$C, respectively. The electron and hole concentrations of undoped and Mg-doped In$_{0.08}$Ga$_{0.92}$N were $n_e = 5 \times 10^{17}$ cm$^{-3}$ and $n_0 = 5 \times 10^{18}$ cm$^{-3}$, respectively. InN and GaN grown by MOCVD and hydride vapor phase epitaxy (HVPE) were also studied [12,13].

With a monoenergetic positron beam, the Doppler broadening spectra of the annihilation radiation were measured as a function of the incident positron energy $E$. The low-momentum part of the spectra was characterized by the $S$ parameter, defined as the number of annihilation events over the energy range of 511 keV $\pm$ $\Delta E_r$ (where $\Delta E_r = 0.76$ keV) around the centre of the peak, and the high-momentum part was characterized using the $W$ parameters, defined as the annihilation events in the range of 3.4 keV $\leq |\Delta E_r| \leq 6.8$ keV. The relationship between $S$ and $E$ was analysed by VEPFIT [14].

Doppler broadening spectra corresponding to the annihilation of positrons were theoretically calculated using QMAS (Quantum MATERials Simulator) code, which uses valence-electron wavefunctions determined by the projector augmented-wave (PAW) method [15]. Details of the calculation method and its application to group-III nitrides are described elsewhere [11-13]. The structural optimization was done for a cell containing about 128 atoms by means of ab initio quenched molecular dynamics. For In$_{0.5}$Ga$_{0.5}$N, the initial bulk structure containing 128 atoms has been generated by means of the special-quasirandom-structure (SQS) approach [16]. The simulation was also perfumed for ordered In$_{0.5}$Ga$_{0.5}$N, where In- and Ga-faces were assumed to locate in c-faces alternately.

3. Results and Discussion
The $S$ values of HVPE-GaN and Mg-doped GaN before and after annealing as a function of $E$ are shown in Fig. 1. The mean implantation depth of positrons is shown on the upper horizontal axis. For HVPE-GaN, the $S$ value saturated at $E > 20$ keV, suggesting that almost all positrons annihilate in the bulk in this energy range. The solid curve is a fit to the experimental data, and the diffusion length of positrons $L_d$ was obtained as 72$\pm$1 nm. The derived value is the typical one for defect-free GaN [11-13]. For Mg-doped GaN after annealing, the $S$ value near the surface ($< 1$ keV) decreased rapidly with increasing $E$. For this sample, the $L_d$ value was derived as 2.3$\pm$0.1 nm. This very short diffusion length indicates the suppression of thermalized positrons diffusing toward the surface. A schematic of the band structure for p-type GaN is shown as an inset of Fig. 1. Because of the electric field caused by the band bending, the positrons implanted into the depletion region are dragged toward the inside of the sample, and this decreases the $L_d$ value for p-GaN after annealing.

For p-GaN before annealing, the $S$ values at $E \approx 2$ keV were almost the same as those after annealing; above this energy, however, they increased with increasing $E$ (<12 keV), suggesting the trapping of positrons by vacancy-type defects. When the Fermi level position inside the sample was higher than that near the surface, the diffusion of positrons toward the surface would be enhanced. According to this model, the region sampled by the positrons was divided into three blocks; the first and second blocks correspond to the positron annihilation in the Mg-doped layer, and the third block corresponds to that in the Si-doped layer. The derived $S$ values for the first and second layers were close to the $S$ values at $E = 2$ keV and 12 keV, respectively. The interface between the first and second layers was obtained as 6.4$\pm$0.4 nm. The $L_d$ value in the first layer was fixed to the value for the sample after
annealing, and that in the second layer was derived as 127±5 nm. The long diffusion length of positrons in the second layer can be attributed to the enhanced diffusion toward the surface due to the band structure. The $S$ value for the first layer was close to that for the sample after annealing, suggesting that the vacancy concentration in the subsurface region (<6 nm) were close to those in the film after annealing. The phenomena observed for the sample before annealing can be attributed to the partial activation of Mg in the subsurface region. Mg is known to segregate on the growth surface of GaN. Thus, because of a combination between the high Mg concentration and an enhanced reaction between Mg and vacancies at the Fermi level position in the subsurface region could decrease without annealing.

Figure 2 shows the $S$–$E$ curves for undoped InN and Mg-doped InN (p-InN, [Mg] = 3.1×10¹⁹ cm⁻³) after annealing, where the activation of Mg in p-InN was confirmed using electrolyte-based capacitance-voltage analysis[12]. For the undoped sample, the $L_d$ value was derived as 34±4 nm, and this short diffusion length is considered to be related to the surface band bending for InN [17]. The $S$–$E$ curve for p-InN can be fitted using the model applied to p-GaN before annealing. The width of the first region and the $L_d$ value in the second block were obtained as 70±7 nm and 127±8 nm, respectively. Thus, a similar band structure discussed for p-type GaN before annealing is expected for p-InN. Because of the electron accumulation at the surface of InN, the confirmation of carrier species in InN is difficult [17]. The present results suggests that the analysis of the $S$–$E$ curve can provide useful information about the band structure near the surface.

Figure 3 shows undoped and Mg-doped InₓGa₁₋ₓN as a function of incident positron energy $E$. For Mg:In₀.₀₈Ga₀.₉₂N, the $S$ value near the surface decreased rapidly with increasing $E$. This is the typical behavior of $S$ for p-type GaN and InN, and was attributed to the suppression of the positron diffusion toward the surface due to the band bending near the surface. For In₀.₁₄Ga₀.₈₆N, the $S$ value was almost flat at $E = 1-3$ keV, which suggests that almost all positrons annihilated in the In₀.₁₄Ga₀.₈₆N layer without diffusing back to the surface. For all samples, the dips in the $S$–$E$ curves were observed at $E = 10-15$ keV, which can be attributed to the annihilation of positrons near the InₓGa₁₋ₓN/GaN interface.

**Figure 1.** $S$ as a function of incident positron energy $E$ for undoped HVPE-GaN, Mg-doped GaN (p-GaN) before and after annealing. The solid curves are fits to the experimental data. An inset shows a schematic viewgraph for the band structure for p-type GaN.

**Figure 2.** $S$ parameters as a function of $E$ for undoped and Mg-doped InN (p-InN) after activation of Mg.
Annihilation characteristics of positrons in layered structures can be discussed by graphical analysis of the relationship between the $S$ and $W$ parameters. Figure 4 shows the $S$--$W$ relationship for In$_{0.14}$Ga$_{0.86}$N, In$_{0.08}$Ga$_{0.92}$N, and Mg:In$_{0.08}$Ga$_{0.92}$N. The $(S,W)$ value for HVPE-GaN (defect-free GaN) is also shown. Arrows show directions of the increase of $E$. For Mg:In$_{0.08}$Ga$_{0.92}$N, the $(S,W)$ trajectory can be represented by a straight line [an identical line was also shown in Fig. 4(a) and (b)]. The value approached the defect-free $(S,W)$ for GaN with increasing $E$ ($E \leq 10$ keV). For In$_{0.14}$Ga$_{0.86}$N, although the $(S,W)$ value saturated at $E = 2.9-5.4$ keV (corresponding $(S,W)$ value was shown in dotted lines), above $E = 5.9$ keV, it started to approach the defect-free $(S,W)$ value. For undoped In$_{0.08}$Ga$_{0.92}$N, although no clear indication of the annihilation of positrons in the In$_{0.08}$Ga$_{0.92}$N layer observed in the $S$--$E$ curve, the deviation from the line was observed in the $S$--$W$ plot. This suggests that positrons implanted into the In$_{x}$Ga$_{1-x}$N layer were under strong influence of the In$_{x}$Ga$_{1-x}$N/GaN interface. Because the $(S,W)$ value tend to approach the value for HVPE-GaN, the momentum distribution of electrons near the In$_{x}$Ga$_{1-x}$N/GaN interface is considered to be close to that for defect free In$_{x}$Ga$_{1-x}$N or GaN.

The $S$--$E$ curves for In$_{x}$Ga$_{1-x}$N/GaN were fitted, and the region sampled by the positrons was divided into four blocks; they respectively correspond to the positron annihilation in the In$_{x}$Ga$_{1-x}$N layer, the In$_{x}$Ga$_{1-x}$N/GaN interface, the GaN layer, and the sapphire substrate. The widths of the blocks and the corresponding $S$ values were determined by the fitting. The derived depth distributions of $S$ are shown

![Figure 3. $S$ parameters as a function of $E$ for undoped In$_{x}$Ga$_{1-x}$N $(x=0.08$ and $0.14)$ and Mg-doped In$_{0.08}$Ga$_{0.92}$N. Dips at $E = 9-15$ keV in the curves were attributed to the annihilation of positrons at the In$_{x}$Ga$_{1-x}$N/GaN interface. An inset shows the piezoelectric field $E_z$ and the electric field generated from the spontaneous polarization $E_0$.](image1)

![Figure 4. Relationships between $S$ and $W$ for (a) In$_{0.14}$Ga$_{0.86}$N, (b) In$_{0.08}$Ga$_{0.92}$N, and (b) Mg-doped In$_{0.08}$Ga$_{0.92}$N. The $(S,W)$ values for HVPE-GaN (defect-free) is also shown. Arrows show the increase in the incident energy of positrons.](image2)
in Fig. 5. For all samples, although the second block represents the In$_x$Ga$_{1-x}$N/GaN interface, their widths were obtained as about 200 nm. Makkonen et al. [9] reported the localization of positrons at the InN/GaN interface due to the built-in electric field caused by the piezoelectric effect. Because this effect was not included in the fitting model, the accumulation of positrons near the interface appeared as the wide width of the second block. Because a compressive stress is introduced in the In$_x$Ga$_{1-x}$N layer grown on the +c-plane GaN template, the positrons in the layer are dragged toward the interface by the piezoelectric field $E_z$, where the spontaneous electric field $E_0$ is far smaller than $E_z$ (inset of Fig. 3). This is the major cause of the lack of clear signals for the positron annihilation in the In$_{0.08}$Ga$_{0.92}$N layer.

Figure 6 shows the ($S, W$) values calculated from the coincidence Doppler broadening spectra using the PAW method. The values correspond to the annihilation of positrons in the delocalized state (defect-free: DF) and that of positrons trapped by $V_{Ga}$ as calculated for In$_{0.125}$Ga$_{0.875}$N. The result for DF-GaN is also shown. Arrows show the effect of $V_N$ coupled with $V_{Ga}$. The ($S, W$) values for In$_{0.14}$Ga$_{0.86}$N, Mg-doped In$_{0.08}$Ga$_{0.92}$N, and HVPE-GaN are also shown.

Using first-principles calculation [18], it was reported that the formation energy of $V_N$ decreased as the number of In adjacent to $V_N$ increased. Thus, both the bond-length/angle distortions and the decrease
in the formation energy of $V_N$ are expected to promote the introduction of $V_N$ with increasing InN content. Although positrons are not trapped by isolated $V_N$, some of them preferentially couple with cation vacancies and form stable complexes. Thus, we can conclude that the observed behaviour of defects in In$_x$Ga$_{1-x}$N is considered to be the introduction of $V_N$ and related formation of cation-vacancy-$V_N$ complexes.

4. Summary
We studied vacancy-type defects in In$_x$Ga$_{1-x}$N grown by MOCVD using a monoenergetic positron beam. The major defect species in the In$_x$Ga$_{1-x}$N film was identified as cation vacancies coupled with $V_N$s, and their concentration increased with increasing InN content. The defect concentration, however, was decreased by Mg-doping. The intrinsic ($S,W$) value corresponding to the annihilation of positrons at the In$_x$Ga$_{1-x}$N/GaN interface was close to that for defect-free GaN or In$_x$Ga$_{1-x}$N, suggesting the localization of positrons at the interface due to the piezoelectric field. From the measurements of Mg-doped InN, In$_x$Ga$_{1-x}$N, and GaN, it was found that the diffusion property of positrons is sensitive to variation in the band structures in the subsurface region. We have shown that the positron annihilation parameters are sensitive to vacancy-type defects in In$_x$Ga$_{1-x}$N films, meaning that this technique can be a useful tool for evaluating In$_x$Ga$_{1-x}$N-based devices.

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