Room temperature photoluminescence lifetime for the near-band-edge emission of epitaxial and ion-implanted GaN on GaN structures

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For accelerating the development of GaN power-switching devices, current knowledge on the origins and dynamic properties of the major intrinsic nonradiative recombination centers (NRCs) in Mg-doped GaN (GaN:Mg) are reviewed, as lightly to heavily doped p-type planar GaN segments are required but certain compensating defects including NRCs hinder their formation. The results of complementary time-resolved photoluminescence and positron annihilation spectroscopy measurements on the epitaxial and ion-implanted GaN:Mg formed on low dislocation density GaN substrates indicate the following: major intrinsic NRCs are the clusters of Ga vacancies (VGa)s and N vacancies (VN), namely VGa(VN)s in the epitaxial GaN:Mg and (VGa)3(VN)3 in the ion-implanted GaN:Mg after appropriate thermal annealings. The minimum electron capture-cross-section of the major intrinsic NRCs in n-type GaN, namely VGa(VN)s, is approximately 7×10−14 cm2.

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1. Introduction

In order to solve the energy crisis problem, the exploitation of high-power devices is one of the delightful ways of decreasing the total energy consumption. For such devices, GaN is suited according to its outstanding characteristics such as the large bandgap energy (3.4 eV), high breakdown field (3.3 MV cm−1), and high saturation electron velocity (2.5×107 cm s−1). A normally-off GaN-based transistor on a freestanding (FS) GaN substrate with low specific on-state resistance (1.0 mΩ cm2) and high off-state breakdown voltage (1.7 kV) has been demonstrated using p-type GaN (p-GaN)/AlGaN/GaN layers overgrown on the V-shaped groove formed over the drift layer. Moreover, GaN vertical metal-oxide-semiconductor field-effect-transistors (MOSFETs) capable of large current switching have been explored.

Although most of the previous GaN devices have been examined using Mg-doped p-GaN (p-GaN:Mg) epitaxial layers, selective-area impurity doping is an indispensable technique from the viewpoint of versatile designing and processing of devices at a low cost. In particular, ion implantation (I/I) with appropriate activation annealing is preferred for fabricating both vertically and laterally current-flowing transistors. In this connection, both heavily and lightly doped p-type layers are crucial, because the former realizes low resistance for contacting and hole-injecting layers while the latter is applicable for forming inversion channels and for electric field spreading as a guard ring. However, p-type doping by I/I of Mg has long been difficult, partially because donor-type defects introduced by I/I and/or donor impurities such as O or Si that might be diffused from the protective overlayer during the post-implantation annealing (PIA) likely compensate holes. Another issue is that only Mg serves as an acceptor in GaN.

Several approaches to avoid the compensation have been examined recently. Reference 16 fabricated p-GaN:Mg by using a shallow, sequential implantation of Mg and H ions to (000̅) N-polar plane of FS-GaN, and demonstrated pn junction diodes with a distinct rectification property. Their explanation was that the use of the (000̅) plane allowed a capping-less PIA because of its high thermal stability, which suppressed unwanted hole compensation. Also, the addition of H was assigned to decrease the formation energy of MgGa acceptors. Reference 21 have measured the cathodoluminescence (CL) spectra of those N-polar I/I GaN:Mg samples at 10 K, and showed the peak originating from the recombinination of excitons bound to a MgGa acceptor (ABEs) at 3.465 eV (Refs. 22–24) and the ultraviolet luminescence (UVL) band at around 3.26 eV that originates from a free electron or a shallow donor to a MgGa acceptor transition. However, they simultaneously observed considerable green luminescence (GL) band at around 2.4 eV, which is routinely observed in I/I GaN:Mg and has been assigned to a transition involving N vacancies (VN). Similar to their reports, definitive evidence of p-type conductivity with a reliable hole concentration (p) measurement has not been shown, and the device characteristics containing p-GaN:Mg fabricated using I/I have been reported only recently.

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For the reliable fabrication of p-GaN:Mg by I/I, an accurate understanding of I/I induced defects is essential, as such defects likely form trapping levels and/or nonradiative recombination centers (NRCs), both of which decrease $p$. With respect to point defects in GaN: Mg, Refs. 27, 28 have detected vacancy-type defects in p-GaN:Mg homoepitaxial films grown by metalorganic vapor phase epitaxy (MOVPE) and I/I GaN:Mg (Refs. 27 and 28) formed on unintentionally doped (UID) homoepitaxial films on Ga-polar (0001) plane of a FS-GaN substrate by means of positron (e') annihilation spectroscopy (PAS) measurement. They have shown that major vacancy-type defects in the epilayers (0001) were multiple vacancies consisting of a Ga vacancy ($V_{Ga}$) and two or three $V_{Ga}$s, namely $V_{Ga}(VN)_2$ or $V_{Ga}(VN)_3$,27 while those in the as-implanted GaN:Mg were $V_{Ga}VN$ divacancies but they agglomerated into larger vacancy clusters such as ($V_{Ga}h)(VN)$ after a PIA at 1300 °C.28

Combined with the results of time-resolved photoluminescence (TRPL) measurement, Ref. 37 have assigned $V_{Ga}(VN)_2$ to the major NRCs in the GaN:Mg epilayer and quantified their electron capture-cross-section ($\sigma_e$) approximately the middle of $10^{-13}$ cm$^2$ at 300 K, which was larger than the hole capture cross-section ($\sigma_h$) of the major NRCs in n-type GaN (n-GaN), namely $V_{Ga}VN$, $V_{Ga}VN$, $V_{Ga}VN$, being $7 \times 10^{-14}$ cm$^2$.36,37,38 However, because the near-band-edge (NBE) emission has scarcely been observed at 300 K from I/I GaN:Mg for a long time,24,26 neither $\tau_{PL}$ nor $\sigma_h$ of ($V_{Ga}h)(VN)$ has been quantified until recently.39

In this progress review, the origins and $\sigma_h$ of the major intrinsic NRCs in epitaxial and I/I p-GaN:Mg formed on low threading dislocation (TD) density FS-GaN substrates are described, and compared with the major intrinsic NRCs in n-GaN.22,34,36,38 The epitaxial p-GaN:Mg commonly exhibited the NBE and/or UVL emissions at low temperatures and the NBE emission at 300 K irrespective of Mg doping concentration, [Mg]. Accordingly, photoluminescence (PL) lifetimes ($\tau_{PL}$) at 300 K were measurable.37 By contrast, both (0001) Ga-polar20 and (0001) N-polar16,21 I/I GaN:Mg with the average implantation depths larger than 500 nm have never exhibited the NBE emission at 300 K,26 and the results have hampered quantifying $\tau_{PL}$ or judging the conductivity type. Quite recently, sequential shallow implantation of Mg and H into the (0001) plane with subsequent capping-less PIA has enabled the formation19 of p-type I/I GaN:Mg. Accordingly, $\tau_{PL}$ and $\sigma_h$ of ($V_{Ga}h)(VN)$ defects were quantified very recently.39 The $\sigma_h$ values of $V_{Ga}VN$ and ($V_{Ga}h)(VN)h$ are commonly approximately the middle of $10^{-13}$ cm$^2$ at 300 K, which is approximately four times larger than $\sigma_h$ of the major intrinsic NRCs ($V_{Ga}VN$) in n-GaN.

2. Experiments and analyses

2.1. Samples

The GaN:Mg epilayers were grown by MOVPE by two suppliers, as shown in Fig. 1(a). From supplier A, approximately 1 to 4-μm-thick GaN:Mg epilayers grown on a 2-μm-thick UID GaN epilayer on a Ga-polar c-plane FS-GaN substrate grown by the hydride vapor phase epitaxy (HVPE) method [Mitsubishi Chemical Corp. (MCC)]40 were provided (sample set A). Potential influences of TDs on the PL properties41 may be minimized, as the TD density was in the range of $10^6$ cm$^{-2}$.40 The [Mg] values were controlled from $3 \times 10^{16}$ to $7 \times 10^{19}$ cm$^{-3}$, which were quantified by using the secondary-ion mass spectrometry (SIMS). As a control sample, a UID GaN film was prepared. From supplier B, approximately 2-μm-thick UID GaN epilayers grown on a 2-μm-thick UID GaN epilayer on the same c-plane FS-GaN (MCC)40 were provided. The [Mg] values were $5 \times 10^{17}$, $5 \times 10^{18}$, and $4 \times 10^{19}$ cm$^{-3}$ (sample set B). All epilayer samples were thermally annealed at $T_A = 700$ °C for 30 min in a N$_2$ gas ambient for activating the MgGa acceptor. The I/I GaN:Mg samples were supplied from suppliers A and C. At supplier A, the samples were formed on a 4-μm-thick UID GaN film grown on the same Ga-polar FS-GaN (MCC)40 as shown in Fig. 1(b). Mg$^+$ ions were implanted into the UID GaN film with several energies ranging from 20 to 430 keV, in order to form a 500-nm-deep box-type profile with [Mg] of $1 \times 10^{17}$, $1 \times 10^{18}$, and $1 \times 10^{19}$ cm$^{-3}$. The I/I GaN was carried out at room temperature and followed by the deposition of a 300-nm-thick AlN decomposition shield by a sputtering method. All samples were annealed under various temperatures ($T_A$) between 1000 and 1300 °C for 5 min with N$_2$ gas at atmospheric pressure. The AlN film was chemically removed after annealing. By supplier C, approximately 100-nm-deep N-polar I/I GaN:Mg of a box-type profile was prepared by implanting Mg and H ions sequentially to the (0001) plane of an n-type FS-GaN substrate grown by HVPE [Furukawa Denshi Co. Ltd. (Furukawa)] through the 30-nm-thick SiN$_x$ film, as shown in Fig. 1(c). The total TD density of the edge and screw components was typically $2 \times 10^6$ cm$^{-2}$, which is low enough to maintain the internal quantum efficiency ($\eta_{int}$) of the NBE emission,41 and almost no structural defects were observed. The concentrations of Mg and H in the constant profile region were [Mg] = $1.4 \times 10^{19}$ cm$^{-3}$ and [H] = $2.1 \times 10^{20}$ cm$^{-3}$. The I/I GaN was carried out without any protective overlayer at $T_A$ between 800 and 1260 °C for 30 s in a N$_2$ ambient. The details of the sample fabrication process can be found elsewhere.16 For comparison, the following four samples were prepared. One was a control Ga-polar GaN:Mg epilayer ([Mg] = $1.5 \times 10^{19}$ cm$^{-3}$) grown by MOVPE on a FS-GaN substrate (manufacturer undisclosed). Another was a Ga-polar edition of the principal sample, namely, an approximately 100-nm-deep Mg- and H-implanted GaN of a box-type profile, which was fabricated on a (0001) FS-GaN (Furukawa). The other two were deep-implantation editions.
namely, 710-nm-deep Mg- and H-implanted (0001) and (000$	ext{f}$) FS-GaN (Furukawa). These comparative II samples were annealed at 1230°C without any capping layers. After the annealing, the (0001) surface became porous, while the (000$	ext{f}$) surface did not exhibit serious degradation.21

2.2. Steady-state and time-resolved photoluminescence measurements

Steady-state PL was excited by using the 325.0 nm line of a cw He-Cd laser with the power density of 38 W cm$^{-2}$. For understanding the origin and dynamic properties of the major intrinsic NRCs in a direct bandgap semiconductor, the complementary use of TRPL and PAS measurements is suited, as PAS is sensitive to vacancy-type defects and TRPL quantifies $\tau_{PL}$ of the NBE emission that represents the minority carrier lifetime ($\tau_{\text{minority}}$). The TRPL measurement was carried out at 300 K using approximately 100 fs pulses of a frequency-tripled (3ω) mode-locked $\text{Al}_{2}\text{O}_{3}\cdot\text{Ti}$ laser ($\lambda = 267$ nm), of which the repetition rate was decreased to 8 MHz. The power density was approximately 120 nJ cm$^{-2}$ (per pulse), where the excited carrier concentration is estimated at a few times $10^{15}$ cm$^{-3}$ when $\tau_{PL}$ is 100 ps. We note that both steady-state PL and TRPL measurements were carried out under weak excitation conditions to underline the nonradiative recombination processes.36 The spot diameter was 1 mm, and the obtained PL and TRPL signals are most likely composed of various signals from corresponding areas with different concentrations of Shockley-Read-Hall (SRH)-type NRCs ($N_{\text{NRC}}$). The TRPL signal was collected using a synchro-scan streak camera with the temporal resolution better than 1 ps. As shown in Fig. 2, an inverse of $\tau_{PL}$ is the PL decay rate, which is a sum of the radiative and nonradiative recombination rates ($R_{R}$ and $R_{NR}$, respectively), expressed by $\tau_{PL}^{-1} = \tau_{R}^{-1} + \tau_{NR}^{-1}$, where $\tau_{R}$ and $\tau_{NR}$ are the respective lifetimes. Because $\tau_{R}$ of the NBE emission in a good quality bulk material is a unique value; e.g. approximately 40–50 ns at 300 K for the case of GaN under weak excitation conditions, $\tau_{NR}$ can be derived from measured $\tau_{PL}$. Here, $\tau_{NR}$ is governed by the capture coefficient for minority carriers ($C_{\text{minority}}$) and $N_{\text{NRC}}$ under the relationship $\tau_{NR} = (C_{\text{minority}} \cdot N_{\text{NRC}})^{-1}$. Here, $C_{\text{minority}}$ is assumed to be a product of the minority carrier capture-cross section ($\sigma_{\text{minority}}$) and thermal velocity ($v_{\text{minority}}$) and the capture-cross-section $\sigma_{\text{minority}}$. In the case of n-type GaN, in which minority carriers are holes, $\tau_{NR}$ is expressed by $1/\tau_{NR} = \tau_{PL}^{-1} + 1/\tau_{\text{NR}}$.31

![Fig. 2](image)

(Color online) (a) Schematic representation of the relationship among the generation of an electron-hole pair or an exciton by a photon $h\nu$ with the rate $G$, nonradiative recombination at a SRH-type NRC with the rate $R_{NR}$ (lifetime $\tau_{NR}$), and radiative recombination with the rate $R_{R}$ (lifetime $\tau_{R}$). (b) Schematic model of a NRC capturing minority carriers of a thermal velocity $v_{\text{minority}}$ and the capture-cross-section $\sigma_{\text{minority}}$. In the case of n-type GaN, in which minority carriers are holes, $\tau_{NR}$ is expressed by $\frac{1}{\tau_{NR}} = \frac{1}{\tau_{PL}} + \frac{1}{\tau_{\text{NR}}}$.

For identifying the origin and quantifying the concentration of the major vacancy-type defects, PAS measurement35–39 was carried out. A monoenergetic $e^{-}$ beam line at University of Tsukuba25,26,28–31,34,36,37,39 was used to measure the Doppler broadening spectra of the annihilating $\gamma$-rays of $e^{-}$ and electrons ($e^{-}$). The low- and high-momentum portions of the spectra were characterized by the $S$ and $W$ parameters,29–31,35 respectively, where $S$ reflects the size or concentration of the vacancy-type defects. During the PAS measurement, the samples were illuminated with the same He-Cd laser to supply electrons to neutral or positively charged levels.28 Details of the PAS measurements20–33,35 and the analytical procedures27,28 can be found elsewhere. The species and the concentration of major vacancy-type defects were identified and quantified from the $S$- $W$ relationship20–33,35 and the magnitude of $S$ parameter,20–33,35 respectively. Reference 35 have evaluated the dynamic range of PAS for a neutral defect like a $V_{\text{Ga}}$ in n-GaN from the sensitivity of $e^{-}$ annihilation lifetime to approximately between 10$^{10}$ and 10$^{15}$ cm$^{-3}$, at which implanted $e^{-}$ are nearly fully delocalized in the defect-free (DF) regions and fully trapped by $V_{\text{Ga}}$, respectively. The range may shift toward the lower values when the vacancy is negatively charged.

When $\tau_{NR}$ of the NBE emission is inversely proportional to the concentration of a unique defect, the defect can be assigned to the major NRC.32,34,36,37,39 As a consequence, the capture-cross-section for the minority carriers ($\sigma_{\text{minority}}$) of the NRCs can be derived36–39 from the relationship given in Sect. 2.2. By using this complementary approach described in Sect. 2.2 and 2.3,32,34,36 point-defect complexes containing a $V_{\text{Ga}}$32,34 more precisely $V_{\text{Ga}}V_{N}$,33,36 have been identified as the origin of the major SRH-type NRCs in n-GaN, because $\tau_{NR}$ decreased with increasing the concentration of $V_{\text{Ga}}$-complexes,32,34 more precisely $V_{\text{Ga}}V_{N}$ concentration ($[V_{\text{Ga}}V_{N}]$).36 Accordingly, its hole capture coefficient ($C_{p}$) was determined from the relationship between $\tau_{NR}$ and $N_{\text{NRC}}$. $\tau_{NR} = (C_{p} \cdot N_{\text{NRC}})^{-1}$, and $\sigma_{p}$ was deduced from $C_{p} = \sigma_{p} \cdot v_{p}$, where $v_{p} = \sqrt{3k_{B}T \cdot m_{p}^{-1}}$ is the hole thermal velocity. These parameters are important, as $\eta_{\text{int}}$ of the NBE emission is given by $\eta_{\text{int}} = \frac{\tau_{NR}}{\tau_{R} + \tau_{NR}} \cdot \frac{1}{\tau_{NR}}$. Eventually, $\tau_{PL}$ of the NBE emission is expressed by $\frac{1}{\tau_{PL}} = \frac{1}{\tau_{\text{NR}}} + \frac{1}{\tau_{\text{NR}}} \cdot N_{\text{NRC}}$. In the case of n-GaN, $\sigma_{p}$ of $V_{\text{Ga}}V_{N}$ approximately $7 \times 10^{-14}$ cm$^2$ was determined in this way,36,38 where intrinsic $\tau_{R}$ was taken as 40 ns.34,43

3. Results and discussion

3.1. Mg-doped GaN epitaxial films grown by MOVPE

Both the spectra and decay signals of the NBE PL in sample sets A and B showed principally similar trends with respect to the change in [Mg], as follows. PL spectra at 10 K of UID, GaN:Mg set A, and GaN:Mg set B are shown in Figs. 3(a), 3(b)–3(e), and 3(f)–3(h), respectively, by the upper solid...
lines. The PL intensity (y-axis) has a unit of count per second (cps), and the spectra can be compared with those at different temperatures or other samples. As shown in Fig. 3(a), the UID GaN film exhibited distinct NBE PL peaks and shoulders originating from the recombination of free excitons (FXXs) at 3.478 eV, recombination of excitons bound to a neutral donor (DBEs) at 3.472 eV, and their LO phonon replicas at the energies higher than 3.2 eV. In addition, weak luminescence bands called the blue luminescence (BL) band due to the transition of an electron from a carbon deep donor (CGa) to the valence band (carbon-blue)44) at around 2.9 eV and red luminescence (RL) band25) at around 1.8 eV were detected. By using the first-principles calculations, Ref. 25 have suggested that $V_{Si}$ is the origin of RL band. In this context, the appearance of RL implies higher $V_{Si}$ concentration, $[V_{Si}]$, in the present UID GaN, because state-of-the-art UID GaN films grown by MOVPE do not exhibit RL but exhibit so-called yellow luminescence (YL) band.22,45–49) We note that there are two independent origins of the YL band: one is the transition of an electron in the conduction band (or bound to a shallow donor) to a carbon acceptor on a N site (C$_{Ga}$)40) and the other is the emission due to the complex of a VGa and a donor impurity such as an oxygen on a N site (O$_{N}$), $V_{Ga}O_{N}$.46–48)

The dominant NBE emission at 10 K switched from DBEs in UID to ABEs in GaN:Mg films with $[Mg]$ lower than $5 \times 10^{18}$ cm$^{-3}$, as shown in Figs. 3(b)–3(d), 3(f), and 3(g). Simultaneously, UVL band49) appeared in the PL spectra of GaN:Mg films [Figs. 3(b)–3(h)]. Such an observation of the ABEs and UVL indicates the formation of MgGa acceptors. We note that $[Mg]$ of $3$ to $4 \times 10^{19}$ cm$^{-3}$ is routinely used to obtain a p-GaN hole-injecting layer ($p = 1 \times 10^{18}$ cm$^{-3}$) in light-emitting devices, and the emergence of a BL band (magnesium-blue)23,50) at around 2.8 eV at 300 K (lower solid lines in Fig. 3) is a fingerprint of p-type conductivity of GaN: Mg epilayers. As can be seen in Fig. 3, most of the PL spectra exhibited a weak RL band.25) The enhanced incorporation of $V_{Si}$ in GaN:Mg films compared to n-GaN is reasonable, as the formation energies ($E_{f orm}$) of $V_{Si}$ and $V_{N}$-MgGa decrease with the lowering Fermi level ($E_F$).25,45–47)

Even at 10 K, the integrated spectral NBE emission intensity ($I_{NBE}$) decreased with increasing $[Mg]$ when $[Mg]$ exceeded $1 - 5 \times 10^{18}$ cm$^{-3}$, as shown in Figs. 3(d), 3(e), 3(g), and 3(h). A drastic decrease in $I_{NBE}$ was found in the samples with $[Mg] > 10^{19}$ cm$^{-3}$, indicating higher $R_{NR}$ compared with UID or less Mg-doped samples. For example, $I_{NBE}$ (ABE and UVL) of GaN:Mg with $[Mg]$ of $1 \times 10^{19}$, $4 \times 10^{19}$, and $7 \times 10^{19}$ cm$^{-3}$ were more than one, two, and three orders of magnitude lower than $I_{NBE}$ of UID or less Mg-doped samples, as shown in Figs. 3(d), 3(h), and 3(e), respectively. By using a simplified model described in Refs. 36 and 38, the upper bound of $N_{NR}$ in them can be estimated, as follows. When the average distance of NRCS is far longer than the exciton Bohr diameter ($2a_0$) and excitons do not move at zero carrier temperature, $\eta_{int}$ at 0 K is in principle approximately unity. However, when $N_{NR}$ exceeds a critical value, $\eta_{int}$ at 0 K becomes no longer unity, because an electron-hole pair or an exciton recombinates at the NRCS without diffusion or drift, as depicted in Fig. 4. The probability that a diffusion- or drift-free exciton at 0 K is not captured by NRCS and decays with the radiative recombination gives the maximum $\eta_{int}$ ($\eta_{int}^{max}$) of the emission, which is defined36,38,45) by $\eta_{int}^{max} = 1 - \frac{\pi a_0^2 N_{NR}}{E_{\text{exc}} 4}$. Here, $\eta_{int}^{max}$ is modeled under the assumption that every NRC within the exciton volume causes the nonradiative recombination. From this simple consideration, the assumption that $\eta_{int}$ is close to unity at 2–4 K is not absolutely incorrect when $N_{NR}$ is lower than approximately the middle of $10^{18}$ cm$^{-3}$ for GaN.36,38) Judging from Fig. 4, $N_{NR}$ of the present GaN: Mg of low $I_{NBE}$ is predicted to be between $10^{16}$ and $6 \times 10^{18}$ cm$^{-3}$. This concentration range is within the dynamic range of PAS for $V_{Ga}$35) and agrees with the concentration of unknown donors (or donor-type defects) suggested by Ref. 51 using Hall effect measurements on the...
epitaxial GaN:Mg films, which were grown on FS-GaN substrates manufactured by the same supplier. Such defects may act as NRCs, as the energy level of excitonic and free to acceptor transitions. The TRPL signals appear to be fitted using a multiple-exponential line shape function. In general, the appearance of multiple decay components at 300 K most likely reflects the fact that several portions of different NRCs, which are away beyond the diffusion length of minority carriers ($L_{\text{minority}}$), are simultaneously observed in the macroarea TRPL measurement. In the present case, however, the signals were sufficiently fitted using a bi-exponential function: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where $I(t)$ is the PL intensity at time $t$, and $A_1$ and $A_2$ are the pre-exponential constant and the lifetime, respectively, of the fast (slow) decay component. The results are shown by the gray lines superimposed on the experimental data. We note that in these analyses, only the bulk recombination was considered and the surface recombination was not taken into account, as excited carriers may not diffuse out to the surface because $L_{\text{minority}}$ is limited by the average distance between the NRCs, $1/\sqrt{N_{\text{NRC}}}$, which is approximately 30 nm in GaN:Mg with $N_{\text{NRC}}$ approximately a few times $10^{16}$ cm$^{-3}$, as discussed in the following paragraphs.

The values of $\tau_1$ obtained through the fitting, which mainly limits the cw PL intensity under low excitation conditions, is used as the representative $\tau_n$. The $\gamma_1$ values are plotted as a function of $[\text{Mg}]$ in Fig. 5(b). As is clearly seen, $\gamma_1$ for set B were approximately an order of magnitude longer than those of set A at the same $[\text{Mg}]$, and $[\text{Mg}]$ at which $\gamma_1$ started to decrease rapidly for set B (approximately $10^{19}$ cm$^{-3}$) was higher than that of A (approximately $10^{18}$ cm$^{-3}$). This result indicates higher $R_{\text{KR}}$ at the same $[\text{Mg}]$ for set A. As shown in Fig. 3(a), the NBE emission intensity of UID GaN at 300 K was more than three orders of magnitude lower than that at 10 K, and this thermal quenching is severer than the state-of-the-art UID GaN on GaN structures. Therefore, the sample set A appears to contain higher concentration NRCs or different species of NRCs having larger $\sigma_n$. As discussed
above, the sample set A likely contains higher concentration $V_N$. These results are consistent, because $V_N$ is one of the constituent elements of NRCs in both n-GaN (Refs. 32, 34, 36) and p-GaN (Refs. 37 and 39). Nevertheless, the decrease in $I_{\text{NBE}}$ at 10 K and $\gamma$ at 300 K simultaneously occurred for high [Mg] samples.

The $S$ parameters of the GaN:Mg films with [Mg] less than $5 \times 10^{18}$ cm$^{-3}$ were almost equal to the characteristic $S$ for the annihilation of $e^+$ and $e^-$ in DF states ($S_{\text{DF}}$) being 0.440. However, $S$ increased to approximately 0.442–0.443 for [Mg] higher than $5 \times 10^{18}$ cm$^{-3}$, indicating the increased defect concentration. By using the PAS technique, Ref. 27 have studied the vacancy-type defects in GaN:Mg homoepitaxial films grown using MOVPE by supplier A. They have concluded that the GaN:Mg film with [Mg] $= 4 \times 10^{19}$ cm$^{-3}$ contained multiple vacancies such as $V_{\text{Ga}}(V_N)_{2}$ [or $V_{\text{Ga}}(V_N)_{3}]$ before and after thermal annealing. From $S$ parameters, the concentrations of $V_{\text{Ga}}(V_N)_{2}$ [or $V_{\text{Ga}}(V_N)_{3}]$ in the present GaN:Mg films of [Mg] $= 5 \times 10^{18}$, $1 \times 10^{19}$, and $4 \times 10^{19}$ are estimated at approximately 7.0 $\times 10^{16}$, 7.0 $\times 10^{15}$, and $2.3 \times 10^{16}$ cm$^{-3}$, respectively. Because the decrease in $\gamma_{\text{N}}$ synchronized with the increase in $[V_{\text{Ga}}(V_N)_{2}]$, we attribute $V_{\text{Ga}}(V_N)_{2}$ to the origin of major NRCs in the homoepitaxial p-GaN:Mg films.

The relationship between $\tau_{PL}$ at 300 K and $N_{\text{NRC}}$ of GaN: Mg epilayers is shown by closed squares in Fig. 6, where the right y-axis shows corresponding $\eta_{\text{NRC}}$ using $\eta_{\text{R}} = 40$ ns. In Fig. 6, four ideal curves are drawn for the cases with $\sigma_n$ ranging from $1 \times 10^{12}$ to $1 \times 10^{15}$ cm$^{-3}$ using the relationship $\tau_{PL} = \Gamma^+ + \sigma_n \cdot \tau_{NRC}$, where $\tau_{NRC} = 2.6 \times 10^7$ cm s$^{-1}$ and the electron effective mass $m_e^* = 0.20 m_0$ ($m_0$ is a free electron mass). This relationship predicts that $\tau_{PL}$-NRC shows a straight line under low excitation and high $N_{\text{NRC}}$ conditions, where $\Gamma^+$ dominates $\tau_{PL}$. As shown, the data points are scattered around the lines for $\sigma_n = 10^{13}$ and $10^{12}$ cm$^{-3}$. This large error likely originates from two reasons. One is the fact that $[V_{\text{Ga}}(V_N)_{2}]$ are close to the detection limit of PAS being $10^{15}$ cm$^{-3}$, where the change in $S$ with the change in corresponding $N_{\text{NRC}}$ ($\Gamma^+$) is much smaller than that at the middle of the dynamic range. Another is that set A contains another type of defect. Taking the data for sample set B, $\sigma_n$ of $V_{\text{Ga}}(V_N)_{2}$ is determined at the middle of $10^{13}$ cm$^{-3}$, which is approximately four times larger than $\sigma_n$ of $V_{\text{Ga}}(V_N)_{2}$ in n-GaN being $7 \times 10^{14}$ cm$^{-3}$ (Refs. 36 and 38). Combined with the large $\eta_{\text{N}}$, $\gamma_{\text{N}}$ in p-GaN:Mg becomes much smaller than that in n-GaN.

3.2. Mg-implanted Ga-polar GaN (500-nm-deep box-type profiles)

The Mg implantation drastically modified the electronic properties of GaN, which is characterized by the appearance of undiminishable GL band, as follows. Changes in the PL spectra of I/I GaN:Mg are summarized as functions of $T_a$ (column) and [Mg] (row) using a matrix in Fig. 7. In each panel, PL spectra measured at 10 and 300 K are shown at the top and bottom, respectively. The top traces in the right edge column of Fig. 7, namely Figs. 7(d), 7(h), and 7(l), show the low-temperature PL spectra of I/I GaN:Mg for [Mg] = $1 \times 10^{17}$, $1 \times 10^{18}$, and $1 \times 10^{19}$ cm$^{-3}$, respectively, after PIA at 1300 °C. All samples exhibited the UVL band, implying the formation of $Mg_{Ga}$ acceptors. However, even at 10 K, the absolute intensities of ABEs and UVL were approximately two orders of magnitude lower than those of GaN:Mg epilayers of comparable [Mg] shown in Figs. 3(b)–3(d). At the same time, the GL band, which has not been found in UID or Mg-doped GaN epilayers, appeared in all I/I GaN:Mg [Figs. 7(a)–7(l)] and eventually GL became the dominant emission in the spectra of the samples with [Mg] of $1 \times 10^{19}$ cm$^{-3}$, as shown in the topmost row of Fig. 7, namely Fig. 7(i). These results indicate that I/I of Mg generates NRCs and simultaneously increases the concentration of the point defects relevant to GL. Because these two major change occurred simultaneously by I/I, the NRCs and GL most likely have a common constituent element, namely $V_N$, of which concentration $[V_N]$ is sufficiently low in most of epitaxial GaN:Mg.

Reference 28 examined these samples using PAS measurement and found that I/I of Mg at room temperature generated a very high concentration ($V_{\text{Ga}}(V_N)_{N}$) and that they agglomerated into ($V_{\text{Ga}}(V_N)_{N}$) clusters during PIA, although their concentration, ($[V_{\text{Ga}}(V_N)_{N}]$), could be decreased by increasing the PIA temperature up to $T_a = 1300 \, ^\circ C$. The $S$ parameters of I/I GaN: Mg after PIA (0.46–0.49) were commonly larger than that of epitaxial GaN:Mg of [Mg] = $4 \times 10^{19}$ cm$^{-3}$ (0.449) or $S_{\text{free}}$ (0.440). Accordingly, the present I/I GaN:Mg samples contain high concentrations of ($V_{\text{Ga}}(V_N)_{N}$) clusters and postron-sensitive NRCs. Because ($V_{\text{Ga}}(V_N)_{N}$) defects were quite recently assigned to the major SRH-type NRCs in the (000)1 N-polar GaN:Mg (Refs. 16 and 21) formed by the sequential shallow I/I of Mg and H, ($V_{\text{Ga}}(V_N)_{N}$) likely act as NRCs in these (0001) Ga-polar editions in Fig. 7.

The room-temperature PL spectra of epitaxial and I/I GaN: Mg also showed clear differences, as shown by the bottom lines in Figs. 3 and 7. In principle, I/I GaN:Mg did not exhibit the NBE or UVL peak, as shown in Fig. 7, except for the detectable NBE peaks in Figs. 7(b) and 7(c) for the lowest [Mg] sample. Such low quantum efficiencies of the NBE

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**Fig. 6.** (Color online) PL lifetime $\tau_{PL}$ and corresponding $\eta_{\text{NRC}}$ of the NBE emission in p-type GaN: Mg at 300 K as a function of $N_{\text{NRC}}$. The major NRCs are $V_{\text{Ga}}(V_N)_{2}$ in p-GaN: Mg epilayers and $V_{\text{Ga}}(V_N)_{3}$ in I/I p-GaN: Mg. The experimental data for the epitaxial p-GaN: Mg are shown by closed squares (red for the supplier A and blue for the supplier B online) and those for the 100-nm-deep N-polar I/I-GaN: Mg ($[\text{Mg}]$ samples. The room-temperature PL spectra of epitaxial and I/I GaN: Mg for [Mg] less than $10^{19}$ cm$^{-3}$ are shown by closed circles. Four ideal $\tau_{PL}$-$N_{\text{NRC}}$ curves are drawn for $\sigma_n$ ranging from $1 \times 10^{12}$ to $1 \times 10^{15}$ cm$^{-3}$ as a guide to the eye. As the temporal resolution of our TRPL system is better than 1 ps and the dynamic range of the present PAS measurement is between the middles of $10^{15}$ and $10^{18}$ cm$^{-3}$, the data points in the shaded zone are reliable. All samples appear to have nearly similar parameters, the concentrations of $V_{\text{Ga}}(V_N)_{2}$ [$V_{\text{Ga}}(V_N)_{3}$] being the middle of $10^{16}$ and $10^{19}$ cm$^{-3}$, as shown by the broken line. [Modified with permission from Ref. 39, Appl. Phys. Lett. 113, 191901 (2018). Copyright 2018 AIP Publishing LLC].
emission, UVL, and BL are caused by high $N_{NRC}$. The dominance of the GL band at 300 K in Fig. 7(l) is, therefore, the result of the introduction of VN by Mg I/I.

For the same Mg dose, the NBE and UVL intensities at 10 K were increased by increasing $T_a$, implying that high $T_a$ annealing is effective in decreasing $N_{NRC}$. Then, the increase in GL intensity with increasing $T_a$ in Figs. 7(i)–7(l) is not due to the increase in $[V_N]$ but to the increased capture of carriers by $(V_{Ga})_3(VN)_3$ owing to the reduced $N_{NRC}$. Nonetheless, the NBE emission intensity at 300 K of the sample with $[Mg] = 1 \times 10^{17} \text{cm}^{-3}$ was decreased by the increase in $T_a$ to 1300 °C, presumably because of the increase in $[V_N]$ by N out-diffusion from the surface and/or the downshift of $E_F$ by the activation of Mg. Consequently, the overall I/I process, including PL, must be optimized to decrease $[V_N]$ and $(V_{Ga})_3(VN)_3$ for the reproducible production of p-type conductivity.

### 3.3. Sequentially Mg and H implanted N-polar GaN (100-nm-deep box-type profiles)

PL spectra of the control GaN:Mg epilayer annealed at 850 °C, 710-nm-deep Ga- and N-polar I/I-GaN:Mg annealed at 1230 °C, and 100-nm-deep Ga- and N-polar I/I-GaN:Mg annealed at 1230 °C are shown in Figs. 8(a)–8(e), respectively. The $[Mg]$ values were commonly $1 \times 10^{19} \text{cm}^{-3}$. In Figs. 8(f)–8(j), the PL spectra of as-implanted and annealed 100-nm-deep N-polar I/I-GaN:Mg of $T_a = 800$, 1000, 1100, and 1260 °C are shown, respectively. In each panel, PL spectra measured at 10 and 300 K are shown at the top and bottom, respectively. As shown in Fig. 8(a), the Ga-polar GaN:Mg epilayer after annealing exhibited the UVL band and ABE peak at 10 K, both of which are associated with MgGa acceptors.22–24,50 The emissions from deep energy states such as GL or RL were absent. These spectral features agree with those shown in Fig. 3(d). The 710-nm-deep Ga- and N-polar I/I-GaN:Mg also exhibited the UVL band at 10 K, as shown in Figs. 8(b) and 8(c), respectively, implying the formation of MgGa acceptors.22–24,50 However, their intensities were three orders of magnitude lower than the epilayer [Figs. 3(d) and 8(a)]. Moreover, the distinct GL band peculiar to I/I GaN:Mg (Refs. 21 and 26) was dominant and the RL band with almost equal intensity as UVL was found in both spectra. In contrast, the 100-nm-deep Ga- and N-polar I/I-GaN:Mg exhibited a distinct UVL band at 10 K, of which intensities were approximately one and two orders of magnitude higher than the 710-nm-deep ones, as shown in Figs. 8(d) and 8(e), respectively. Moreover, the peak at 10 K was much higher in the 100-nm-deep samples, where both GL and RL were significantly suppressed. Therefore, the depth of I/I, i.e., total doses and energies used, seriously affected PL intensities.21 To form constant $[Mg]$ and $[H]$ profiles, higher total doses and a greater number of times of I/I with higher energies are required for deeper profile samples, meaning that the samples suffer from severer I/I damage.21

At 300 K, the dominant PL peak of the control GaN:Mg epilayer was the BL band, as shown in Fig. 8(a). Although the 710-nm-deep Ga- and N-polar I/I-GaN:Mg did not exhibit any NBE emissions at 300 K, as shown in Figs. 8(b) and 8(c), respectively, the 100-nm-deep samples did, as shown in Figs. 8(d) and 8(e). These results again indicate lower $N_{NRC}$ in the 100-nm-deep samples. Because the NBE emission intensity at 300 K of the 100-nm-deep N-polar I/I-GaN:Mg [Fig. 8(e)] was an order of magnitude higher than the Ga-polar edition [Fig. 8(d)], $N_{NRC}$ in the N-polar one is likely lower than the Ga-polar one, provided that the major NRCs in both samples have a common origin. Reference 39 carried out PAS analyses of the present samples and concluded from the $S$-$W$ relationship that major defect species in the N-polar I/I-GaN:Mg after PIA at $T_a = 1000$ °C was the same as that in the Ga-polar one.28
Mg. The Ga-polar epilayer displayed in panel (a) was annealed at 850 °C for 5 min in a N2 ambient. The [Mg] values were (a) 1.5 × 1019 cm−3, (i) 1100 °C, and (j) 1260 °C. The [Mg] values were (a) 1.5 × 1019 cm−3 and (b)−(j) 1.0 × 1019 cm−3. All samples were fabricated on FS-GaN substrates. The PL intensity (γ) axis has a unit of count per second (cps), and all spectra can be quantitatively compared. [Reproduced with permission from Ref. 39, Appl. Phys. Lett. 113, 191901 (2018). Copyright 2018 AIP Publishing LLC].

![Fig. 8.](PROGRESS REVIEW)

Fig. 8. (Color online) Steady-state PL spectra at 10 K (top traces) and 300 K (bottom traces) of (a) Ga-polar GaN:Mg epilayer, 710-nm-deep (b) Ga-polar and (c) N-polar, and 100-nm-deep (d) Ga-polar and (e) N-polar I/I-GaN:Mg annealed at T4 = 1230 °C. (e)−(j) PL spectra of the 100-nm-deep N-polar I/I-GaN:Mg. The Ga-polar epilayer displayed in panel (a) was annealed at 850 °C for 5 min in a N2 ambient. The T4 values were (e) 1230 °C, (g) 800 °C, (h) 1000 °C, (i) 1100 °C, and (j) 1260 °C. The [Mg] values were (a) 1.5 × 1019 cm−3 and (b)−(j) 1.0 × 1019 cm−3. All samples were fabricated on FS-GaN substrates. The PL intensity (γ) axis has a unit of count per second (cps), and all spectra can be quantitatively compared. (Reproduced with permission from Ref. 39, Appl. Phys. Lett. 113, 191901 (2018). Copyright 2018 AIP Publishing LLC).
analyses of the present samples and concluded that the major defect species is \((\text{VGa})_3(\text{VN})_3\). By comparing the measured and theoretically calculated\(^{27,28}\) \(S\) parameters, \([\text{VGa}]/[\text{VN}]\) in the 100-nm-deep N-polar I/I-GaN:Mg annealed at 800, 1000, 1100, and 1230 °C were estimated at a few times \(10^{16}\) cm\(^{-3}\) and decreased with increasing \(T_a\). For comparison, the signal for the 100-nm-deep Ga-polar I/I-GaN:Mg annealed at \(T_a = 1230\) °C is shown. The spectral integration was carried out between 3.2 and 3.6 eV, in order to cover all NBE emissions such as excitation and free to acceptor transitions. The signal denoted by “System” indicates the overall system response. The decay curves were fitted using a bi-exponential line shape function, and the results are shown by gray lines superimposed on the experimental data. (b) Fast and slow decay components \((\tau_f\) and \(\tau_s\), respectively) as a function of \(T_a\). (c) Fraction of the time-integrated PL intensities arising from the slow decay component, \(\tau_f/\tau_f + \tau_s\), as a function of \(T_a\). Closed and open legends in (b) and (c) represent the data for the N- and Ga-polar I/I-GaN:Mg, respectively. [Reproduced with permission from Ref. 39, Appl. Phys. Lett. 113, 191901 (2018). Copyright 2018 AIP Publishing LLC.]

**4. Conclusion**

Current knowledge on the origins and dynamic properties of the major intrinsic NRCs in the epitaxial and ion-implanted p-type GaN:Mg fabricated on FS-GaN substrates are summarized. The results of complementary TRPL and PAS measurements indicate that the major intrinsic NRCs are the clusters of \(\text{VGa}\) and \(\text{VN}\), namely \(\text{VGa}^*\) and \(\text{VN}^*\) in the epitaxial p-GaN:Mg and \(\text{VGa}^*\) and \(\text{VN}^*\) in the I/I p-GaN:Mg after appropriate PIA. Different from the case of 4H-SiC, atomic structures of the major intrinsic NRCs in the p-type GaN:Mg epilayer and n-type GaN are different: \(\text{VGa}^*\) and \(\text{VN}^*\) in the former and \(\text{VGa}^*\) and \(\text{VN}^*\) in the latter. The minimum \(\tau_p\) values of \(\text{VGa}^*\) and \(\text{VN}^*\) are estimated commonly at the middle of \(10^{-13}\) cm\(^2\) at 300 K, which is approximately four times larger than \(\tau_p\) of \(\text{VGa}^*\) in n-GaN being \(7 \times 10^{-14}\) cm\(^2\). Although GaN:Mg layers formed by I/I deeper than 500 nm never exhibited the NBE, UVL, or BL emission at 300 K, those fabricated by the shallow (≈100 nm) and sequential Mg and H implantation followed by the capping-less high temperature PIA gave rise to the observation of the NBE and BL emissions at 300 K and p-type conductivity. As \(\tau_p\) of the best (0001) I/I-GaN:Mg \((\text{Mg}[\text{Mg}] = 1 \times 10^{19}\) cm\(^{-3}\)) that was annealed at \(T_a = 1230\) °C increased to 18 ps, which nearly agrees with typical \(\tau_p\) being 20 ps in (0001) Ga-polar p-GaN:Mg epilayers of the same [Mg], good performance vertically current-flowing GaN transistors using I/I p-GaN:Mg will appear in the market shortly.

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1) S. J. Pearton, J. C. Zolper, R. J. Shul, and F. Ren, J. Appl. Phys. 86, 1 (1999).
2) Y. Saitoh, K. Sumiyoshi, M. Okuda, T. Horii, T. Miyazaki, H. Shiomi, M. Ueno, K. Katayama, M. Kiyama, and T. Nakamura, Appl. Phys. Express 3, 081001 (2010).
3) J. Kolnik, I. H. Ojuzman, K. F. Brennan, R. Wang, P. P. Ruden, and Y. Wang, J. Appl. Phys. 78, 1033 (1995).
4) D. Shihata, R. Kajitani, M. Ogora, K. Tanaka, S. Tamura, T. Hatsuda, M. Ishida, and T. Ueda, IDDM Technical Digest, 2016, p. 248.
5) M. Kodama, M. Sugimoto, E. Hayashi, N. Soejima, O. Ishiguro, M. Kanechika, K. Itoh, H. Ueda, T. Uesugi, and T. Kachi, Appl. Phys. Express 1, 021104 (2008).
6) T. Oka, T. Ina, Y. Ueno, and J. Nishii, Appl. Phys. Express 8, 054101 (2015).
7) H. Amano et al., J. Phys. D: Appl. Phys. 51, 165001 (2018).
