

## Thermal annealing of GaN implanted with Be

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### Abstract

GaN samples were implanted with Be and annealed in different conditions in order to activate the shallow Be<sub>Ga</sub> acceptor. Low-temperature photoluminescence spectra were studied to find Be<sub>Ga</sub>-related defects in the implanted samples. A yellow band with a maximum at about 2.2 eV (the YL<sub>Be</sub> band) was observed in nearly all samples protected with an AlN cap during the annealing and in samples annealed under ultrahigh N<sub>2</sub> pressure. A green band with a maximum at 2.35 eV (the GL2 band), attributed to the nitrogen vacancy, was the dominant defect-related luminescence band in GaN samples annealed without a protective AlN layer. The ultraviolet luminescence (UVL<sub>Be</sub>) band with a maximum at 3.38 eV attributed to the shallow Be<sub>Ga</sub> acceptor with the ionization energy of 0.113 eV appeared in implanted samples only after annealing at high temperatures and ultrahigh N<sub>2</sub> pressure. This is the first observation of the UVL<sub>Be</sub> band in Be-implanted GaN, indicating successful activation of the Be<sub>Ga</sub> acceptor.

## INTRODUCTION

The production of high-quality *p*-type GaN by ion implantation remains a challenge. Currently, the only *p*-type dopant in GaN is Mg. However, relatively high ionization energy (0.22 eV) of the Mg<sub>Ga</sub> acceptor requires high doping concentrations to achieve *p*-type conductivity suitable for practical applications. It is expected that doping of wide-bandgap nitrides such as GaN,<sup>1,2,3,4,5</sup> AlN,<sup>6,7</sup> BN,<sup>8</sup> and their alloys with Be may produce high-conductivity *p*-type materials and cause a breakthrough in the development of bright UV emitters. First-principles calculations predict that Be<sub>Ga</sub> in GaN is a deep acceptor with the ionization energy  $E_A \approx 450\text{-}550$  meV.<sup>9,10</sup> However, photoluminescence (PL) studies provide strong evidence for the Be-related acceptor level at  $\sim 0.1$  eV above the valence band in Be-doped GaN.<sup>1,11,12,13,14,15,16</sup>

Recently, we showed that Be in GaN exhibits a shallow acceptor state at  $113 \pm 5$  meV above the valence band, which is responsible for a PL band (labeled UVL<sub>Be</sub>) with a sharp peak at 3.38 eV, followed by a series of LO phonon replicas.<sup>1</sup> The UVL<sub>Be</sub> band is often observed in Be-doped GaN layers grown by molecular beam epitaxy (MBE).<sup>1,11,12,14,15,16</sup> However, we are not aware of any work in which the UVL<sub>Be</sub> band was observed in GaN after implantation with Be. The reason may include the low mobility of Be in GaN and the low fraction of Be substituting for Ga atoms.<sup>17,18</sup>

Post-implantation annealing is necessary to remove crystal defects such as vacancies and vacancy complexes. For GaN, to recover from the ion implantation damage, the annealing temperature,  $T_{ann}$ , should be well above 1000 °C.<sup>19,20</sup> However, decomposition of GaN begins at  $T_{ann} \approx 900$  °C in N<sub>2</sub>, Ar, or He ambient under atmospheric pressure.<sup>21,22</sup> In H<sub>2</sub> ambient, the decomposition starts already at 800 °C.<sup>22</sup> Higher annealing temperatures can be achieved by

employing an AlN cap layer, yet the GaN decomposition is still observed at 1200 °C.<sup>23</sup> To resolve the problem, ultra-high-pressure-annealing (UHPA) of GaN has been recently proposed.<sup>24</sup> Sakurai *et al.*<sup>25</sup> demonstrated that cap-free annealing of Mg-implanted GaN under a nitrogen pressure of 1 GPa at  $T_{ann} = 1200 - 1480$  °C removes implantation-induced crystal damage and activates Mg acceptors without thermal decomposition of GaN. At such high temperatures, the diffusion of implanted species and other impurities may also be significant.<sup>25</sup>

There is limited research on the Be diffusion in GaN. Early studies demonstrated no significant diffusion of Be during rapid thermal annealing (RTA) at temperatures up to 1200 °C.<sup>26,27</sup> Koskelo *et al.*<sup>28</sup> investigated the Be diffusion at 850 and 950 °C by annealing for six days and 2.5 hours, respectively, under Ar-gas atmosphere after ion implantation of <sup>7</sup>Be and <sup>7</sup>Li ions. Jakiela *et al.*<sup>17</sup> studied the Be diffusion at temperatures between 1200 and 1400 °C under UHPA in nitrogen ambient during 15-30 min after <sup>9</sup>Be implantation to GaN with very low density of dislocations. They concluded that the Be diffusion occurs by two mechanisms: rapid interstitial and slow interstitial-substitutional diffusion. By combining the experimental data from these two works, we conclude that the diffusion coefficient  $D$  for Be in GaN varies with temperature as<sup>17,28</sup>

$$D = D_0 \exp\left(\frac{-E_A}{kT}\right). \quad (1)$$

with pre-exponential factor  $D_0 \approx 0.01$  and the activation energy  $E_A \approx 2.8$  eV.

In this work, we demonstrate that activation of the Be<sub>Ga</sub> acceptors in Be-implanted GaN can be successfully achieved by post-implantation annealing at high temperatures and ultra-high nitrogen pressure.

## I. EXPERIMENTAL DETAILS

Nominally undoped GaN layers were grown on sapphire and ammonothermal GaN (Am-GaN) substrates by halide vapor phase epitaxy (HVPE) (Table I). The samples were implanted at room temperature with different doses and energies of  $^9\text{Be}^+$  ions at a  $7^\circ$  tilt angle. Samples of series E were additionally implanted with  $^{14}\text{N}$ . After the implantation, the samples were annealed in different conditions. Samples of series A-D were cut into  $5\times 5$  mm squares and annealed in  $\text{N}_2$  ambient at temperatures from 950 to 1100 °C for 1-4 h, by RTA at 900-1225 °C for 1.5-2 min, or under ultrahigh  $\text{N}_2$  pressure (1 GPa) at temperatures from 1250 to 1400 °C. In some cases, a protective  $\sim 80$  nm-thick AlN cap layer was deposited onto the sample surface before the annealing. Samples of series E were annealed by the UHPA method at  $T_{ann} = 1250 - 1400$  °C without any protective layer.

**TABLE I.** Implantation parameters

Sample series	HVPE GaN thickness ( $\mu\text{m}$ )	Substrate	$^9\text{Be}$ energy (keV)	$^9\text{Be}$ dose ( $\text{cm}^{-2}$ )	$^{14}\text{N}$ energy (keV)	$^{14}\text{N}$ dose ( $\text{cm}^{-2}$ )	$[\text{Be}]^{\text{a)}$ ( $\text{cm}^{-3}$ )
A	5	Sapphire	40	$10^{12}$	-	-	$\sim 10^{16}$
B	5	Sapphire	40	$10^{13}$	-	-	$\sim 10^{17}$
C	5	Sapphire	180	$10^{13}$	-	-	$\sim 10^{16}$
D	5	Sapphire	40	$10^{14}$	-	-	$\sim 10^{18}$
E	50	Am-GaN	500	$2\times 10^{15}$	500	$2\times 10^{15}$	$\sim 10^{18}$

<sup>a)</sup> The concentration of Be in the near-surface 200 nm-thick layer estimated from SRIM simulations and SIMS measurements on selected samples

Steady-state PL was excited with a HeCd laser. Other details of PL experiments can be found elsewhere.<sup>29,30</sup> The as-measured PL spectra were corrected for the measurement system's spectral response, and PL intensity was additionally multiplied by  $\lambda^3$ , where  $\lambda$  is the light

wavelength, to present the PL spectra in units proportional to the number of emitted photons as a function of photon energy.<sup>29</sup> For selected samples, PL spectra were also measured before and after implantation (before any annealing experiments). The original HVPE GaN samples from Kyma showed typical for such material PL spectra with weak RL1, YL1, GL1, and UVL bands.<sup>30</sup> After ion implantation, the PL signal from samples of series B, C, and D dropped by at least three orders of magnitude, and no PL bands could be recognized. In samples implanted with the lowest Be dose (series A), the RL1, YL1, and UVL bands could be resolved with intensities by order of magnitude lower than in as-grown samples.

We assume that PL signal is collected from the depth of up to  $\sim 200$  nm, which is limited by significant light absorption at 325 nm and small charge carrier diffusion length in Be-implanted GaN samples. From the SRIM Monte Carlo simulations, the depth profile of Be is expected to have a maximum at 125, 500, and 1100 nm for Be ion energies of 40, 180, and 500 keV, respectively. The concentration of Be in the maximum is expected to be  $7 \times 10^{16}$ ,  $7 \times 10^{17}$ ,  $3.5 \times 10^{17}$ ,  $7 \times 10^{18}$ , and  $5 \times 10^{19}$  cm<sup>-3</sup> for samples from series A, B, C, D, E, respectively. For samples of Series E, the implantation profiles after annealing are expected to be similar to those in samples implanted with Be and annealed in similar conditions.<sup>17</sup> The depth profiles were also measured for selected samples using secondary ion mass spectrometry (SIMS). Only for samples of series D (with the implantation dose of  $10^{14}$  cm<sup>-2</sup>) the presence of Be with the concentration of  $1-5 \times 10^{18}$  cm<sup>-3</sup> in the near-surface region up to  $\sim 200$  nm could be reliably found. For other samples (series A-C), the concentration of Be was close to or below the detection limit ( $10^{16}$  -  $10^{17}$  cm<sup>-3</sup>). In the last column of Table I, a rough estimate (order of magnitude) for the concentration of Be in the near-surface 200 nm-thick layer is presented based on combined information from the SRIM simulations and SIMS measurements.

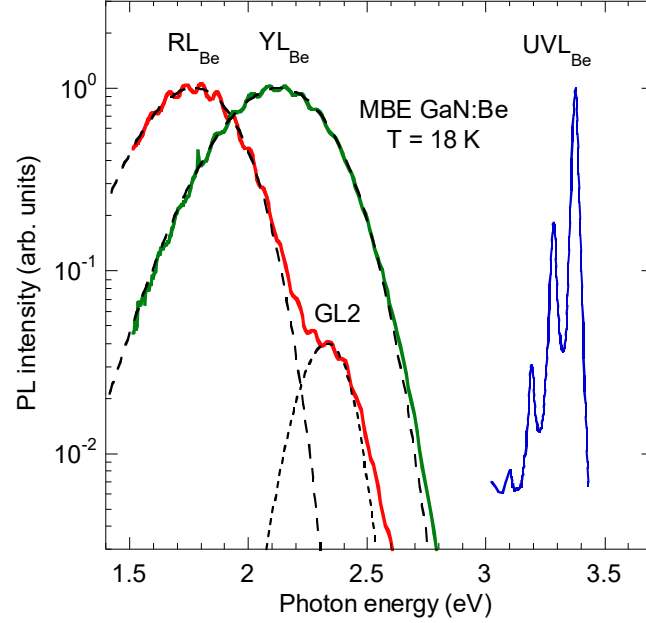
## II. RESULTS AND DISCUSSION

### A. Be-related PL bands in GaN:Be

PL bands from defects in GaN have reproducible features such as PL band shape, the temperature dependence of PL intensity, PL lifetime, electron- and hole-capture coefficients.<sup>30</sup> These features serve as fingerprints to identify defects or recognize the PL bands caused by unknown defects. In this section, we will briefly review the main features of defects observed in Be-doped GaN grown by MBE.<sup>1,31</sup>

Figure 1 shows the main defect-related PL bands in MBE GaN:Be samples.<sup>31</sup> At low temperature (18 K), three Be-related PL bands are observed: the UVL<sub>Be</sub> band with the main peak at 3.38 eV followed by several LO phonon replicas, the broad YL<sub>Be</sub> band with a maximum at 2.15 eV, and the RL<sub>Be</sub> band with a maximum at 1.8 eV (Fig. 1). In samples with the strong RL<sub>Be</sub> band, we also observed the GL2 band with a maximum at 2.33 eV. The shapes of the broad PL bands can be fitted with the following expression obtained in a one-dimensional configuration coordinate model.<sup>32</sup>

$$I^{PL}(\hbar) \propto \hbar \left[ -2S_e \left( \sqrt{\frac{E_0^* - \hbar}{d_{FC}^g}} \quad 1 \right)^2 \right]. \quad (2)$$



**Fig. 1.** Defect-related PL bands (normalized intensity) observed in Be-doped GaN. The PL spectra are from three GaN:Be samples grown by MBE. The dashed lines show the shapes of the  $RL_{Be}$ ,  $YL_{Be}$ , and  $GL2$  bands calculated by using Eq. (2) with parameters in Table II.

Here,  $S_e$  is the Huang-Rhys factor in the excited state of the defect,  $d_{FC}^g = E_0^* - \hbar$  is the Frank-Condon shift in the ground state,  $E_0^* = E_0 + 0.5\hbar$ ,  $E_0$  is the zero-phonon line (ZPL) energy,  $\hbar$  is the energy of the effective phonon mode in the excited state,  $\hbar$  and  $\hbar$  are the photon energy and position of the PL band maximum, respectively. The  $\Delta$  is a small shift of the PL band maximum due to sample-dependent reasons such as in-plane biaxial strain in thin GaN layers grown on sapphire substrates. According to Eq. (2), the shape of a PL band with a maximum at  $\hbar$  depends only on parameters  $S_e$  and  $d_{FC}^g$ . Table II presents these parameters for the broad PL bands in Be-doped GaN and updated parameters for other PL bands commonly observed in undoped GaN.

**TABLE II.** Main PL bands in Be-doped GaN (first two rows) and in undoped GaN, parameters defining the bands' positions and shapes, ZPL (when observed), and the charge transition level above the top of the valence band ( $E_A$ ).

PL band	Preliminary attribution	$\hbar$ (eV)	$S_e$	$E_0^*$ (eV)	ZPL (eV)	$E_A$ (eV)
RL <sub>Be</sub>	Be <sub>Ga</sub> V <sub>N</sub>	1.77	~20	~2.6	-	~0.9
YL <sub>Be</sub>	Be <sub>Ga</sub> complex	2.15	24	3.2	-	0.3
RL1	Cl-related?	1.73	9.5	2.3	-	~1.2
RL2	V <sub>N</sub> complex	1.72	~23	~2.5	-	~0.9
YL1	C <sub>N</sub>	2.17	7.8	2.67	2.59	0.916
YL3	Fe-related	2.07	6.2	2.41	2.38	1.130
GL1	Unknown	2.35	10.3	2.97	-	~0.5
GL2	V <sub>N</sub>	2.33	26.5	2.85	-	~0.45
BL1	Zn <sub>Ga</sub>	2.86	3.2	3.14	3.10	0.400
BL2	C <sub>N</sub> H <sub>i</sub>	3.0	4.6	3.38	3.33	0.150

The parameters of the YL<sub>Be</sub> band and the C<sub>N</sub>-related yellow band (labeled YL1) differ, although positions of their maxima coincide. The PL bands are also different in terms of other properties. The YL1 band in *n*-type GaN quenches at temperatures above 500 K due to thermal emission of holes from the  $-/0$  level of the C<sub>N</sub> acceptor at 0.9 eV above the valence band.<sup>33</sup> The quenching of the YL<sub>Be</sub> band in *n*-type GaN:Be begins at 200 K, and the activation energy of this quenching is 0.3 eV.<sup>31</sup> We preliminarily proposed that the Be<sub>Ga</sub>V<sub>N</sub>Be<sub>Ga</sub> complex with a ground state at ~1.5 eV and an excited state at 0.3 eV above the valence band is responsible for the YL<sub>Be</sub> band in MBE-grown GaN:Be.<sup>31</sup> Teisseyre *et al.* attributed the yellow band in bulk Be-doped GaN grown by the high-nitrogen-pressure-solution method to the Be<sub>Ga</sub>O<sub>N</sub> complex.<sup>34</sup> Note that the YL<sub>Be</sub>

band in the MBE GaN and yellow band in bulk GaN:Be are apparently caused by different defects.<sup>31</sup> In particular, the quenching of the yellow band in bulk GaN:Be begins only at  $T > 500$  K.<sup>35</sup>

The shape of the UVL<sub>Be</sub> band in GaN is unique. This defect has the smallest Huang-Rhys factor (the ratio of the first phonon replica intensity to the ZPL intensity) and the shallowest energy level ( $E_A = 113 \pm 5$  meV) among defects in GaN. We attribute this band to the shallow state of the Be<sub>Ga</sub> acceptor, while the deep state is not observed in PL experiments, possibly due to the low hole-capture cross-section.<sup>1</sup>

In MBE-grown GaN:Be samples studied in Refs. 1 and 31, the UVL<sub>Be</sub> and YL<sub>Be</sub> bands were the main defect-related bands, whereas the RL<sub>Be</sub> band was strong only in samples also containing the GL2 band (Fig. 1). The GL2 band can be easily recognized by a relatively narrow width, Gaussian shape, and exponential decay of PL after a laser pulse, with a characteristic lifetime of 250  $\mu$ s.<sup>32</sup> The GL2 and RL<sub>Be</sub> bands are attributed to the isolated nitrogen vacancy ( $V_N$ ) and its complex with Be<sub>Ga</sub>, respectively.<sup>31,32</sup> The Be<sub>Ga</sub> $V_N$  complex is a deep donor with the ground 0/+ level at about 2.5 eV below the conduction band and an excited state close to the conduction band. In time-resolved PL experiments, this band can be recognized by an exponential decay with the characteristic time of 2  $\mu$ s at  $T = 18$  K.<sup>31</sup> It may be difficult to distinguish the RL<sub>Be</sub> band in Be-doped GaN and the RL2 band in semi-insulating undoped GaN samples.<sup>36</sup> A detailed study of the  $V_N$ -related red PL bands in GaN will be presented elsewhere.<sup>37</sup> In contrast, the YL<sub>Be</sub> and UVL<sub>Be</sub> bands have specific properties that allow us to recognize them confidently.

As a result of ion implantation and post-implantation thermal annealing, various defects are created. The Be atoms may substitute for Ga, N, occupy interstitial positions, or form

complexes. We searched for the  $UVL_{Be}$  and  $YL_{Be}$  bands in PL spectra as signatures of the  $Be_{Ga}$  defects. In particular, the  $Be_{Ga}$ -related  $UVL_{Be}$  band has never been observed in GaN implanted with Be before, while this shallow acceptor state is often observed in Be-doped GaN grown by MBE.

## **B. Annealing in nitrogen under atmospheric pressure**

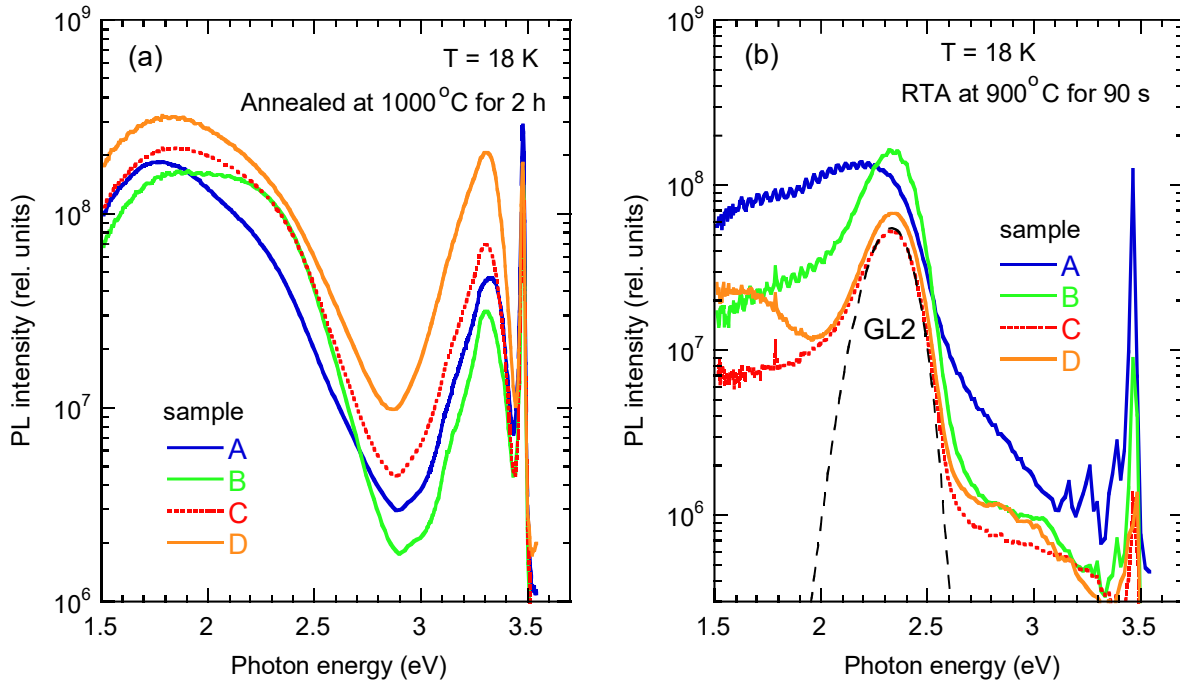
Low-temperature PL spectra from as-grown HVPE GaN layers on sapphire substrates contained intense excitonic lines and defect-related PL bands typical for this material: the RL1, YL1, BL1, and UVL bands (Table I). By using the approach described in Refs. 38 and 39, we estimated the concentrations of related defects as  $6 \times 10^{15}$ ,  $1.5 \times 10^{15}$ ,  $1.5 \times 10^{13}$ , and  $7 \times 10^{12} \text{ cm}^{-3}$ , respectively. A weak GL1 band can also be resolved in these PL spectra at high excitation intensities. After Be implantation, the PL from GaN samples became very weak, with total radiative efficiency lower than  $10^{-4}$ . The exciton emission was  $10^4$  times weaker than in material before implantation, and no familiar defect-related PL bands could be found.

Samples of series A-D, after Be implantation, were annealed under atmospheric pressure in  $N_2$  ambient at temperatures between 950 and 1100 °C in different conditions, including RTA and long annealing, with and without an 80-nm-thick AlN cap. The PL spectra were studied in detail for all these samples, and the main results are presented below.

### *1. Annealing of GaN with a bare surface*

In the first annealing experiments, samples from series A-D were annealed after Be ion implantation without AlN cap for two hours in  $N_2$  ambient at temperatures from 950 to 1100 °C with a step of 50 °C. We could not find the  $YL_{Be}$  and  $UVL_{Be}$  bands in these samples. Representative

PL spectra for  $T_{ann} = 1000$  °C are shown in Fig. 2a. In this and the following figures, PL intensities are presented in the same relative units.



**Fig. 2.** PL spectra from GaN samples implanted with Be and annealed without AlN cap. (a) Annealing in atmospheric-pressure  $N_2$  at 1000 °C for 2 hours. (b) RTA at 900 °C for 90 s. The GL2 band is caused by the isolated  $V_N$ . All the measurements were done in identical conditions.

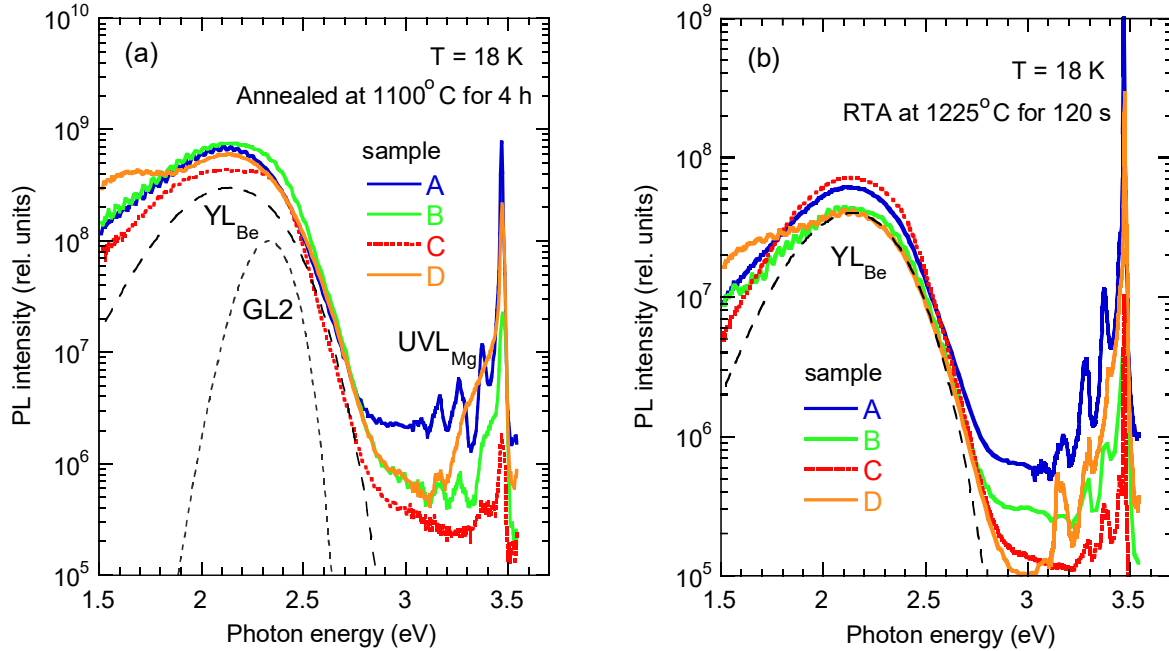
In addition to excitonic emission with a maximum at 3.47 eV (by a factor of 100 weaker than in the samples before the irradiation), a structureless band was observed in the UV region. This band markedly shifts with excitation intensity (from  $\sim 3.2$  to 3.4 eV with increasing excitation intensity,  $P_{exc}$ , from  $10^{-4}$  to 100 W/cm<sup>2</sup>). Although this band's position roughly matches the UVL<sub>Be</sub> band's position, no characteristic fine structure could be revealed. We attribute this band to diagonal transitions from the conduction band to the valence band in regions with large potential

fluctuations in semi-insulating material.<sup>30</sup> Another broad PL band at lower photon energies consists of at least two bands. The origin of the red band at  $\sim 1.8$  eV could not be established, whereas the band at  $\sim 2.35$  eV was identified as the GL2 band caused by the  $V_N$  defect.

Samples from series A-D without AlN cap were also annealed by RTA for 90 s in  $N_2$  at  $T_{ann} = 900$  °C. The GL2 band was the dominant defect-related PL band in these samples (Fig. 2b). We conclude that the  $V_N$  defects are formed abundantly at these temperatures when GaN is annealed without a protective cap layer. Note that the GL2 band is not observed in conductive  $n$ -type GaN. This is because the Fermi level in such samples is located above the  $0/+$  level of the  $V_N$ , and the capture of photogenerated holes by the neutral  $V_N$  is very inefficient.

## 2. Annealing of GaN with AlN cap

In the following experiments, 80-nm-thick AlN films were deposited on the samples from series A-D to prevent GaN decomposition. These samples were annealed at 1100 °C for 1 and 4 hours and alternatively at 1225 °C by RTA. Typical PL spectra from these samples are shown in Fig. 3. The  $YL_{Be}$  band was the dominant defect-related band in the samples annealed at relatively high temperatures with an AlN cap. The  $V_N$ -related GL2 band was observed in some samples. It could be better resolved at low excitation intensities and at temperatures close to 200 K when the  $YL_{Be}$  band is quenched. No  $UVL_{Be}$  band could be found in these samples. Rarely, a weak Mg-related UVL band ( $UVL_{Mg}$ ) with a maximum at  $\sim 3.27$  eV was observed in this spectral region (Fig. 3a).

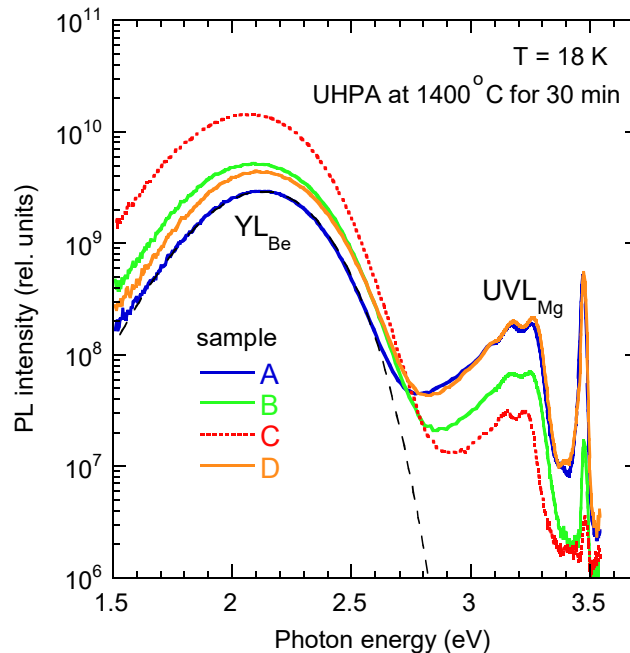


**Fig. 3.** PL spectra from GaN implanted with Be, covered with protective AlN cap, and annealed in  $N_2$  at atmospheric pressure. (a) Samples annealed at  $1100\text{ }^\circ\text{C}$  for 4 hours. (b) Samples annealed by RTA at  $1225\text{ }^\circ\text{C}$  for 120 s. The dashed lines show the shapes of the  $YL_{Be}$  and GL2 bands calculated using Eq. (2) with parameters given in Table II.

### C. Annealing under ultrahigh $N_2$ pressure

#### 1. Samples of series A-D treated by UHPA

The Be-implanted GaN samples of series A-D were also annealed at high temperatures (1250-1400  $^\circ\text{C}$ ) under ultrahigh  $N_2$  pressure to avoid the decomposition of GaN. Representative PL spectra for the highest annealing temperature are shown in Fig. 4. Similar trends were observed for all other  $T_{ann}$ .



**Fig. 4.** PL spectra from GaN samples implanted with Be and annealed under ultrahigh  $N_2$  pressure (1 GPa) at 1400 °C for 30 min.

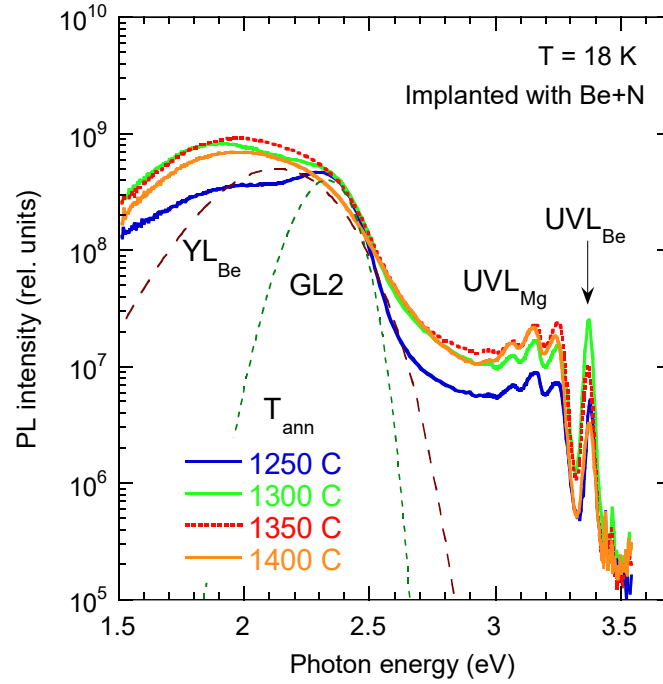
The  $YL_{Be}$  intensity significantly increased compared to the samples annealed at lower temperatures and atmospheric pressure (Fig. 3). The  $YL_{Be}$  band peak intensity of  $\sim 10^{10}$  in this and other figures roughly corresponds to the quantum efficiency close to unity according to our calibrations.<sup>30</sup> For samples implanted with the same  $Be^+$  ion energy (40 keV), we consistently observed a proportional decrease of the exciton emission intensity with the implantation dose increase and a monotonous increase of the  $YL_{Be}$  intensity (the increase could not be linearly proportional because its quantum efficiency approached unity). With increasing  $T_{ann}$  from 1250 to 1400 °C, for each series of samples in the group A-D, the  $YL_{Be}$  intensity monotonously increased (totally by a factor of 1.5-3). Since the  $YL_{Be}$  band is caused by  $Be_{Ga}$ -related defects,<sup>31,34</sup> the significant increase of its intensity indicates activation of the  $Be_{Ga}$  after UHPA.

Interestingly, the Mg-related  $UVL_{Mg}$  band appeared in the PL spectra of samples annealed using the UHPA method. We observed a relatively intense  $UVL_{Mg}$  band in all samples annealed by this method. The  $UVL_{Mg}$  band intensity monotonously increased with increasing  $T_{ann}$  for each implantation set (totally by about an order of magnitude for  $T_{ann}$  varied from 1250 to 1400 °C). The Mg likely originates from GaN powder covering the samples during UHPA. With increasing  $T_{ann}$ , diffusion of Mg to the Be-implanted samples increases. While the quantum efficiency of the  $YL_{Be}$  band approaches unity in some UHPA-treated samples, that of the  $UVL_{Mg}$  band remains below  $\sim 0.02$ , which corresponds to the concentrations of Mg lower than  $10^{15} \text{ cm}^{-3}$  (Ref. 39).

## 2. Samples of series E treated by UHPA

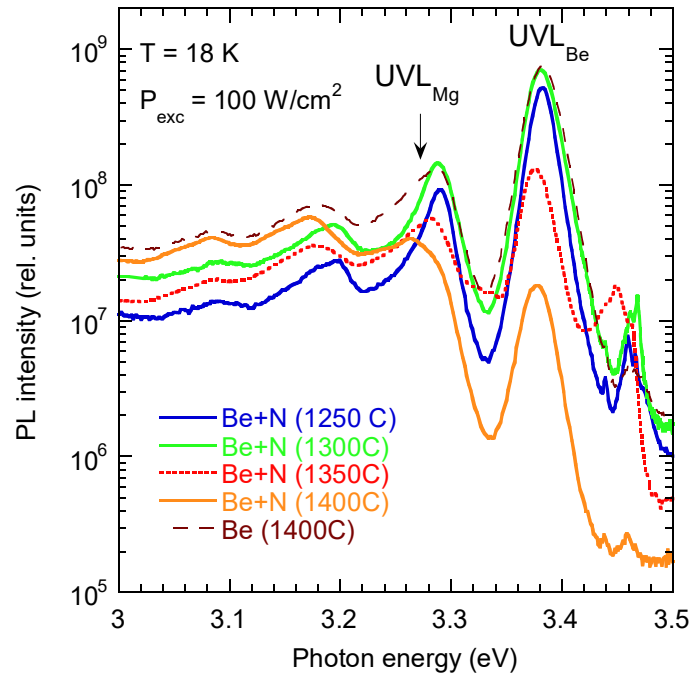
Samples of series E were co-implanted with Be and N. The purpose of the implantation with nitrogen ions was to reduce the formation of the  $V_N$ . It is known that sequential implantation of Mg and N ions into GaN improves the  $Mg_{Ga}$  acceptor activation and significantly decreases the contribution of the  $V_N$ -related GL2 band in the PL spectrum.<sup>40,41,42</sup> Note that similar effects have been observed for GaN implanted at high temperature with Mg and F.<sup>43</sup>

Representative PL spectra are shown in Fig. 5. In this sample set, the  $YL_{Be}$  band overlaps with a red PL band of unknown origin. The measurements of PL spectra in a wide range of temperatures revealed the  $V_N$ -related GL2 band only in samples annealed at 1250 and 1300 °C (in Fig. 5, the GL2 band contribution in the spectrum from the sample annealed at 1250 °C is shown with a dashed curve). Remarkably, the  $UVL_{Be}$  band was observed in all GaN samples co-implanted with Be and N. The highest intensity of this band was achieved in the sample annealed at 1300 °C (Fig. 5). One of the samples was implanted with only Be under the same conditions as other samples of series E and annealed by UHPA at 1400 °C. There was no significant difference in PL spectra between this sample and the sample co-implanted with Be and N and annealed at 1400 °C.



**Fig. 5.** PL spectra from GaN samples of series E co-implanted with Be and N and annealed under ultrahigh  $N_2$  pressure (1 GPa) for 30 min.  $P_{exc} = 0.005 \text{ W/cm}^2$ .

The relative contribution of the  $UVL_{Be}$  band to PL spectra increased with increasing excitation intensity because the broad bands at photon energies below 3 eV could be easily saturated, whereas the  $UVL_{Be}$  band intensity increases superlinearly with  $P_{exc}$ .<sup>31</sup> PL spectra in the UV region obtained with a focused HeCd laser beam ( $P_{exc} \approx 100 \text{ W/cm}^2$ ) are shown in Fig. 6. The main peak of the  $UVL_{Be}$  band at 3.38 eV is followed by LO phonon replicas at distances multiple of 92 meV. These replicas overlap with the main peak of the  $UVL_{Mg}$  band at 3.27 eV, also followed by LO phonon replicas. As can be seen from this figure, the relative intensity of the  $UVL_{Be}$  band decreases significantly in samples annealed at  $T_{ann} > 1300 \text{ }^\circ\text{C}$ . Interestingly, the intensity of this band in the sample implanted with only Be remains high for  $T_{ann} = 1400 \text{ }^\circ\text{C}$ .



**Fig. 6.** PL spectra from GaN samples of series E co-implanted with Be and N (one sample is implanted with Be only) and annealed under ultrahigh  $N_2$  pressure (1 GPa) for 30 min.  $P_{exc} \approx 100 \text{ W/cm}^2$ . The relative units in this figure cannot be compared to the relative units in Figs. 2-5 because conditions for collection PL were not the same for unfocused and focused laser beams.

This is the first observation of the  $Be_{Ga}$ -related  $UVL_{Be}$  band in GaN implanted with Be to the best of our knowledge. Previously, this band was observed only in Be-doped GaN. It is not clear why the  $UVL_{Be}$  band appeared in samples of series E but was not observed in samples of series A-D annealed in the same conditions by UHPA. The samples of series E were implanted with a higher dose and energy of Be ions (Table I). They are also expected to have much lower dislocation density because the HVPE layers were grown on bulk ammonothermal GaN templates as opposed to sapphire substrates for the series A-D. No electrical measurements have been conducted so far on the studied samples. However, the observation of the GL2 band indicates that the samples are

semi-insulating. Further studies will explore optimal implantation and annealing conditions to find a route for efficient *p*-type GaN.

### III. CONCLUSION

In MBE-grown GaN samples doped with Be, the PL spectrum contains the UVL<sub>Be</sub> band caused by the shallow Be<sub>Ga</sub> acceptor and the YL<sub>Be</sub> band caused by a Be-containing complex. We implanted Be into HVPE-grown GaN and annealed the implanted samples in different conditions. The YL<sub>Be</sub> band was observed in nearly all samples protected with an AlN cap during the annealing and in samples annealed under ultrahigh N<sub>2</sub> pressure. The UVL<sub>Be</sub> band was observed only after annealing at high temperatures and ultrahigh N<sub>2</sub> pressure. The ultra-high pressure annealing favors the formation of the Be<sub>Ga</sub> acceptors, and thus it is a promising route for activating beryllium implanted in GaN.

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### AUTHOR DECLARATIONS

#### Conflict of Interest

The authors have no conflicts to disclose.

## DATA AVAILABILITY

The data supporting this study's findings are available from the corresponding author upon reasonable request.

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