The Mg Solid Solution for the P-type Activation of GaN Thin Films Grown by Metal-Organic Chemical Vapor Deposition

Keunjoo Kim*
Department of Semiconductor Technology, Ulsan College, Ulsan 680-749, R. O. Korea

Sang Jo Chung
Applied Technology Corporation, Hwasung, 445-913, R. O. Korea

E-mail : kkim@mail.ulsan-c.ac.kr

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GaN films were grown for various Mg doping concentrations in metal-organic chemical vapor deposition. Below the Mg concentration of $10^{19}/cm^3$, the thermally annealed sample shows the compensated phase to n-type GaN in Hall measurement. In the Mg concentration of $4\times10^{19}/cm^3$ corresponding to the hole carrier concentration of $2.6\times10^{19}/cm^3$, there exists a photoluminescence center of the donor and the acceptor pair transition of the 3.28-eV band. This center is correlated with the defects for a shallow donor of the V_{Ga} and for an acceptor of Mg_{Ga}. The acceptor level shows the binding energy of 0.2-0.25 eV, which was observed by the photon energy of the photocurrent signal of 3.02-3.31 eV. Above the Mg concentration of $4\times10^{19}/cm^3$, both the Mg doping level and Mg concentration were saturated and there is a photoluminescence center of a deep donor and an acceptor pair transition of the 2.76-eV blue band.

Keywords : Mg doped GaN, MOCVD, photoluminescence, photocurrent, Mg solid solution

1. INTRODUCTION

GaN-based semiconductor technology has been extensively developed for wide band gap engineering such as blue light opto-electronic and high power electronic devices [1,2]. The progress in the research focused on the device applications, which have caused commercial devices to be available. Two technical issues, such as the introduction of the low-temperature buffer layer on large geometrical mismatch at the interface between sapphire substrate and GaN film [1,3], and the successful p-type conduction [4,5] have enhanced the progress.

In order to achieve the p-type activation, Mg doped GaN film has been processed after the epitaxial growth [4,5]. The Mg doped is highly resistive to an as-grown GaN epilayer by metal-organic chemical vapor deposition (MOCVD) due to the compensating role of hydrogen as a donor [5,6]. The thermal annealing provides the p-type activation of Mg dopant in GaN films and possibly dissociates an Mg-H complex. The Mg acceptor in p-type GaN films has the thermal ionization energy of about 160 meV in Hall measurement[7]. The time-resolved photoluminescence (PL) provided an optical ionization energy of about 290 meV for the shallow Mg acceptors and 550 meV for doping induced deep center [8]. The photoconductivity spectra from the photocurrent (PC) measurement [9], show the level at 0.255 eV above the valence band edge. In spite of many elaborated experiments, the difficulty in the achievement of high doping is still uncertain.

In this work, we carried out the epitaxial growths of Mg-doped GaN films by MOCVD for various Mg source flow rates and thermally annealed the samples in order to p-type activation. As increasing the Mg doping level, the dislocation-correlated Mg center can be activated and shifted from a 3.21-eV band to a 2.76-eV band. PL spectra are very sensitive to Mg doping concentration and the dislocation-associated PL center peaked at 3.01 eV showing the strong enhancement for a critical hole carrier concentration of $2.6\times10^{17}/cm^3$. The photocurrent measurement also shows the two-types of donors activated at the energies of 142 and 29 meV.

2. EXPERIMENTAL

The p-type epitaxial films were grown by MOCVD on sapphire substrates with 40-nm GaN buffer layers. The nucleation layer at a low temperature of 520°C was introduced for geometrical bonding at the surface of sapphire due to the large lattice mismatch between sapphire (Al_2O_3) substrate and GaN epitaxial film. The subsequent high-temperature epitaxial growth of Mg doped GaN film was performed by adding the Mg doping source of Cp_2Mg into the main stream of hydrogen, ammonia and trimethylgallium (TMGa). Several samples were grown for various Mg source flow rates of 0, 0.5, 1(sample A), 3(sample B), 5(sample C), 2 nmole/min (sample D). These samples were thermally annealed in a vacuum chamber at a temperature of 850°C for 10 min.

The PL spectra were measured by using the 325 nm line excitation of an He-Cd laser. The luminescence was analyzed by a 250-mm grating monochrometer and detected by a photon counter. The low-temperature PL measurement at 30 K was performed in the pumping system of helium gas. The SIMS measurement at surfaces and the Hall effect measurement at room temperature were performed on the annealed samples. The room-temperature PC spectra were measured on the as-grown and annealed sample C under a dc bias of 1.5 V and Halogen lamp illumination. The photo-excited electron in the conduction band tail can be measured for the photocurrent without dark current mixing under the dc bias.

3. RESULTS AND DISCUSSION

Fig. 1 shows Hall effect measurements on hole carrier concentrations and mobility for Mg-doped GaN samples for various flow rates of Cp_2Mg. The undoped sample and the very low Mg-doped sample with a flow rate 0.5 nmole / min, corresponding to the Mg concentration of $7\times10^{18}/cm^3$ exhibit the n-type electrical behavior. As the flow rate of Mg source is increased, the p-type conversion occurs. For the Mg source flow rates in the range of 1~3 nmole/min, the Mg concentration, the hole carrier concentration and the mobility can be located in the range of about $2\sim20\times10^{19}/cm^3$, $1\sim6\times10^{17}/cm^3$ and around 8~15 cm^2/V-sec, respectively.

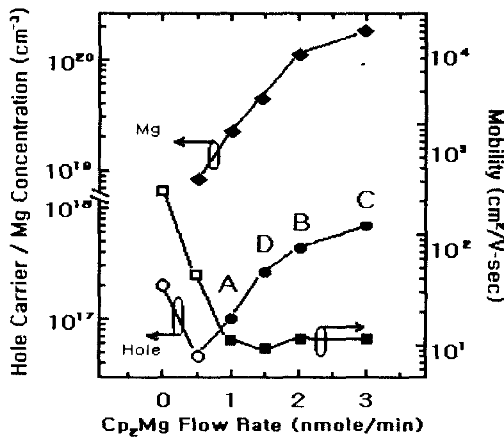

Fig. 1. The Hall effect measurements on the hole carrier concentrations and the mobility for Mg-doped GaN samples for various flow rates of Cp_2Mg. The open and solid symbols indicate the n- and p-type GaN films, respectively.

The very low percentage of the Mg solid solution rate in GaN film results in the low activation electrically and introduces the transparent p-contact layer [10]. The hole concentration of the order of $10^{17}/cm^3$ corresponds to the Mg concentration of the order of $10^{19}/cm^3$. The introduced Mg atoms can be preferably occupied to Ga sites by accompanying the atomic hydrogen and reduces the native Ga vacancy. In spite of the similar electrical property for various samples, the optical property is quite different.

Fig. 2 shows room-temperature PL spectra for various Mg-doped GaN samples with hole carrier (Mg) concentrations of $2.1\times10^{17}/cm^3$ ($2\times10^{19}/cm^3$) for sample A, $3.8\times10^{17}/cm^3$ ($1.2\times10^{20}/cm^3$) for sample B and $6.5\times10^{17}/cm^3$ ($2.0\times10^{20}/cm^3$) for sample C, respectively. With the increase of the Mg flow rate, the neutral donor-bound excitonic level of 3.42 eV disappears and the blue emission PL band around 2.75 eV becomes dominant.

The sample A shows four small PL peaks appeared in the spectral range of 3.1-3.4 eV. The peaks P1 correspond to a band-edge emission of 3.389 eV and the P2 is the phonon replica of P1 with an energy difference of about 130 meV. The peaks P3 and P4 are donor-acceptor transitions of 3.195 and 3.07 eV, respectively. The sample B shows a PL spectrum peaked at 2.75 eV with interference

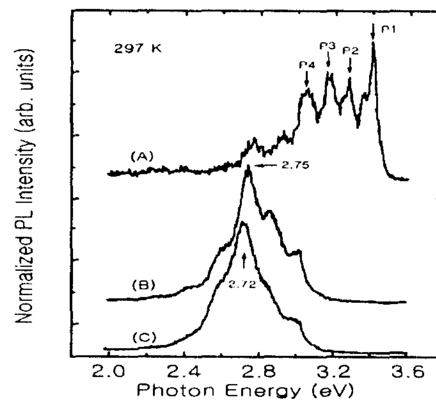

Fig. 2. The room-temperature PL spectra for various annealed samples of Mg-doped GaN film. As increasing Mg doping level, there is a certain transition of PL centers to blue band of 2.76 eV.

fringes. The sample C also shows a PL spectrum peaked at 2.72 eV with interference fringes. The effective p-type Sample A shows shallow donor levels below the conduction band. The shallow donor-related PL bands above 3.01 eV from valence band can be made to disappear by increasing the Mg doping concentration as shown in Fig. 2(B) and (C). This indicates that the native Ga vacancy can not be completely replaced by Mg atoms in a low doping rate. The samples B and C with relatively high doping rates show the stable room temperature PL at 2.72-eV band indicating that donor levels are deep states from the conduction band. The deep donor-acceptor pair (DAP) transition at 2.72 eV is associated with high doping rates, which may lower the crystalline quality and lead to the effect of dislocation into Mg-related defect center.

According to Kaufmann *et al.* [11], this blue emission comes from the DAP transition between Mg_{Ga}-V_N deep donor and Mg_{Ga} acceptor with a Frank-Condon shift of 180 meV. Furthermore, Colton and Yu [12] provided a DAP transition model of a mobility gap in the band tails which gives rise to a bottleneck in the relaxation. They suggested a PL transition from localized states to delocalized states occurring within the Urbach tail at the blue emission at the energy of 2.8 eV.

Fig. 3 shows PL spectra for Mg-doped GaN samples A, B and C at a low temperature of 30 K. To compare with the room-temperature PL in Fig. 2, sample A shows a main PL band peaked at the energy of 3.19 eV with a minor peak at 3.28 eV. For sample B, PL bands of 2.81 and 3.01 eV are dominant with a shoulder of 2.7 eV. Sample C shows similar PL spectra on 2.76 and 3.01 eV with the sample (B). While increasing the Mg doping rate, a blue emission band peaked at 2.76 eV becoming dominant rather than 3.01 eV and a PL band of 3.19 eV is quenched and a broad PL band around 2.76 eV becomes dominant. This indicates the PL property is highly sensitive to the Mg doping concentration and the corresponding Mg related structural defect is associated with the formation of a broad PL band below the 3.01 eV PL center. Therefore, the formation of an N vacancy by increasing the Mg doping concentration induces a structural defect formation such as a misfit stacking fault or pyramidal inclusion [13].

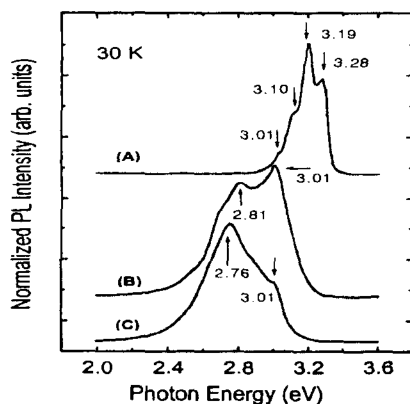

Fig. 3. PL spectra measured at the low temperature of 30 K for various annealed samples of Mg-doped GaN films.

Generally, the very broad PL band is related to the structural defect such as a dislocation or island, but not to a point defect. Furthermore, the dislocation effect on the PL shift is very inert to the temperature dependence on the PL measurement, indicating the dislocation-related PL could not be changed by the thermal annealing. In very low doped sample, the blue PL band can be established and the Mg substitution on the Ga site can form a very tiny strain and this developed a nucleation of an island inclusion or a Mg-related dislocation.

In order to understand the critical doping level for the shift of PL band transitions, sample D with Mg source flow rate of 1.5 nmole/min was prepared. The hole carrier concentration for the annealed sample was measured to a value of $2.6\times10^{17}/cm^3$, corresponding to the Mg doping concentration of $4.0\times10^{19}/cm^3$. As shown in Fig. 4(A), the room temperature PL band in the as-grown sample of Mg doped GaN is formed at an energy peak of 2.71 eV. This is quite different to Fig. 2(A), where the annealed sample shows a tiny blue band of 2.78 eV. However, as shown in Fig. 4(B), the annealed sample shows a blue band of 2.63 eV without the satellites of PL bands above 3.01 eV.

This phenomenon indicates that at a critical Mg doping concentration, the multiple Mg related point defects coalesce and formulate structural defects. These multiple point defects can behave as a point defect level at low temperatures and as a structural defect at room temperature. This phenomenon indicates that at a critical Mg doping concentration, the phase of the native Ga

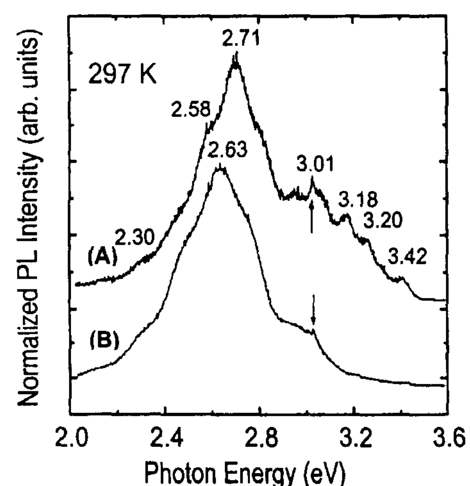

Fig. 4 .The room-temperature PL spectra for the sample D, epitaxially grown at the flow rate of Mg source of 1.5 nmole/min.

vacancy coexists with the compensated Mg-H complex in as-grown sample and with Mg atoms in the post-annealed sample. However the dislocation-induced PL peaked at 3.01 eV is not changed by the thermal annealing effect indicating that the Mg-related defect level can be incorporated with the misfit dislocation, because the dislocation-associated PL center could not be quenched by thermal annealing [14].

Fig. 5 shows the low-temperature PL for sample D and a PL band at 3.12 eV is dominant. This shows the temperature-dependent PL property for a certain Mg doping concentration. Both the as-grown and the annealed samples show similar PL spectra and the intensity was reduced in the annealed sample. The low-temperature emission of PL spectra of sample D is similar with sample A in Fig. 3(A). However, a PL band of 3.01 eV is quite intense and comparable with sample B in Fig. 3(B). Therefore, in Mg doped GaN samples, there are twofold PL bands, which are separable along the energy line of 3.01 eV.

Above the energy level of 3.01 eV, the low doped sample provides a PL band around 3.12 eV, which may be correlated with the dislocation free DAP transition. Below the energy level, the highly doped sample shows a blue PL band around 2.71 eV, which may be classified as a dislocation-related or structural defect including deep donor and acceptor pair transition. Sample D has the intermediate doping level, where a transition in PL spectra from 3.12 eV to 2.71 eV has occurred so that PL spectra are temperature-dependent and the peak positions are independent on the annealing process. From the temperature dependent study, the PL band transition can occur with the temperature of 140 K, indicating the thermal activation energy of 0.4 eV [15,16].

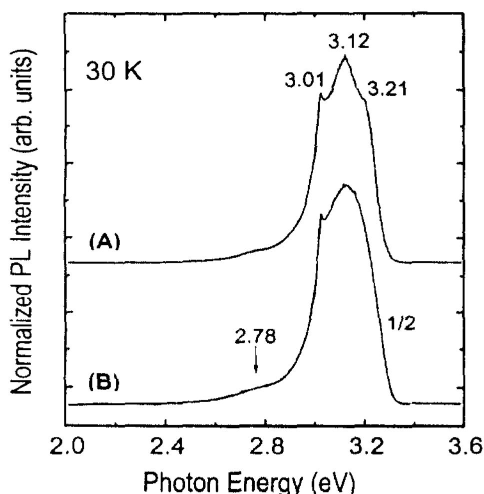

Fig. 5. The low-temperature PL spectra for the sample D, epitaxially grown at the flow rate of Mg source of 1.5 nmole/min..

In the analysis of the microstructure of the defect center, group II acceptor substitutes the group III atoms in III-V compound semiconductor and formulates the complex with hydrogen in a BC site between the acceptor and one of the group V neighbors [17] as shown in Fig. 6. However, due to the more ionic covalent character of as-grown Mg doped GaN system, the Mg atom relaxes toward the three other N neighbors and this relaxation indicates that the neutralized Mg is trigonally threefold coordinated. Therefore, the general BC site as shown in Fig. 6 can be changed for the hydrogen bonding which is on the opposite side to the Mg atom. The Mg-N-H complex is normal to the trigonal configuration instead of the Mg-H-N complex. This trigonal symmetry can be broken to the thermal annealing and the Mg atom is displaced into the Ga site. However, there is still the residual stress for the partial relaxation due to the isolated Mg atom. This results in the increase of the c axis lattice parameter of about 12% [18] and the Raman shift from 570.31 cm^{-1} for undoped GaN to 570.90 cm^{-1} for the annealed sample of Mg-doped GaN. This is consistent with the TEM measurement on the pyramidal defect [13], where a translation of the planar (0002) of c/8 close to the basal boundary is observed but not in plain translation.

In p-type GaN, the hydrogen atom behaves as a donor (H^+), compensating acceptors. Hydrogen can bind to the Mg acceptors with a binding energy of 0.7 eV. N vacancy also acts as a compensating center and plays an important role on the blue PL band. While increasing Mg doping conceration, the formation of the N vacancy is enhanced due to the very small solid solubility of Mg in GaN and the corporation of hydrogen to the strong formation of N-H bonds or the corresponding ammonia molecule. The ionic bond ratio between two atoms is

$$I = 0.166\,x + 0.12\,x^2 - 0.024\,x^3 \qquad (1)$$

where x is the difference of electro-negativity between two atoms. The ionic bond ratio of Ga-N is 0.341 and 0.522 for Mg-N bond. This indicates that the N atom or Ga-N dimmer during the diffusion process in the reactor

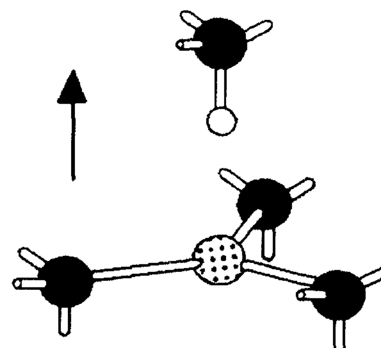

Fig. 6. Schematic representation of III-V complex with hydrogen in a BC site. The black spheres represent V atoms the dotted one the acceptor and the small white one the hydrogen atom. In Mg-N-H complex in GaN, the hydrogen is located on the opposite side to the acceptor.

hardly participates in the chemical bonding with the Mg atom at surface. For the introduction of hydrogen as a surfactant into GaN, the hydrogen compensation on the Mg-N-H complex is preferred to the N vacancy-associated compensation. At a relatively low doping level, the partial compensation of Ga vacancy by Mg-H complex occurred and both defect centers of V_{Ga} and Mg_{Ga} exist in an annealed GaN thin film. At a relatively high doping level, the Ga vacancy can be fully compensated by Mg-H complex and further forms the N vacancy at the nearest neighbor of Mg atom, so that the annealed samples have two types of defect centers: Mg_{Ga}-V_N and Mg_{Ga}.

The acceptor level of Mg_{Ga} has been extensively characterized. According to Zhu *et al.* [19], the multiple deep levels originating from the Mg-N-H complex, from the analysis of dominant deep level transient spectroscopy (DLTS) signal. While increasing the annealing duration with the annealing temperature of 800°C, the broad deep levels of 0.41, 0.49 and 0.59 eV is reconciled to 0.23 and 0.42 eV, and finally converged to the energy of 0.22 eV, indicating the Mg deep center. The higher energy levels correspond to the bond of hydrogen atoms and the long term annealing process enables more H to escape from the Mg-H-N complex. The binding energy of Mg acceptor in GaN is about 0.25 eV in PL measurement [20]. This ionization energy indicates the corresponding observation of the photo-excitation signal at the photon energy of about 3.15 eV in PC measurement.

From the *ab-initio* calculation [21], the electronic band structure on the Mg-doped wurtzite GaN shows the same band shape as that of the undoped GaN except for the energy region near band edges. The impurity state is delocalized on sites of N atoms at the top of the valence band. The wurtzite GaN shows the ionic favor and the electro-static Madelung energy shift due to the Mg doping provides the destabilization of ionic charge distribution. The repulsive force at N site increases both energies of *s* and *p* valence orbitals. This destabilization can enhance the native defect formation of N vacancy as a donor. Further theoretical calculations [22,23] suggested that the lowest defect level in p-type GaN may originate from a donor state of N-site vacancy, V_N. This defect shows two different relaxed structures with +1 and +3 charge states. The most stable structure is a +3 charge state in p-type GaN and provides an unoccupied deep level at 0.8 eV above the valence band maximum [22].

In order to verify the N vacancy model on the deep level at 0.8 eV above the valence band, the PC measurement for the photo-excitation mechanism in p-GaN has been carried out at room temperature under the dc bias of 1.5 V. Fig. 7 shows the PC spectra for the as-grown and the annealed states of sample D. For PC spectra above half of the band gap of 3.42 eV in GaN, the majority carrier is the electron which can be excited to conduction band from the deep donor levels by photo-excitation. The PC bands belonging to this class are 3.02 and 3.31 eV in as-grown samples and 3.02, 3.15 and 3.30 eV in annealed samples. Furthermore, the low energy PC bands of 0.87 and 0.91eV in the annealed sample come from the hole transition from deep levels to the valence band edge [9]. This signal may provide a clue to the p-type activation of Mg doped GaN. And also these PC signals of 0.91 and 0.87 eV are consistent with the theoretical prediction on the N vacancy formation, V_N. The dark currents can be activated from both a deep donor with the energy of 142 meV above the temperature of 140 K and a shallow donor with 29 meV below the temperature.

Fig. 8 shows the PC spectra for the Mg doped sample with various carrier concentrations. Samples A, B and C were annealed at 850°C for 10 min and hole carrier concentrations of 2.1×10^{17}, 3.8×10^{17} and $6.5\times10^{17}/cm^3$ were obtained, respectively. The typical PC spectral centers were observed to the energies of 3.31,

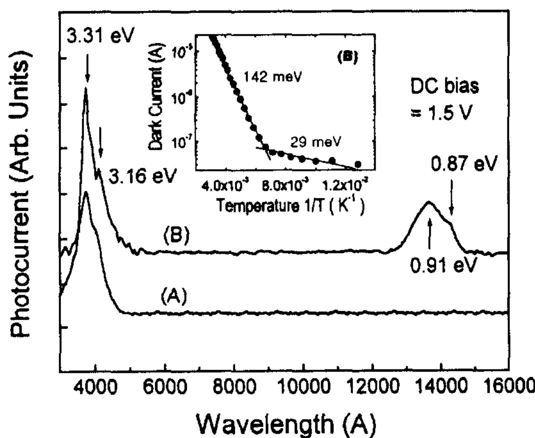

Fig. 7. The room-temperature PC spectra for (A) as-grown and (B) annealed sample D. The PC spectra were obtained by applying the dc bias of 1.5 V.

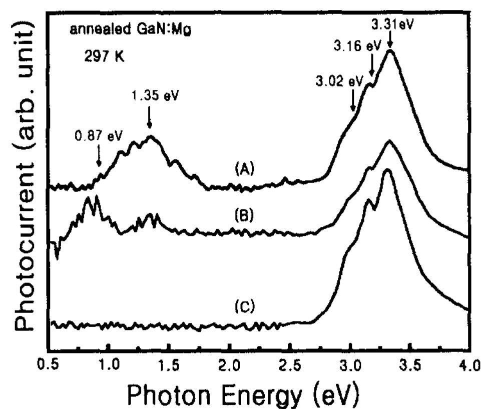

Fig. 8 The room-temperature PC spectra for annealed samples A, B and C.

3.16, 3.02, 1.35 and 0.87 eV, respectively. The common PC signals for the energies of 3.02, 3.16 and 3.31 eV are correlated with Mg-N-H complex or H-dissociated Mg_{Ga} center and these provide the acceptor level above the valence band edge with the energy difference of 0.11-0.4 eV. The low energy signals of 1.35 and 0.87 eV were observed in relatively low doped samples A and B, which is consistent with the unoccupied deep level predicted by theoretical calculation [22].

4. CONCLUSION

Mg doping effects on the electrical and optical properties were investigated for various p-GaN thin films. Below the Mg doping concentration of $10^{19}/cm^3$, the thermally annealed sample shows the compensated phase to n-type GaN in Hall measurement. In the Mg concentration of $4.0\times10^{19}/cm^3$ corresponding to the hole carrier concentration of $2.6\times10^{19}/cm^3$, there exists a photoluminescence center of the donor and the acceptor pair transition of the 3.28-eV band. This center is correlated with the defects for a shallow donor of the V_{Ga} and for an acceptor of Mg_{Ga}. The acceptor level shows the binding energy of 0.2-0.25 eV, which was observed by the photon energy of the photocurrent signal of 3.02-3.31 eV. Above the Mg concentration of $4.0\times10^{19}/cm^3$, both the Mg doping level and Mg concentration were saturated and there is a photoluminescence center of a deep donor and an acceptor pair transition of the 2.76-eV blue band. This center is attributed to the defect centers of Mg_{Ga}-V_N for the deep donor and Mg_{Ga} for the acceptor. The light emission from the dislocation center was observed at the energy of 3.01 eV and the transition effect is magnified at a critical point of Mg doping level. Furthermore, the photocurrent measurement provides the acceptor levels of 0.87-1.35 eV above the valence band for the annealed and relatively low doped samples. This sheds a light on the clue to p-type activation of the Mg doped GaN sample.

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