

Hole Compensation Mechanism of P-Type GaN Films

To cite this article: Shuji Nakamura *et al* 1992 *Jpn. J. Appl. Phys.* **31** 1258

View the [article online](#) for updates and enhancements.

You may also like

- [The development of a -biomimetic uncooled IR-Sensor inspired by the infrared receptors of *Melanophila acuminata*](#)
Georg Siebke, Peter Holik, Sam Schmitz et al.
- [Non-classical behaviour of higher valence dopants in chromium \(III\) oxide by a Cr vacancy compensation mechanism](#)
John J Carey and Michael Nolan
- [Effect of Cobalt Content on Charge Compensation Mechanism of \$\text{LiNi}_{1-x}\text{Mn}_x\text{Co}_2\text{O}_2\$ Cathode for Lithium Ion Battery](#)
Yoshiyuki Morita, Koji Nakanishi, Megan Aubin et al.

Hole Compensation Mechanism of P-Type GaN Films

Shuji NAKAMURA, Naruhito IWASA, Masayuki SENOH and Takashi MUKAI

Nichia Chemical Industries, Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774

(Received January 13, 1992; accepted for publication February 15, 1992)

Low-resistivity p-type GaN films, which were obtained by N_2 -ambient thermal annealing or low-energy electron-beam irradiation (LEEBI) treatment, showed a resistivity as high as $1 \times 10^6 \Omega \cdot \text{cm}$ after NH_3 -ambient thermal annealing at temperatures above 600°C . In the case of N_2 -ambient thermal annealing at temperatures between room temperature and 1000°C , the low-resistivity p-type GaN films showed no change in resistivity, which was almost constant between $2 \Omega \cdot \text{cm}$ and $8 \Omega \cdot \text{cm}$. These results indicate that atomic hydrogen produced by NH_3 dissociation at temperatures above 400°C is related to the hole compensation mechanism. A hydrogenation process whereby acceptor-H neutral complexes are formed in p-type GaN films was proposed. The formation of acceptor-H neutral complexes causes hole compensation, and deep-level and weak blue emissions in photoluminescence.

KEYWORDS: p-type GaN, thermal annealing, hydrogenation, atomic hydrogen, Hall measurement, photoluminescence

§1. Introduction

Wide-band-gap semiconducting GaN shows promise for use in blue light-emitting diodes (LEDs) and UV-emitting laser diodes (LDs). In order to realize production of these emitting devices, a method for obtaining high-quality GaN films and highly p-typed GaN films must be developed. It has been very difficult to obtain high-quality GaN films because of the large lattice mismatch and large difference in thermal expansion coefficients between GaN and substrate. For these same reasons, it has been impossible to obtain a p-type GaN film. Numerous substrate materials have been used for the deposition of GaN, the most common being (0001) C-face sapphire. The surface morphology of these GaN films was markedly improved when an AlN buffer layer was initially deposited on the sapphire, as shown initially by Yoshida *et al.*^{1,2)} More recently, Amano *et al.*^{3,4)} and Akasaki *et al.*⁵⁾ have obtained high-quality GaN films using this AlN buffer layer by means of the metalorganic chemical vapor deposition (MOCVD) method. They showed that the uniformity, crystalline quality, luminescence and electrical properties of GaN films were remarkably improved, and they developed GaN p-n junction LEDs for the first time using this AlN buffer layer technique.^{6–8)} Amano *et al.*^{6,7)} and Amano and Akasaki⁸⁾ grew Mg-doped GaN films using AlN buffer layers on a sapphire substrate. After the growth, the low-energy electron-beam irradiation (LEEBI) treatment was performed on these GaN films to obtain a p-type GaN film.

The present authors succeeded for the first time in obtaining high-quality GaN films using GaN buffer layers instead of AlN buffer layers.^{9,10)} The crystal quality and p-type conductivity control of GaN films grown with GaN buffer layers were far superior to those of films grown with AlN buffer layers.^{9,10)} Using this GaN buffer layer technique, GaN p-n junction blue LEDs suitable for practical use were fabricated for the first time.¹¹⁾ To achieve higher external quantum efficiency of GaN LEDs and UV LDs, further improvement in crystal quality and p-type conductivity control of GaN films is required.

Usually, these as-grown Mg or Zn-doped p-type GaN films show resistivity levels greater than $10^4 \Omega \cdot \text{cm}$.^{6–8,10)} Therefore, LEEBI treatment has been performed for these as-grown p-type GaN films to obtain low-resistivity p-type GaN films.^{6–8,10)} However, the mechanism of the LEEBI treatment effects on p-type GaN films has not been established. On the other hand, the present authors have discovered that N_2 -ambient or vacuum-ambient thermal annealing at temperatures above approximately 700°C is effective in obtaining low-resistivity p-type GaN films identical to those produced by the LEEBI treatment.¹²⁾

The mechanism of thermal annealing effects on p-type GaN films is also not well established. To obtain highly p-typed GaN films for fabricating emitting devices, the mechanisms of LEEBI treatment and thermal annealing effects on these films must be understood.

In this study, the ambient gas of thermal annealing was varied to examine the mechanism of thermal annealing effects on low-resistivity p-type GaN films. The purpose of this study is to clarify the mechanisms underlying LEEBI treatment and thermal annealing effects on p-type GaN films, and the hole compensation in p-type GaN films.

§2. Experimental

GaN films were grown by the two-flow metalorganic chemical vapor deposition (TF-MOCVD) method. The details of TF-MOCVD are described in other papers.^{13,14)} The growth was conducted at atmospheric pressure. Sapphire with (0001) orientation (C face), which had a two-inch diameter, was used as a substrate. Trimethylgallium (TMG), ammonia (NH_3) and bis-cyclopentadienyl magnesium (Cp_2Mg) were used as Ga, N and Mg sources, respectively. First, the substrate was heated to 1050°C in a stream of hydrogen. Then, the substrate temperature was lowered to 510°C to grow the GaN buffer layer. The thickness of the GaN buffer layer was approximately $250 \text{ \AA}$. Next, the substrate temperature was elevated to 1035°C to grow GaN films. During the deposition, the flow rates of H_2 , NH_3 and TMG of the main flow were

maintained at 2.0 l/min, 4.0 l/min and 54 $\mu\text{mol/min}$, respectively. The flow rates of H_2 and N_2 of the subflow were maintained at 10 l/min and 10 l/min, respectively. P-type GaN film was grown for 60 minutes by flowing Cp_2Mg gas at a flow rate of 3.6 $\mu\text{mol/min}$. The total thickness was approximately 4 μm . After the growth, the LEEBI treatment was performed to obtain low-resistivity p-type GaN films under the condition that the accelerating voltage of incident electrons was maintained at 15 kV. After LEEBI treatment, thermal annealing was performed at different temperatures. N_2 and NH_3 were used as ambient gases of thermal annealing. The annealing time was 20 min at each temperature. The flow rates of N_2 gas and NH_3 gas were 1 l/min and 2 l/min, respectively, during thermal annealing. The temperature of thermal annealing was varied between room temperature and 1000°C. No change in the surface morphologies of GaN films was observed after thermal annealing between these temperatures. After thermal annealing, each sample was evaluated by Hall-effect and photoluminescence measurements at room temperature. Hall-effect measurement was performed by the van der Pauw method.

§3. Results and Discussion

Resistivity change as a function of annealing temperature is shown in Fig. 1. Before thermal annealing, the LEEBI treatment was performed for as-grown GaN films whose resistivity was as high as $1 \times 10^6 \Omega \cdot \text{cm}$ to obtain low-resistivity p-type GaN films. The hole carrier concentration and resistivity were calculated assuming that the thickness of the p-layer was 4 μm , although the penetration depth of the incidence electrons was roughly 0.8 μm

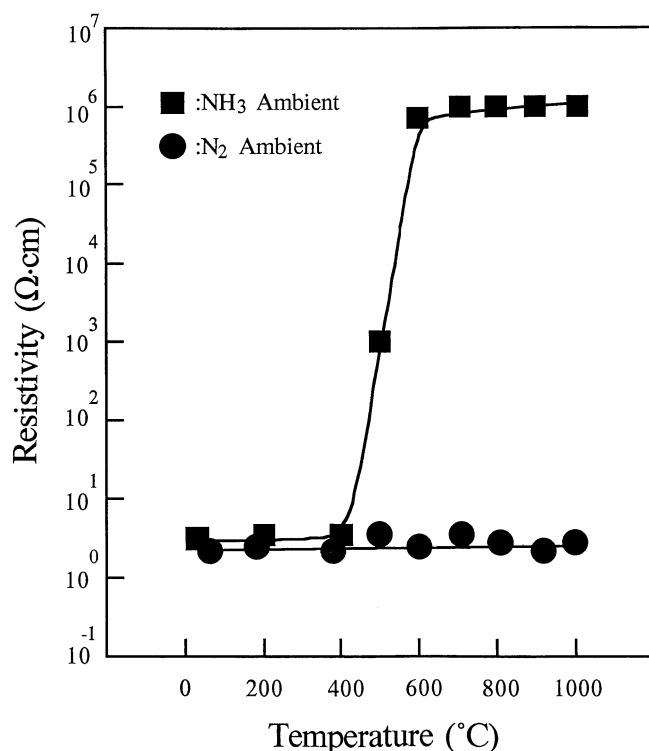


Fig. 1. The resistivity change in LEEBI-treated Mg-doped GaN films as a function of annealing temperature. The ambient gases, NH_3 and N_2 , were used for thermal annealing.

at this accelerating voltage in LEEBI treatment.⁷⁾ Typical values of resistivity, hole carrier concentration and hole mobility were $2 \Omega \cdot \text{cm}$, $3 \times 10^{17}/\text{cm}^3$ and $10 \text{ cm}^2/\text{V} \cdot \text{s}$ after the LEEBI treatment. In NH_3 -ambient thermal annealing, the resistivity was almost constant at temperatures between room temperature and 400°C. When the annealing temperature was increased to 500°C, the resistivity suddenly began to increase. At 600°C, the resistivity increased to approximately $1 \times 10^6 \Omega \cdot \text{cm}$. At temperatures above 600°C, the resistivity was almost constant at as high a value as $1 \times 10^6 \Omega \cdot \text{cm}$. On the other hand, the resistivity was almost constant between $2 \Omega \cdot \text{cm}$ and $8 \Omega \cdot \text{cm}$ in N_2 -ambient thermal annealing at temperatures between room temperature and 1000°C. When the thermal annealing ambient gas used was NH_3/N_2 mixed gas or NH_3/H_2 mixed gas, the change in resistivity as a function of annealing temperature was almost the same as that in NH_3 -ambient thermal annealing. When the thermal annealing ambient was a vacuum, the resistivity change as a function of annealing temperature was almost the same as that in N_2 -ambient thermal annealing. Therefore, these results indicate that the abrupt resistivity increase in NH_3 -ambient thermal annealing at temperatures above 400°C is caused by NH_3 gas flow.

Another interesting phenomenon occurs in thermal annealing. After NH_3 -ambient thermal annealing at temperatures above 600°C, resistivity becomes as high as $1 \times 10^6 \Omega \cdot \text{cm}$ (see Fig. 1). These high-resistivity GaN films resulting from NH_3 -ambient thermal annealing at temperatures above 600°C were annealed again in N_2 -ambient at temperatures above 700°C. The resistivity of these twice-annealed GaN films, whose second annealing ambient gas was changed to N_2 , became as low as $2 \Omega \cdot \text{cm}$ to $8 \Omega \cdot \text{cm}$. These values of resistivity were almost the same as those of LEEBI-treated samples before annealing. Therefore, these changes between high resistivity (about $1 \times 10^6 \Omega \cdot \text{cm}$) and low resistivity (about $2 \Omega \cdot \text{cm}$) were reversible by changing the annealing ambient gas at temperatures above 700°C. The present authors have already reported that N_2 -ambient thermal annealing at temperatures above 700°C was effective in significantly reducing the resistivity of as-grown Mg-doped GaN films.¹²⁾

For these thermal annealing experiments, shown in Fig. 1, LEEBI-treated low-resistivity GaN films were used for NH_3 -ambient and N_2 -ambient thermal annealing. Even without use of the LEEBI treatment, low-resistivity p-type GaN films can be obtained by N_2 -ambient or vacuum-ambient thermal annealing above 700°C.¹²⁾ When the thermal-annealed low-resistivity GaN films were used for NH_3 -ambient and N_2 -ambient thermal annealing experiments, the results were almost the same as for the resistivity change of LEEBI-treated GaN films in NH_3 -ambient and N_2 -ambient thermal annealing, as seen in Fig. 1. Therefore, it is assumed that the effects of LEEBI treatment and N_2 -ambient thermal annealing for Mg-doped GaN films are almost the same, and that the mechanism by which high-resistivity GaN films become low-resistivity GaN films is almost identical for the LEEBI treatment and thermal annealing.

Photoluminescence (PL) measurements were performed at room temperature for the above-mentioned GaN

films. A He-Cd laser was used as an excitation source. Typical examples of PL spectra are shown in Figs. 2 and 3. Figure 2(a) shows the PL spectrum of LEEBI-treated GaN film before thermal annealing, Fig. 2(b) shows the film after NH_3 -ambient thermal annealing at 800°C for the sample in Fig. 2(a), and Fig. 2(c) shows the film after N_2 -ambient thermal annealing at 800°C for the sample in Fig. 2(b). Before NH_3 -ambient thermal annealing, the intensity of blue emissions at 450 nm is strong, and broad deep-level emissions (DL emissions) are not observed around 750 nm (see Fig. 2(a)). After NH_3 -ambient thermal annealing at 800°C for the sample in Fig. 2(a), the intensity of blue emissions becomes weaker (by approximately one order), and DL emissions around 750 nm appear (see Fig. 2(b)). After N_2 -ambient thermal annealing at 800°C for the sample in Fig. 2(b), the intensity of blue emissions becomes stronger in comparison with that of Fig. 2(b), and DL emissions disappear. The resistivities of Mg-doped GaN films of Figs. 2(a), 2(b) and 2(c) were

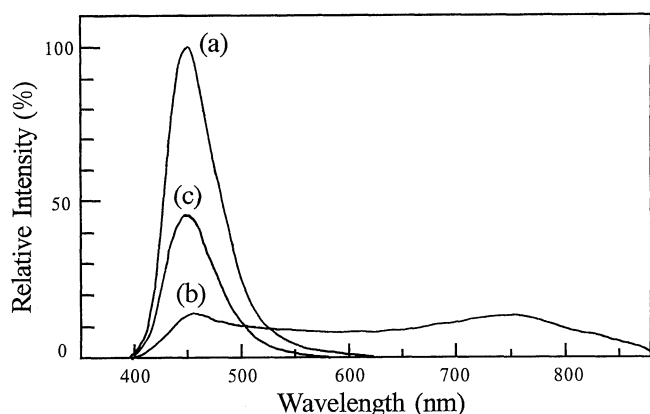


Fig. 2. PL spectra of Mg-doped GaN films which were continuously annealed under different conditions: (a) LEEBI-treated GaN film before thermal annealing, (b) GaN film after 800°C NH_3 -ambient thermal annealing of the GaN film in Fig. 2(a), (c) GaN film after 800°C N_2 -ambient thermal annealing of the GaN film in Fig. 2(b).

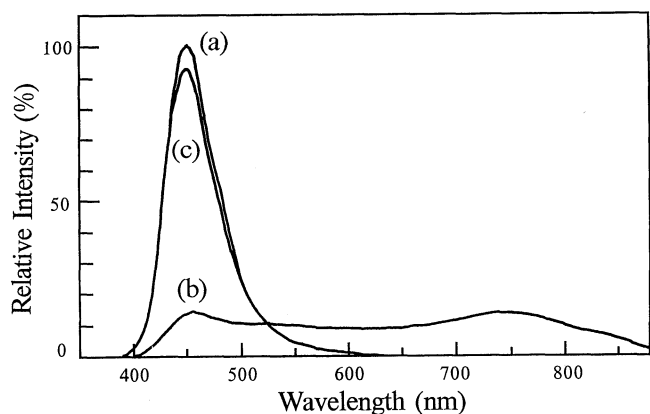


Fig. 3. PL spectra of Mg-doped GaN films which were continuously annealed under different conditions: (a) GaN film after 800°C N_2 -ambient thermal annealing of the LEEBI-treated GaN film, (b) GaN film after 800°C NH_3 -ambient thermal annealing of the GaN film in Fig. 3(a), (c) GaN film after 800°C N_2 -ambient thermal annealing of the GaN film in Fig. 3(b).

$3\ \Omega\cdot\text{cm}$, $1 \times 10^6\ \Omega\cdot\text{cm}$ and $4\ \Omega\cdot\text{cm}$, respectively. The results of PL measurement in Fig. 2 show that resistivity becomes high when DL emissions appear, and the intensity of blue emissions of LEEBI-treated GaN films becomes weak as a result of N_2 -ambient thermal annealing.

Figure 3(a) shows the PL spectrum of 800°C N_2 -ambient thermal-annealed GaN film, Fig. 3(b) shows the film after NH_3 -ambient thermal annealing at 800°C for the sample in Fig. 3(a), and Fig. 3(c) shows the film after N_2 -ambient thermal annealing at 800°C for the sample in Fig. 3(b). Before NH_3 -ambient thermal annealing, the intensity of blue emissions is strong, and broad DL emissions are not observed around 750 nm (see Fig. 3(a)). After NH_3 -ambient thermal annealing at 800°C for the sample in Fig. 3(a), the intensity of blue emissions becomes weaker, and DL emissions around 750 nm appear (see Fig. 3(b)). After N_2 -ambient thermal annealing at 800°C for the sample in Fig. 3(b), the intensity of blue emissions becomes stronger in comparison with that of Fig. 3(b), and DL emissions disappear. The resistivities of Mg-doped GaN films of Figs. 3(a), 3(b) and 3(c) were $2\ \Omega\cdot\text{cm}$, $1 \times 10^6\ \Omega\cdot\text{cm}$ and $4\ \Omega\cdot\text{cm}$, respectively. The results of PL measurement in Fig. 3 show that resistivity becomes high when DL emissions appear, and the intensity of blue emissions is almost constant in spite of repeated N_2 -ambient thermal annealing at the same temperature. Furthermore, these changes in PL spectra were found to be reversible with change in the annealing ambient gas from NH_3 to N_2 , as is the case with the resistivity change (see Fig. 1).

Next, the annealing temperature dependence of the intensity of blue and DL emissions of PL spectra was measured for the above-mentioned GaN films in Fig. 1. The NH_3 -ambient thermal annealing temperature dependence of the intensity of blue and DL emissions is shown in Fig. 4. The intensity dependence of blue emissions on NH_3 -ambient thermal annealing temperature is shown in Fig. 4(a). Between room temperature and 400°C , the intensity of blue emissions is constant. At temperatures above 400°C , the intensity of blue emissions suddenly decreases to approximately one-fifth of that below 400°C . The intensity dependence of DL emissions on NH_3 -ambient thermal annealing temperature is shown in Fig. 4(b). Between room temperature and 400°C , DL emissions were not observed at this slit width of the monochromator. At temperatures above 400°C , DL emissions could be observed. These changes in the NH_3 -ambient thermal annealing temperature dependence of the intensity of blue and DL emissions exactly correspond to those in resistivity in Fig. 1. At temperatures above 400°C in NH_3 -ambient thermal annealing, the resistivities of Mg-doped GaN films reach a maximum of $1 \times 10^6\ \Omega\cdot\text{cm}$, the intensity of blue emissions in PL spectra becomes weak, and DL emissions can be observed. At temperatures below 400°C in NH_3 -ambient thermal annealing, the resistivity of Mg-doped GaN films does not change, the intensity of blue emissions in PL spectra does not change, and DL emissions cannot be observed.

The N_2 -ambient thermal annealing temperature dependence of the intensity of blue emissions is shown in

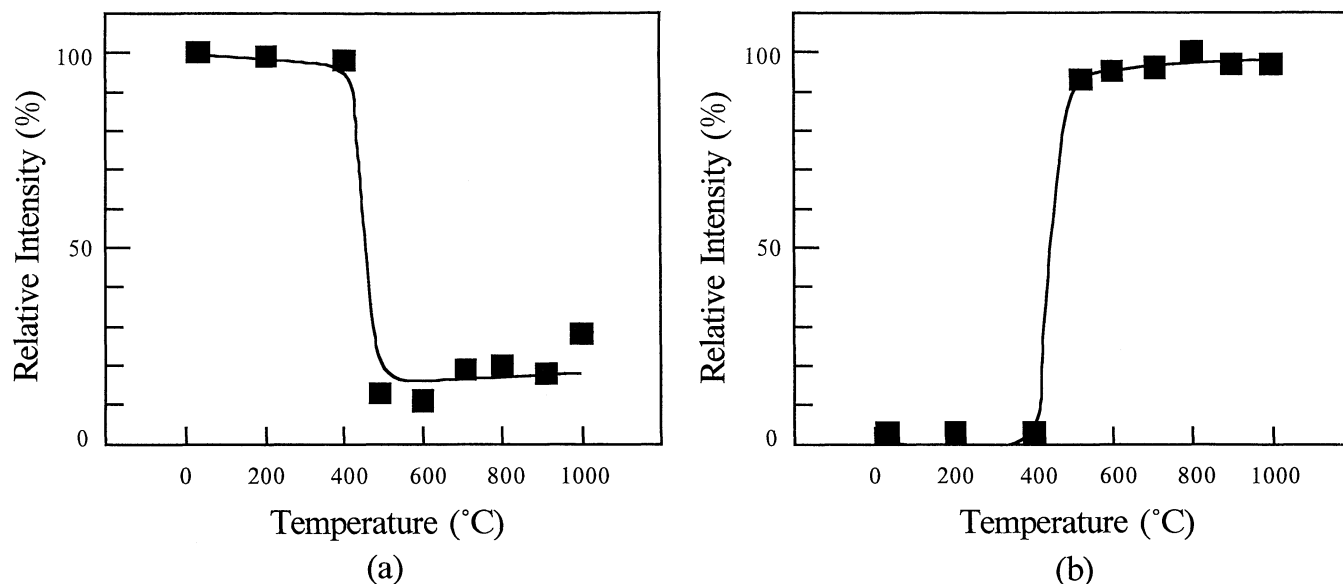


Fig. 4. The relative intensities of (a) 450 nm blue emissions and (b) 750 nm deep-level emissions in PL measurements of LEEBI-treated Mg-doped GaN films as a function of NH_3 -ambient thermal annealing temperature.

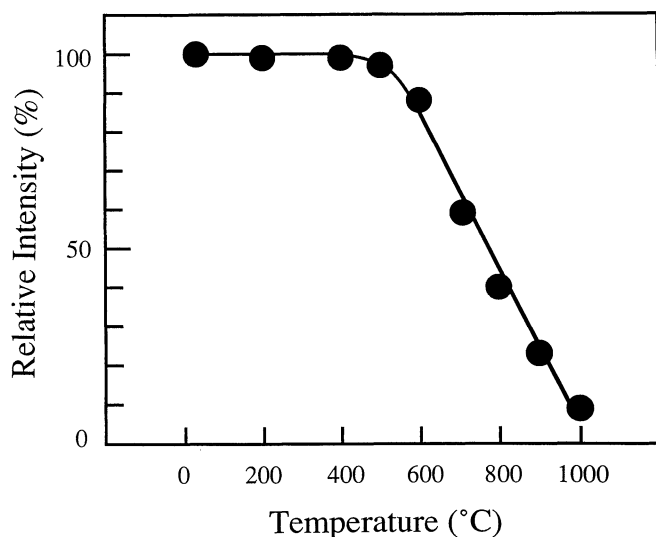


Fig. 5. The relative intensity of 450 nm blue emissions in PL measurements of LEEBI-treated Mg-doped GaN films as a function of N_2 -ambient thermal annealing temperature.

Fig. 5. Between room temperature and 500°C, the intensity of blue emissions is constant. At temperatures above 500°C, the intensity of blue emissions gradually decreases. At 1000°C, the intensity of blue emissions is approximately one order lower than that below 500°C. These gradual decreases in intensity at temperatures above 500°C do not correspond to the resistivity change in Fig. 1. The resistivity is almost constant with minimum values between $2\ \Omega\cdot\text{cm}$ and $8\ \Omega\cdot\text{cm}$ at temperatures between room temperature and 1000°C in Fig. 1. Therefore, it is concluded that the gradual decrease in intensity of blue emissions at temperatures above 500°C in N_2 -ambient thermal annealing is not directly related to the p-type conduction mechanism.

The 800°C N_2 -ambient thermal-annealed GaN film was

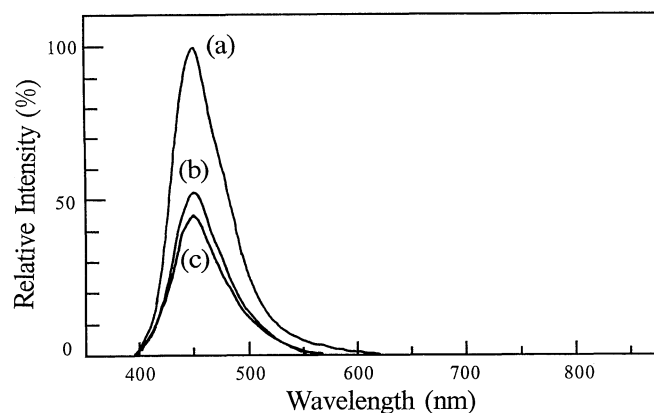


Fig. 6. PL spectra of Mg-doped GaN films which were continuously treated under different conditions: (a) LEEBI-treated GaN film before thermal annealing, (b) GaN film after 800°C N_2 -ambient thermal annealing of the GaN film in Fig. 6(a), (c) GaN film after LEEBI treatment of the GaN film in Fig. 6(b).

treated with LEEBI to ascertain whether the intensity change in blue emissions is reversible. Figure 6(a) shows the PL spectrum of LEEBI-treated GaN film before thermal annealing, Fig. 6(b) shows the film after N_2 -ambient thermal annealing at 800°C for the sample in Fig. 6(a), and Fig. 6(c) is the film after the LEEBI treatment for the sample in Fig. 6(b). Before N_2 -ambient thermal annealing, the intensity of blue emissions at 450 nm is strong, and broad DL emissions are not observed around 750 nm (see Fig. 6(a)). After N_2 -ambient thermal annealing at 800°C for the sample in Fig. 6(a), the intensity of blue emissions becomes weaker (by approximately one-half) (see Fig. 6(b)). After LEEBI treatment for the sample in Fig. 6(b), the intensity of blue emissions is almost constant in comparison with that of Fig. 6(b) (see Fig. 6(c)). The resistivities of Mg-doped GaN films of Figs. 6(a), 6(b) and 6(c) were $2\ \Omega\cdot\text{cm}$, $3\ \Omega\cdot\text{cm}$ and $3\ \Omega\cdot\text{cm}$, respec-

tively. After LEEBI treatment for the sample in Fig. 6(b), the intensity of blue emissions was still weak (Fig. 6(c)) in comparison with that before N₂-ambient thermal annealing at 800°C (Fig. 6(a)). This indicates that the change in the intensity of blue emissions due to N₂-ambient thermal annealing above 500°C is not reversible. In PL measurements of GaN films after N₂-ambient thermal annealing between room temperature and 1000°C in Fig. 5, the DL emissions could not be observed at this slit width of the monochromator.

From the above-mentioned results of resistivity and PL measurement as a function of annealing temperature, the following conclusions are made:

(1) NH₃ gas flow yields high-resistivity (approximately $1 \times 10^6 \Omega \cdot \text{cm}$) p-type GaN films.

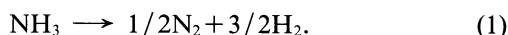
(2) The changes between high resistivity (approximately $1 \times 10^6 \Omega \cdot \text{cm}$) and low resistivity (approximately $2 \Omega \cdot \text{cm}$) were reversible with changes in annealing ambient gas at temperatures above 700°C.

(3) The presence of broad DL emissions at approximately 750 nm is directly related to the p-type conduction mechanism. When DL emissions are observed, the resistivity of Mg-doped p-type GaN films reaches a maximum of approximately $1 \times 10^6 \Omega \cdot \text{cm}$. When DL emissions are not observed, the resistivity of Mg-doped p-type GaN films reaches a minimum of approximately $2 \Omega \cdot \text{cm}$.

(4) The presence of blue emissions at 450 nm is directly related to the p-type conduction mechanism when the thermal annealing gas used was NH₃. When the intensity of blue emissions is strong, the resistivity of Mg-doped p-type GaN films reaches a minimum of approximately $2 \Omega \cdot \text{cm}$. When the intensity of blue emissions is weak, the resistivity of Mg-doped p-type GaN films attains a maximum of approximately $1 \times 10^6 \Omega \cdot \text{cm}$. On the other hand, the intensity of blue emissions is not directly related to the p-type conduction mechanism when the thermal annealing gas used is N₂. A gradual decrease in the intensity of blue emissions at temperatures above 500°C was observed under N₂-ambient thermal annealing.

These results suggest different models for the hole compensation mechanism. Below, we examine the hole compensation mechanism in light of the above results. First, the dissociation process of NH₃ must be considered because NH₃ gas flow creates high-resistivity (approximately $1 \times 10^6 \Omega \cdot \text{cm}$) p-type GaN films and causes changes in PL spectra.

Above 200°C, NH₃ can dissociate into N₂ and H₂ by the reaction



The amount of dissociation increases with temperature. With an NH₃ atmosphere heated to 800°C, at equilibrium, more than 99.9% of the NH₃ dissociates.¹⁵⁾ Although H₂ and N₂ can be produced by this reaction, these gases are inactive with GaN films during thermal annealing, and the dissociation temperature (800°C) of NH₃ is too high in comparison with the changing temperature of PL intensity in Fig. 4, and that of resistivity in Fig. 1 (approximately 400°C). Therefore, other dissocia-

tion processes of NH₃ must be considered. The dissociation of NH₃ on a silicon surface has been observed by Bozso and Avouris at temperatures as low as -173°C ; this process produces radicals such as NH, NH₂ and H.¹⁶⁾ This dissociation is attributable to the existence of dangling Si bonds on the surface.¹⁶⁾ On the Si surface, the species of NH, NH₂ and H are adsorbed to the Si dangling bond, and a large amount of hydrogen in the surface layer of Si is observed from temperatures as low as -173°C .¹⁶⁾ Furthermore, the surface of Si is hydrogen passivated from these low temperatures.¹⁶⁾ In addition, NH species adsorbed to the Si dangling bond begin to dissociate at approximately 200°C, and NH₂ species adsorbed to the Si dangling bond begin to dissociate at approximately 400°C.¹⁶⁾ Also, hydrogen atoms adsorbed to the Si dangling bond begin to desorb above 400°C.¹⁷⁾ Therefore, at approximately 400°C on Si surfaces, there are many hydrogen atoms, which are adsorbed to or desorbed from Si dangling bonds. Using this dissociation mechanism for NH₃, AlN growth was performed on sapphire substrate at low temperatures (between 300°C and 500°C).¹⁵⁾ According to Yu *et al.*'s study, the temperature dependence of the growth rate of AlN crystal showed that the growth rate of AlN increased gradually above 300°C, and saturated at approximately 400°C.¹⁵⁾ Therefore, it is speculated that the same dissociation process of NH₃ which occurs on Si surfaces, also occurs on sapphire surfaces. At approximately 400°C, the surface of the sapphire substrate is almost perfectly hydrogen passivated. These same hypotheses are applied to surfaces of AlN films and GaN films because the AlN growth was performed at around 400°C using the same dissociation process of NH₃.¹⁵⁾ At approximately 400°C, the surface of GaN films is almost perfectly passivated by hydrogen atoms. It is suggested that these hydrogen atoms diffuse from the surface into the bulk of GaN film at this temperature because the number of hydrogen atoms is too great at the surface of the GaN films and the size of hydrogen atoms is very small. In addition, the temperature of 400°C perfectly corresponds to the changing temperature in PL intensity in Fig. 4 (approximately 400°C) and that of resistivity in Fig. 1. Therefore, it is concluded that the dissociation of NH₃ into hydrogen atoms causes the change in PL intensity in Fig. 4 and that of resistivity in Fig. 1. At a temperature of 400°C, the following process can be considered: the dissociation of NH₃ into hydrogen atoms occurs at the surface of GaN films because dangling bonds exist mainly at the surface, and the atomic hydrogen easily diffuses into the GaN films because the number of hydrogen atoms is too great at the surface and the size of hydrogen atoms is very small.

On the other hand, it is well established that hydrogenation (the incorporation of atomic hydrogen) results in the passivation (neutralization) of shallow donors and acceptors in III-V materials and Si.¹⁷⁻²⁶⁾ The passivation of donors is traced back to direct bonding of H to the defects,¹⁷⁾ while Zn acceptors are neutralized as a consequence of the formation of acceptor-H neutral complexes.^{17,18)} It has been shown that the hydrogen atom, when diffused into p-type silicon, is able to

passivate the electrical activity of the material; in n-type Si the passivation effect is less dramatic.^{17,25)} For example, GaAs was hydrogenated by means of microwave plasma at 300°C for 30 min.^{11,18)} In n-type and semi-insulating GaAs films, H was not detectable beyond the immediate surface, whereas in p-type GaAs, H penetrated to a depth greater than 5 μm , and hole concentration was reduced dramatically by the formation of Zn-H neutral complexes.^{17,18)} Thus, it appears that the diffusion coefficient for H is larger in p-type than in semi-insulating or n-type GaAs.^{17,18)} As another example, hydrogen diffusion in InP:Zn has been performed by means of hydrogen plasma exposure at a temperature of 300°C for 20 min.^{17,20)} Passivation of shallow acceptors occurred in the hydrogen-diffused region of InP:Zn, where H penetrated from the surface to a depth of approximately 3 μm . Before hydrogenation of InP:Zn, the resistivity of this p-type InP epilayer was 0.04 $\Omega\cdot\text{cm}$. After hydrogenation, the resistivity became higher than 10⁵ $\Omega\cdot\text{cm}$. Also, the PL spectra showed a difference between states before and after hydrogenation.^{17,22)} This was interpreted as being due to the formation of Zn-H complexes. In addition, reactivation of the hydrogenated acceptors can be performed under thermal annealing, where atomic hydrogen is removed from acceptor-H complexes.^{17,20,22)} After such thermal annealing, the properties of p-type epilayers can approximate those before hydrogenation. For example, in Zn-doped GaAs, atomic hydrogen can be removed by annealing at temperatures near 400°C.¹⁷⁾ These reactivation temperatures, where atomic hydrogen is removed from acceptor-H complexes, show a trend such that as the width of the band gap of the materials increases, the thermal stability of hydrogen passivation of defects in the semiconductor increases.¹⁷⁾ Therefore, it is expected that wide band-gap materials, *e.g.*, GaN, show higher temperatures of reactivation of acceptors in comparison with those of Zn-doped GaAs (approximately 400°C). From the above-mentioned results, it is speculated that the reactivation temperature of the acceptors of Mg-doped GaN films is between 400°C and 700°C.¹²⁾

With the incorporation of the above-mentioned hydrogenation process, the hole compensation mechanism of p-type GaN films can easily be explained. First, the atomic hydrogen, produced by dissociation of NH₃ at temperatures above 400°C, diffuses into p-type GaN films. Second, the formation of acceptor-H neutral complexes, *i.e.*, Mg-H complexes in GaN films occurs. As a result, the formation of Mg-H complexes causes hole compensation, and the resistivity of Mg-doped GaN films reaches a maximum of $1 \times 10^6 \Omega\cdot\text{cm}$ (see Fig. 1). For PL measurements, it is assumed that DL emissions are caused by related levels of Mg-H complexes, and blue emissions are caused by Mg-related levels. When these proposals are applied to the results of the PL measurements in Figs. 2, 3, 4 and 5, the results are quite well explained.

In the NH₃-ambient thermal annealing of Fig. 4, Mg-H complexes are not formed below 400°C, and Mg-H complexes are formed above 400°C in Mg-doped GaN films because the amount of atomic hydrogen diffused into the bulk of the GaN films is not great until tempera-

ture exceeds 400°C. As a result, the intensity of blue emissions of NH₃-ambient thermal-annealed GaN films above 400°C becomes weaker than that of NH₃-ambient thermal-annealed GaN films below 400°C because the number of Mg-related levels is reduced by formation of Mg-H complexes at temperatures above 400°C (see Fig. 4(a)). At temperatures above 400°C, DL emissions can be observed because Mg-H complexes are formed at these temperatures. At temperatures below 400°C, DL emissions cannot be observed because Mg-H complexes are not formed (see Fig. 4(b)).

In the N₂-ambient thermal annealing of Fig. 5, there are no Mg-H complexes in the GaN films because no atomic hydrogen is produced by the dissociation of NH₃. Therefore, related emissions of Mg-H complexes cannot appear in these PL measurements. Following this model, DL emissions were not observed in these N₂-ambient thermal-annealed GaN films between room temperature and 1000°C. However, a gradual decrease in the intensity of blue emissions was observed above 500°C (see Fig. 5). Therefore, this decrease in intensity of blue emissions is not related to the Mg-H complexes model, and other proposals are required to explain this process above 500°C. Considering that this decrease in intensity of blue emissions is not a reversible change, the dissociation of GaN is a possible explanation because the dissociation pressure of GaN becomes high at these temperatures (above 500°C).²⁷⁾ Dissociation pressure is higher when temperature is higher. Therefore, the intensity of blue emissions is weaker when the temperature is higher, *i.e.*, above 500°C, because the dissociation of GaN films causes many N-vacancies in GaN films (mainly near the surface), and the number of radiative recombination centers (Mg-related centers) positioned at Ga-sites, surrounded by four N-atoms, is reduced.

The present authors have already reported that N₂-ambient thermal annealing above 500°C was effective in greatly reducing the resistivity of as-grown high-resistivity GaN films, and the intensity of blue emissions of the PL spectrum showed a maximum around 700°C.¹²⁾ This relationship of intensity of blue emissions as a function of annealing temperature is shown in Fig. 7. The change in intensity is easily explained using the above-mentioned models. When the N₂-ambient thermal annealing temperature exceeds 400°C, removal of atomic hydrogen from Mg-H complexes begins, the number of blue emission centers which are Mg-related radiative recombination centers begins to increase, and the intensity of blue emissions of the PL spectrum gradually increases. However, when the temperature reaches approximately 700°C, the effects of N-vacancies produced by the dissociation of GaN films (mainly near the surface) begin to exceed those of the increased number of Mg-related radiative recombination centers. As a result, the intensity of blue emissions shows a maximum around 700°C in N₂-ambient thermal annealing of as-grown GaN films (see Fig. 7).

In the dissociation of GaN films, there is an interesting result, shown in Fig. 8. Figure 8(a) shows the PL spectrum of LEEBI-treated GaN film before thermal annealing, Fig. 8(b) shows the film after N₂-ambient thermal annealing at 700°C for the sample in Fig. 8(a), and Fig. 8(c)

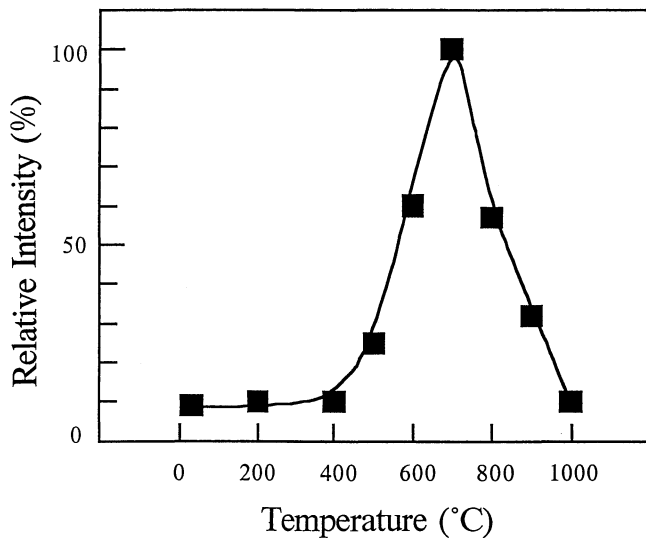


Fig. 7. The relative intensity of 450 nm blue emissions in PL measurements of as-grown Mg-doped GaN films as a function of N_2 -ambient thermal annealing temperature.

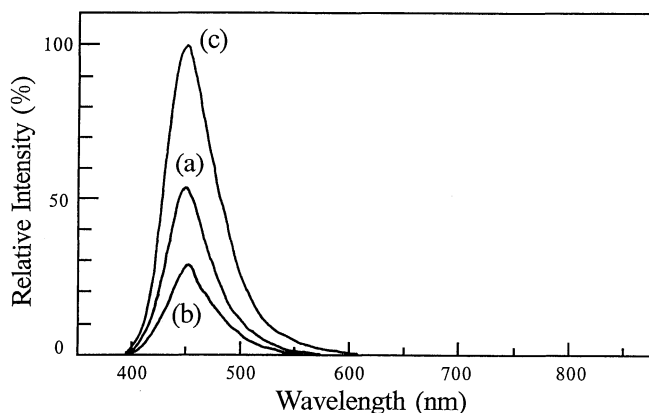


Fig. 8. PL spectra of Mg-doped GaN films which were continuously treated under different conditions: (a) LEEBI-treated GaN film before thermal annealing, (b) GaN film after 700°C N_2 -ambient thermal annealing of the GaN film in Fig. 8(a), (c) GaN film after 1 μ m etching of the GaN film in Fig. 8(b).

shows the film after 1 μ m etching for the sample in Fig. 8(b). After N_2 -ambient thermal annealing at 700°C for the sample in Fig. 8(a), the intensity of blue emissions becomes weaker (by approximately one-half) (see Fig. 8(b)) because GaN near the surface of GaN film dissociates. After 1 μ m etching for the sample in Fig. 8(b), the intensity of blue emissions becomes stronger in comparison with those in Figs. 8(b) and 8(a). This is because the GaN-dissociated area was removed by 1 μ m etching. Another interesting finding shows that the intensity of blue emissions in Fig. 8(c) is stronger than that in Fig. 8(a). This indicates that GaN dissociation also occurs as a result of LEEBI treatment. The resistivities of the Mg-doped GaN films in Figs. 8(a), 8(b) and 8(c) were 3 $\Omega \cdot \text{cm}$, 3 $\Omega \cdot \text{cm}$ and 8 $\Omega \cdot \text{cm}$, respectively.

To ascertain whether dissociation of GaN causes weak intensity levels in blue emissions in PL measurements at

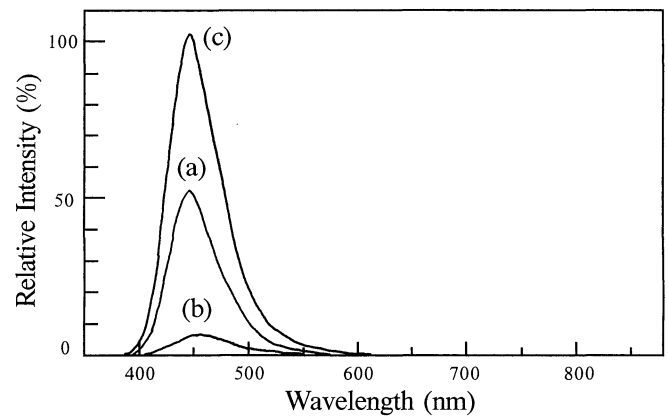


Fig. 9. PL spectra of Mg-doped GaN films which were treated under different conditions: (a) GaN film after LEEBI treatment of as-grown GaN film, (b) GaN film after 1 atm N_2 -ambient thermal annealing at 1000°C of as-grown GaN film, (c) GaN film after 90 atm N_2 -ambient thermal annealing at 1000°C of as-grown GaN film.

temperatures above 500°C, the GaN film was annealed under the conditions of a high-pressure N_2 atmosphere (N_2 pressure is 90 atm) at a temperature of 1000°C, using a high-pressure vessel. The annealing time was 20 min. The results are shown in Fig. 9. Figure 9(a) shows the PL spectrum of the GaN film after LEEBI treatment for as-grown GaN film, Fig. 9(b) shows the film after 1 atm N_2 -ambient thermal annealing at 1000°C for as-grown GaN film, and Fig. 9(c) shows the film after 90 atm N_2 -ambient thermal annealing at 1000°C for as-grown GaN film. The 1 atm N_2 -ambient-annealed GaN film at 1000°C shows an intensity of blue emissions at 450 nm which becomes as weak as approximately 1/10 that of the LEEBI-treated GaN film (see Figs. 9(b) and 9(a)). On the other hand, the 90 atm N_2 -ambient-annealed GaN film at 1000°C shows an intensity of blue emissions which becomes as strong as roughly twice that of the LEEBI-treated GaN film (see Figs. 9(c) and 9(a)). These results indicate that the dissociation of GaN causes the decrease in intensity of blue emissions in N_2 -ambient thermal annealing at temperatures above 500°C (see Fig. 5). The resistivities of the Mg-doped GaN films of Figs. 9(a), 9(b) and 9(c) were 2 $\Omega \cdot \text{cm}$, 3 $\Omega \cdot \text{cm}$ and 8 $\Omega \cdot \text{cm}$, respectively.

The reactivation of the acceptors is shown in Figs. 2 and 3. After NH_3 -ambient thermal annealing for low-resistivity p-type GaN films at 800°C, the intensity of blue emissions becomes weak, and broad DL emissions appear around 750 nm (see Figs. 2(b) and 3(b)) because Mg-H complexes are formed as a result of this annealing process. After N_2 -ambient thermal annealing for these NH_3 -ambient thermal-annealed GaN films at 800°C, the intensity of blue emissions becomes strong and DL emissions disappear because H atoms are removed from Mg-H complexes by N_2 -ambient thermal annealing.

In other experiments on acceptor dopants for GaN films, Amano *et al.* reported that the intensity of Zn-related blue emissions of PL spectra in Zn-doped GaN films was enhanced by LEEBI treatment.²⁸⁾ Therefore, models can be applied to Zn-doped GaN films similar to those for Mg-doped GaN films. The formation of accep-

tor-H neutral complexes, Zn-H complexes in this case, is responsible for the hole compensation mechanism and the decrease in the intensity of blue emissions. Usually, NH_3 is used as the N-source for GaN growth in MOCVD. Therefore, an *in situ* hydrogenation process, in which Zn-H complexes are formed during MOCVD growth, naturally occurs, and the resistivity of as-grown Zn-doped GaN films or Mg-doped GaN films becomes high (almost insulating). After the growth, N_2 -ambient thermal annealing or LEEBI treatment can reactivate the acceptors by removing atomic hydrogen from the acceptor-H neutral complexes in p-type GaN films. As a result, the resistivity of p-type GaN films becomes lower and the intensity of blue emissions becomes stronger. In LEEBI treatment, thermal or electron-beam-induced dissociation of acceptor-H complexes contributes to the fabrication of low-resistivity p-type GaN films. The electron-beam-induced dissociation of Si-H bonding, which was effective even at low temperatures, was studied in detail by Bozso and Avouris.²⁹⁾ However, in this study of hydrogenation of GaN films, either or both of thermal and electron-beam-induced dissociation of acceptor-H complexes contributes to obtaining low-resistivity p-type GaN films by LEEBI treatment.

For the above-mentioned samples, the hole carrier concentration and resistivity were calculated, assuming that p-layer thickness was $4\text{ }\mu\text{m}$, irrespective of the process employed, i.e., LEEBI treatment or thermal annealing. To ascertain whether this assumption is correct, the step etch was performed for samples which were treated with 15 kV LEEBI or annealed under conditions of N_2 ambient at a temperature of 750°C . Before LEEBI treatment or N_2 -ambient thermal annealing, the resistivity of these samples was approximately $1 \times 10^6\text{ }\Omega\cdot\text{cm}$. After each step etch, the resistivity was measured. The typical result is shown in Fig. 10. The results of N_2 -ambient thermal-annealed GaN films show that resistivity is almost constant (approximately $2\text{ }\Omega\cdot\text{cm}$) throughout the $4\text{ }\mu\text{m}$ -thick GaN film. On the other hand, results of the LEEBI-treated GaN films show that resistivity reaches a minimum of $2\text{ }\Omega\cdot\text{cm}$ without etching and a maximum of $300\text{ }\Omega\cdot\text{cm}$ after $0.7\text{ }\mu\text{m}$ etching. The resistivity after etching at a depth greater than $0.7\text{ }\mu\text{m}$ from the surface of LEEBI-treated GaN film is almost constant between $300\text{ }\Omega\cdot\text{cm}$ and $100\text{ }\Omega\cdot\text{cm}$. The resistivity change in LEEBI-treated GaN films as a function of depth shows that thermal annealing effects cause low resistivity in p-type GaN films during LEEBI treatment because the penetration depth of the incidence electrons is approximately $0.8\text{ }\mu\text{m}$ at this accelerating voltage (15 kV)⁷⁾ and the resistivity values range between $2\text{ }\Omega\cdot\text{cm}$ and $300\text{ }\Omega\cdot\text{cm}$ throughout the entire area of the $4\text{ }\mu\text{m}$ -thick GaN film. If no thermal annealing effects occur during LEEBI treatment, the low resistivity is restricted to an area between the surface and a depth of $0.8\text{ }\mu\text{m}$ from the surface. However, the results of LEEBI-treated GaN films show that resistivity values range between 300 and $100\text{ }\Omega\cdot\text{cm}$ throughout the entire area of the $4\text{ }\mu\text{m}$ -thick GaN film, except for the immediate surface, whose resistivity is as low as $2\text{ }\Omega\cdot\text{cm}$. Considering that the penetration depth of the incidence electrons is approximately $0.8\text{ }\mu\text{m}$ at this accelerating

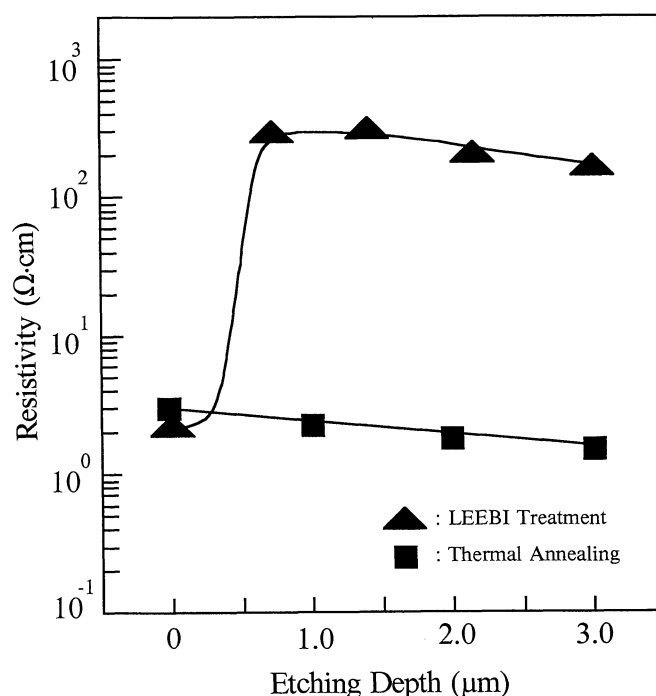


Fig. 10. Resistivity change in a LEEBI-treated GaN film and a 750°C N_2 -ambient thermal-annealed GaN film as a function of etching depth from the surface.

voltage in LEEBI treatment, it is possible that the temperature near the immediate surface of the GaN film becomes very high due to electron incidence in comparison with that far below the surface of the film (i.e., more than $0.8\text{ }\mu\text{m}$ from the surface), and the resistivity near the immediate surface becomes very low due to the thermal annealing effects above 700°C , in comparison with that far below the surface (see Fig. 10). Even if another one of the above-mentioned models proposing electron-beam-induced dissociation of acceptor-H complexes could be applied, this effect would have to be restricted to the area between the surface and a depth of $0.8\text{ }\mu\text{m}$ from the surface. Therefore, if this electron-beam-induced dissociation model can be applied to this case, it is assumed that both thermal and electron-beam-induced dissociation of acceptor-H complexes cause the low resistivity in p-type GaN films only near the immediate surface of the film as a result of the LEEBI treatment.

In the results of LEEBI treatment shown in Fig. 10, taking the midpoint between $0\text{ }\mu\text{m}$ and $0.7\text{ }\mu\text{m}$, we can estimate that the thickness of the p-layer is approximately $0.35\text{ }\mu\text{m}$. If this value for p-layer thickness is applied to the calculation of hole carrier concentration and resistivity, it follows that the hole carrier concentration becomes approximately one order higher than the above-mentioned values ($3 \times 10^{17}/\text{cm}^3$) and the resistivity becomes approximately one order lower than the above-mentioned values ($2\text{ }\Omega\cdot\text{cm}$).

Next, to ascertain whether hydrogen passivation occurs in as-grown GaN films as mentioned above, hydrogen passivation of LEEBI-treated low-resistivity p-type GaN film was attempted by means of microwave plasma, which was used for the hydrogen passivation of p-type GaAs.¹⁸⁾ The microwave plasma was operated at

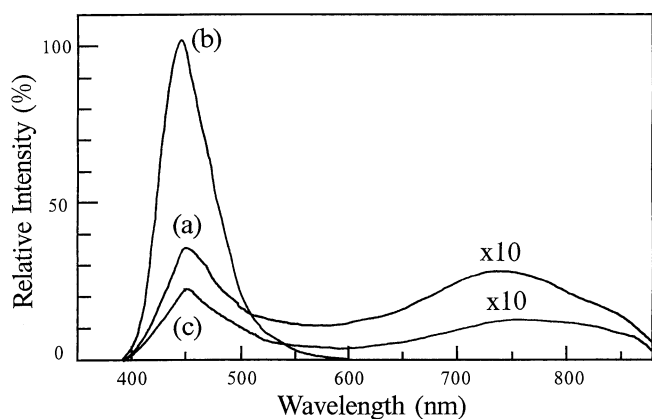


Fig. 11. PL spectra of Mg-doped GaN films which were treated under different conditions: (a) as-grown high-resistivity GaN film, (b) GaN film after LEEBI treatment of the sample in Fig. 11(a), (c) GaN film after microwave plasma treatment of the sample in Fig. 11(b).

240 W and at a pressure of 2 Torr. The flow rate of H_2 was $200 \text{ cm}^3/\text{min}$. The passivation temperature and time were 450°C and 30 min, respectively. Results are shown in Fig. 11. Figure 11(a) shows the PL spectrum of as-grown high-resistivity GaN film, Fig. 11(b) shows the film after LEEBI treatment for the sample in Fig. 11(a), and Fig. 11(c) shows the film after microwave plasma treatment for the sample in Fig. 11(b). Before LEEBI treatment, the intensity of blue emissions at 450 nm is weak and broad DL emissions can be observed at approximately 750 nm (see Fig. 11(a)). After LEEBI treatment, the intensity of blue emissions becomes stronger and the broad DL emissions disappear (see Fig. 11(b)). After microwave plasma treatment for the LEEBI-treated GaN film, the intensity of blue emissions becomes weak and broad DL emissions can be observed at approximately 750 nm (see Fig. 11(c)). The shape and intensity of the PL spectrum of microwave plasma-treated GaN film are almost the same as those of as-grown GaN film (see Figs. 11(c) and 11(a)). Therefore, it is speculated that as-grown GaN films are hydrogen passivated, and the above-mentioned proposal of the hydrogenation process occurs during GaN growth by means of MOCVD. The resistivities of Mg-doped GaN films of Figs. 11(a), 11(b) and 11(c) were $1 \times 10^6 \Omega \cdot \text{cm}$, $2 \Omega \cdot \text{cm}$ and $1000 \Omega \cdot \text{cm}$, respectively. The resistivity of the sample in Fig. 11(c) is smaller in comparison than that of Fig. 11(a). It is probable that the hydrogenation process is not perfect, i.e., hydrogen passivation may only occur near the immediate surface of GaN film because diffusion of atomic hydrogen from the surface into the bulk is minimal. If optimum conditions for microwave plasma treatment in hydrogen passivation of p-type GaN films can be found, resistivity will become higher.

§4. Conclusions

Low-resistivity p-type GaN films, which were obtained by N_2 -ambient thermal annealing or LEEBI treatment, showed a resistivity as high as $1 \times 10^6 \Omega \cdot \text{cm}$ after NH_3 -ambient thermal annealing at temperatures above 600°C . On the other hand, after N_2 -ambient thermal annealing at temperatures between room temperature and 1000°C ,

low-resistivity p-type GaN films showed almost no change in resistivity, which was almost constant between $2 \Omega \cdot \text{cm}$ and $8 \Omega \cdot \text{cm}$. The hydrogenation process, i.e., the formation of acceptor-H neutral complexes in p-type GaN films, was proposed to explain these results. The formation of acceptor-H neutral complexes causes high resistivity and weak blue emissions in PL measurements. N_2 -ambient thermal annealing at temperatures above 700°C can remove atomic hydrogen from the acceptor-H neutral complexes, and the resistivity of p-type GaN films becomes lower after this annealing process. The thermal annealing effects on n-type GaN films remain to be studied in the near future.

References

- 1) S. Yoshida, S. Misawa and S. Gonda: Appl. Phys. Lett. **42** (1983) 427.
- 2) S. Yoshida, S. Misawa and S. Gonda: J. Vac. Sci. & Technol. B **1** (1983) 250.
- 3) H. Amano, N. Sawaki, I. Akasaki and Y. Toyoda: Appl. Phys. Lett. **48** (1986) 353.
- 4) H. Amano, I. Akasaki, K. Hiramatsu and N. Koide: Thin Solid Films **163** (1988) 415.
- 5) I. Akasaki, H. Amano, Y. Koide, K. Hiramatsu and N. Sawaki: J. Cryst. Growth **98** (1989) 209.
- 6) H. Amano, M. Kito, K. Hiramatsu and I. Akasaki: Inst. Phys. Conf. Ser. **106** (1989) 725.
- 7) H. Amano, M. Kito, K. Hiramatsu and I. Akasaki: Jpn. J. Appl. Phys. **28** (1989) L2112.
- 8) H. Amano and I. Akasaki: Oyo Buturi **60** (1991) 163 [in Japanese].
- 9) S. Nakamura: Jpn. J. Appl. Phys. **30** (1991) L1705.
- 10) S. Nakamura, M. Senoh and T. Mukai: Jpn. J. Appl. Phys. **30** (1991) L1708.
- 11) S. Nakamura, T. Mukai and M. Senoh: Jpn. J. Appl. Phys. **30** (1991) L1998.
- 12) S. Nakamura, T. Mukai, M. Senoh and N. Iwasa: Jpn. J. Appl. Phys. **31** (1992) L139.
- 13) S. Nakamura: Jpn. J. Appl. Phys. **30** (1991) 1620.
- 14) S. Nakamura, Y. Harada and M. Senoh: Appl. Phys. Lett. **58** (1991) 2021.
- 15) Z. J. Yu, J. H. Edgar, A. U. Ahmed and A. Rys: J. Electrochem. Soc. **138** (1991) 196.
- 16) F. Bozso and P. Avouris: Phys. Rev. B **38** (1988) 3937.
- 17) S. J. Pearton, J. W. Corbett and T. S. Shi: Appl. Phys. A **43** (1987) 153.
- 18) N. M. Johnson, R. D. Burnham, R. A. Street and R. L. Thornton: Phys. Rev. B **33** (1986) 1102.
- 19) P. S. Nandhra, R. C. Newman, R. Murray, B. Pajot, J. Chevallier, R. B. Beall and J. J. Harris: Semicond. Sci. Technol. **3** (1988) 356.
- 20) J. Chevallier, A. Jalil, B. Theys, J. C. Pesant, M. Aucouturier, B. Rose, C. Kazmierski and A. Mircea: Mater. Sci. Forum **38** (1989) 991.
- 21) A. Bosacchi, S. Franchi, E. Gombia, R. Mosca, P. Allegri, V. Avanzini and C. Ghezzi: Mater. Sci. Forum **38** (1989) 1027.
- 22) E. M. Omeljanovsky, A. V. Pakhomov and A. Y. Polyakov: Mater. Sci. Forum **38** (1989) 1063.
- 23) C. T. Sah, J. Y. C. Sun and J. J. T. Tzou: Appl. Phys. Lett. **43** (1983) 204.
- 24) N. M. Johnson, C. Herring and D. J. Chadi: Phys. Rev. Lett. **56** (1986) 769.
- 25) P. J. H. Denteneer, C. G. Van de Walle, Y. Bar-Yam and S. T. Pantelides: Mater. Sci. Forum **38** (1989) 979.
- 26) S. J. Pearton, W. C. Dautremont-Smith, J. Chevallier, C. W. Tu and K. D. Cummings: J. Appl. Phys. **59** (1986) 2821.
- 27) M. R. Lorenz and B. B. Binkowsky: J. Electrochem. Soc. **109** (1962) 24.
- 28) H. Amano, I. Akasaki, T. Kozawa, K. Hiramatsu, N. Sawaki, K. Ikeda and Y. Ishii: J. Lumin. **40** (1988) 121.
- 29) F. Bozso and P. Avouris: Phys. Rev. B **38** (1988) 3943.