Activation of p-Type GaN in a Pure Oxygen Ambient

Activation of p-Type GaN in a Pure Oxygen Ambient

Tzu-Chi WEN, Shih-Chang LEE, Wei-I LEE[1], Tsung-Yu CHEN[2], Shin-Hsiung CHAN[2] and Jian-Shihn TSANG[2]

Department of Electrophysics, National Chiao Tung University, HsinChu, Taiwan 300, Republic of China
[1]*Microelectronics and Information Systems Research Center, National Chiao Tung University, HsinChu, Taiwan 300, Republic of China*
[2]*Advanced Epitaxy Technology Inc., HsinChu, Taiwan 303, Republic of China*

In this study, we activated p-type GaN in a pure oxygen ambient by rapid thermal annealing. The sheet resistance of p-type GaN was greatly reduced from $> 10^7 \, \Omega/\square$ to $7.06 \times 10^4 \, \Omega/\square$ after annealing in oxygen ambient at 500°C. The photoluminescence intensity of blue emission increased by one order of magnitude compared to the as-grown sample. Moreover, the sheet resistance of p-type GaN annealed in pure oxygen ambient is lower than that of p-type GaN annealed in nitrogen ambient. The carrier concentrations of the samples annealed in oxygen ambient are higher than those annealed in nitrogen ambient. The better activation of p-type GaN in oxygen ambient is due to the higher activity of oxygen than that of nitrogen. Oxygen would remove hydrogen that passivates Mg atoms by forming H_2O at a lower temperature.

KEYWORDS: p-type GaN, activation, rapid thermal annealing, oxygen ambient, nitrogen ambient, Hall measurement, photoluminescence, hydrogen

Group III nitrides are highly promising for applications in blue and ultraviolet optoelectronic devices,[1] high-temperature, high-power transistors[2,3] and solar-blind ultraviolet detectors,[4] because of the wide bandgap varying from 1.9 eV for InN to 6.3 eV for AlN. The key progress in the development of GaN-based devices is the achievement of p-type doping material by using magnesium (Mg) as an acceptor dopant in metalorganic chemical vapor deposition (MOCVD).[5,6] However, as-grown Mg-doped GaN films have a high resistivity and do not have any p-type conduction. A post-treatment, either low-energy electron-beam irradiation (LEEBI)[5] or a N_2-ambient thermal annealing,[6] is typically required to activate the dopants. It has been suggested that the hole compensation is largely due to hydrogen passivation of the Mg acceptor during MOCVD growth.[7]

Ho *et al.*[8] and Koide *et al.*[9] recently indicated that annealing in a partial oxygen ambient improves ohmic contacts of p-type GaN. Ho *et al.* and Chen *et al.*[10] found that NiO islands and/or the amorphous Ni–Ga–O phase may lead to a low-resistance ohmic contact to p-GaN. However, Koide *et al.* provided different hypotheses on the reduction of contact resistance, suggesting that the oxygen content ambient might remove the hydrogen atoms in the p-type GaN and cause reactivation of the Mg atoms, subsequently forming a high hole concentration in the surface of p-GaN. Hull *et al.*[11] noted that oxygen heavily influences the activation of p-type GaN. According to their results, the resistivity of p-GaN is low when 10% O_2 is added to the annealing ambient. Moreover, incorporating oxygen into the activation ambient enhances the outdiffusion of H from the p-type GaN.

In this study, we have successfully activated p-type GaN in a pure oxygen ambient by rapid thermal annealing (RTA). This study also demonstrates that oxygen influences the activation of p-type GaN. Hall measurements reveal that the sheet resistance of p-type GaN annealed in a pure O_2 ambient is lower than that of p-type GaN annealed in pure N_2 ambient. Meanwhile, the hole concentration of the p-GaN annealed in pure O_2 is higher than that of the p-type GaN annealed in pure N_2. Furthermore, the temperature required for activation in a pure O_2 ambient (550°C) is lower than that in a N_2 ambient (850°C). Our results further demonstrate that annealing in a pure O_2 ambient is a more efficient means of activating p-type

GaN.

Mg-doped GaN epitaxial layers were grown on a sapphire (0001) substrate by low-pressure MOCVD in an EMCORE D180 reactor system. The growth was carried out at 100–300 Torr, and the temperatures ranged from 1000°C to 1060°C. Trimethylgallium (TMGa), ammonia (NH_3) and bis-cyclopentadienylymagnesium (Cp_2Mg) were used as Ga, N, and Mg sources, respectively. The substrate was initially heated to 1080°C in hydrogen ambient for 1 min and then lowered to 510°C to grow the GaN buffer layer. Finally, the temperature was elevated to 1040°C in order to grow $2 \, \mu m$ unintentionally doped and $1.5 \, \mu m$ Mg-doped GaN films. After growth, the films were semi-insulating with resistivities of $> 10^7 \, \Omega$ at 300 K.

The GaN films were then annealed in a JEPFIRST RTA system under a pure O_2 or N_2 ambient. The annealing temperature ranged from 500 to 900°C, and the annealing time of all samples was 150 seconds. After annealing, each sample was characterized by room-temperature (RT) Hall effect and RT photoluminescence (PL) measurements. PL was measured at room temperature with a 325 nm line of a He-Cd laser. After PL measurement, Pd (20 nm) film was deposited on GaN film by electron-beam evaporation for Hall measurements. Hall measurements were taken by the van der Pauw method.
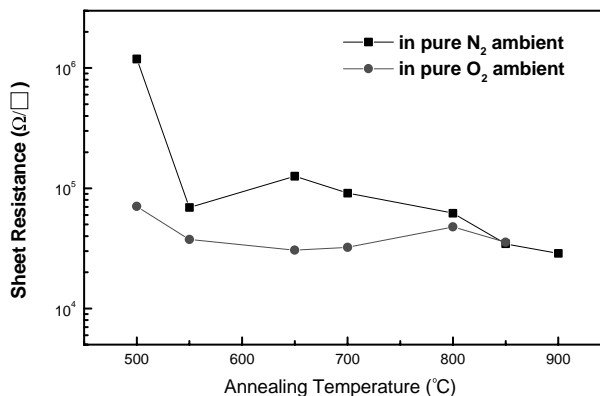

Fig. 1. Sheet resistances of the p-type GaN being as a function of annealing temperature in various annealing ambient gases. The annealing time of all samples was 150 seconds.
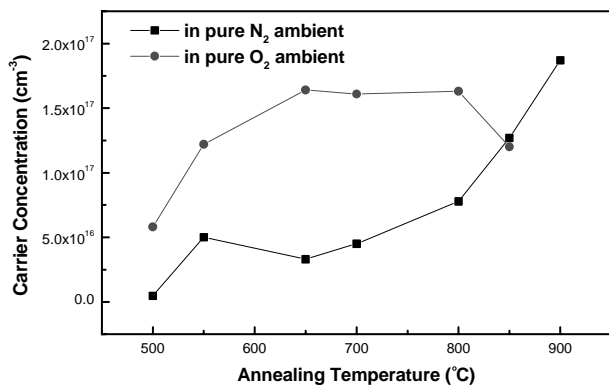
Fig. 2. Hole concentrations against activation temperature in different annealing ambient gases.
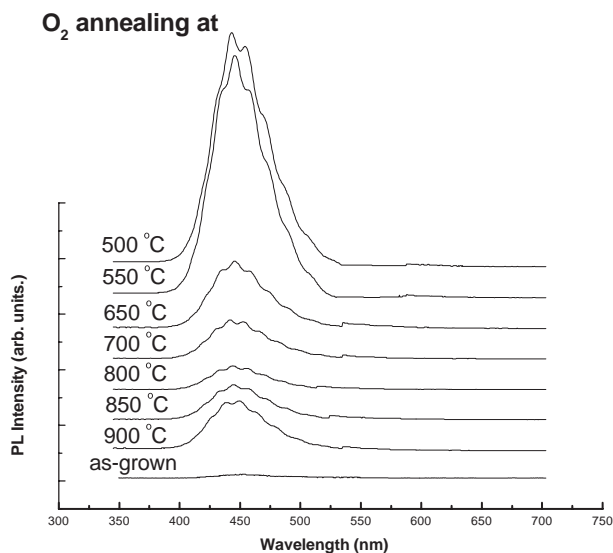
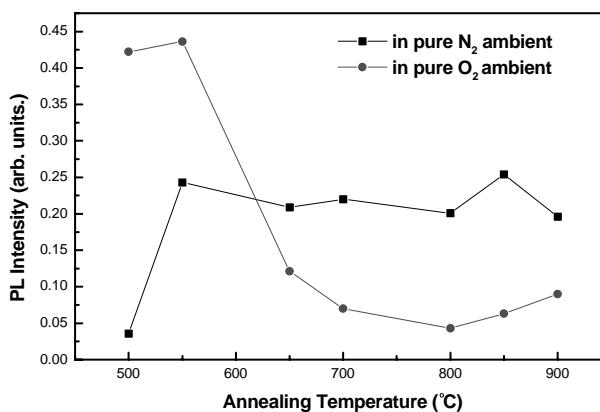Fig. 3. Typical PL spectra of p-type GaN annealed in a pure O_2 ambient.

Fig. 4. PL intensity of blue and deep-level (DL) emissions for p-type GaN as a function of annealing temperature in N_2 and O_2 ambient.

Figure 1 shows the sheet resistance of the p-type GaN as a function of annealing temperature in various annealing ambient gases. In pure N_2-ambient thermal annealing, the sheet resistance exceeds $1 \times 10^6 \, \Omega/\square$ at 500°C. This value resembles that of the as-grown sample. Notably increasing the annealing temperature to 550°C reduces the sheet resistance by over one order of magnitude (from $1.19 \times 10^6 \, \Omega/\square$ at 500°C to $6.94 \times 10^4 \, \Omega/\square$ at 550°C). At temperatures > 600°C, the sheet resistance decreases with an increase of the annealing temperature. In contrast, the sheet resistance is of almost the same order in a pure O_2 ambient at an annealing temperature ranging between 500°C and 850°C. As the annealing temperature reaches 900°C in a pure O_2 ambient, the sheet resistance of p-GaN becomes too high for detection. Moreover, the sheet resistances of the samples annealed in O_2 ambient are lower than those of samples annealed in N_2 ambient from a low temperature (500°C) to a high one (850°C).

Figure 2 illustrates the hole concentrations against the activation temperature in different annealing ambient gases. With the annealing temperature increasing from 500 to 900°C, the hole concentration increases from 4×10^{15} to 1.8×10^{17} cm^{-3} in a pure N_2 ambient. The O_2-annealed samples display the same trend in hole concentration as the N_2-annealed ones ranging from 500 to 650°C. However, the hole concentration becomes saturated at annealing temperatures ranging between 650 and 800°C. At temperatures exceeding 800°C, the hole concentration decreases when increasing the annealing temperature for the O_2 annealing ambient. Notably, the hole concentration of samples annealed in O_2 at 550°C is nearly the same as that of samples annealed in N_2 at 850°C. This finding implies that the activation of p-type GaN in O_2 ambient is more efficient than that in N_2 ambient at a low temperature.

RT PL spectra reveal that the annealing ambient affects the optical properties of p-type GaN. Figure 3 displays a typical PL spectrum of the p-type GaN annealed in pure O_2 ambient. Comparing the PL intensity of the as-grown sample with that of the sample annealed at 500°C reveals that annealing in O_2 ambient enhances the optical properties of these p-type GaN. Moreover, the PL intensity decreases with the annealing temperature from 500 to 800°C but becomes slightly saturated from 800 to 900°C. This decrease suggests that increasing the annealing temperature in O_2 ambient could lead to slight degradation with the generation of optical defects. Therefore, activating p-type GaN in O_2 ambient at a low temperature is

preferable.

Figure 4 shows the PL intensity of blue and deep-level (DL) emissions[7] for p-type GaN as a function of annealing temperature in N_2 and O_2 ambient. As mentioned above, the PL intensity decreases with an increase of the annealing temperature in O_2 ambient. However, the PL intensity is extremely weak for 500°C annealing in N_2 ambient. This intensity resembles that of the as-grown sample. Namely, the sample annealed at 500°C in N_2 ambient is not completely activated. For the temperature exceeding 550°C, the PL intensity is raised by one order of magnitude. This finding suggests that annealing in N_2 ambient should increase the annealing temperature. Furthermore, the trend of PL intensity depends on whether the annealing temperature in N_2 ambient closely corresponds to the tendency of sheet resistance.

It has been reported that forming Mg–H neutral complexes causes hole compensation, as well as DL and weak blue emissions in PL.[7] In this study, the as-grown sample and that annealed in N_2 ambient at 500°C both have an extremely high resistivity in electrical characterization and very weak blue emission in terms of optical properties. This finding suggests that Mg–H neutral complexes degrade the electrical and optical properties in the as-grown sample. After the activation

in O_2 ambient above 500°C or in N_2 ambient above 550°C, the sheet resistance drops to the order of 10^5 $\Omega \cdot cm$. The PL intensity of blue emission also increases one order magnitude higher than that of the as-grown sample. This improvement in electrical and optical properties suggests that p-type GaN can be activated at a suitable temperature in either O_2 or N_2 ambient.

Koide *et al.*[9] have indicated that adding O_2 to N_2 gas reduces the specific contact resistance and sheet resistance of the p-type GaN films after annealing at the 500 to 600°C. According to their results, the O_2 gas removes hydrogen atoms, which bond with Mg atoms and subsequently generates high hole concentrations near the p-type GaN surface. Furthermore, Hull *et al.*[11] recently reported that SIMS data suggested that the presence of oxygen in the activation process enhances the removal of H, which passivates the Mg atoms. Our results present a similar tendency. According to Fig. 1, the sheet resistances of the samples annealing in O_2 ambient are lower than those of the samples annealed in N_2 ambient from 500 to 850°C. In addition, the carrier concentration, samples annealed in O_2 ambient are higher than those annealed in N_2 ambient. At a higher annealing temperature, compressive strain is introduced into the GaN layers.[12] This strain might affect the electrical characterization of p-type GaN. It is worth noticing the electrical characterization of the samples annealed at a low temperature. For conventional processes to activate p-type GaN, annealing for more than 30 min (in a furnace) above 750°C in N_2 ambient is required. However, by using O_2 ambient instead of N_2 ambient, p-type GaN can be activated at a lower temperature and a higher carrier concentration can be obtained. Moreover, the optical property degrades slightly with increasing annealing temperature in O_2 ambient. The reason why this degradation occurs remains unclear. Further studies are required in order to clarify this optical degradation.

On the basis of the above results, we can infer that a mechanism is responsible for activating p-type GaN. As the annealing temperature exceeds a certain temperature, hydrogen atoms that passivate Mg begin to be removed in either O_2 or N_2 ambient. As the annealing temperature increases, more hydrogen is removed and the sheet resistance of the p-type GaN is reduced. However, the activity of oxygen is higher than that of nitrogen. Oxygen would remove hydrogen that passivated Mg atoms by forming H_2O at a low temperature, thus explaining why the annealing temperature in O_2 ambient is lower than that in N_2 ambient.

In summary, this study activated p-type GaN in a pure O_2 ambient. For the O_2-ambient annealed samples, the sheet resistances are lower than those of samples annealed in N_2 ambient from 500 to 850°C. For the carrier concentrations, samples annealed in O_2 ambient have higher carrier concentrations than those in N_2 ambient. The reason for the activation of p-type GaN in O_2 ambient is that the activity of oxygen is higher than that of nitrogen. Furthermore, oxygen would remove hydrogen that passivates Mg atoms by forming H_2O at a low temperature.

1) S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku and Y. Sugimoto: Jpn. J. Appl. Phys. **35** (1996) L74.
2) Z. Fan, S. N. Mohammad, O. Aktas, A. E. Botchkarev, A. Salvador and H. Morkoc: Appl. Phys. Lett. **69** (1996) 1229.
3) Q. Chen, M. A. Khan, J. W. Wang, C. J. Sun, M. S. Shur and H. Park: Appl. Phys. Lett. **69** (1996) 794.
4) G. Y. Xu, A. Salvador, W. Kim, Z. Fan, C. Lu, H. Tang, H. Morkoc, G. Smith and M. Estes: Appl. Phys. Lett. **71** (1997) 2154.
5) H. Amano, M. Kito, K. Hiramatsu and I. Akasaki: Jpn. J. Appl. Phys. **28** (1998) L2112.
6) S. Nakamura, T. Mukai, M. Senoh and N. Iwasa: Jpn. J. Appl. Phys. **31** (1992) L139.
7) S. Nakamura, N. Iwasa, M. Senoh and T. Mukai: Jpn. J. Appl. Phys. **31** (1992) 1258.
8) J.-K. Ho, C.-S. Jong, C. C. Chiu, C.-N. Huang, K. K. Shih, L. C. Chen, F. R. Chen and J. J. Kai: J. Appl. Phys. **86** (1999) 4491.
9) Y. Koide, T. Maeda, T. Kawakami, S. Fujita, T. Uemura, N. Shibata and M. Murakami: J. Electron. Mater. **28** (1999) 341.
10) L. C. Chen, F. R. Chen, J. J Kai, L. Chang, J. K. Ho, C. S. Jong, C. C. Chiu, C. N. Huang, C. Y. Chen and K. K. Shih: J. Appl. Phys. **86** (1999) 3826.
11) B. A. Hull, S. E. Mohney, H. S. Venugopalan and J. C. Ramer: Appl. Phys. Lett. **76** (2000) 2271.
12) J. M. Hayes, M. Kuball, A. Bell, I. Harrison, D. Korakakis and C. T. Foxon: Appl. Phys. Lett. **75** (1999) 2097.