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Performance of InGaN/GaN light-emitting diodes grown using NH_3 with oxygen-containing impurities

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The performance of InGaN/GaN light-emitting diodes (LEDs) fabricated using NH_3 was varied by intentionally adding H_2O, O_2, or CO. The oxygen concentration in the active layer varied with the type of impurity, which was related to the binding energy of the impurity. When a small amount of oxygen was incorporated in the InGaN active layer without Si doping through an oxygen-containing impurity, the light output power of the LED was improved. On the other hand, the light output power of the LED gradually deteriorated with increasing oxygen concentration. The oxygen-containing impurities affected the light output power of the LEDs. When NH_3 with any oxygen-containing impurities was purified using a purification system giving a guaranteed impurity concentration of less than 10 ppb, the light output power of the LED was recovered to that of the LED fabricated with pure NH_3. © 2014 The Japan Society of Applied Physics

1. Introduction

Nitride-based light-emitting diodes (LEDs) emitting in the blue region with a very high external quantum efficiency (EQE) of over 80% have been achieved.[1)] To obtain LEDs with such high light output power, many problems have been overcome. For example, threading dislocations are one of the most critical problems to be solved.[2,3)] Patterned sapphire substrates have been used for improving light extraction efficiency,[4–10)] and many LED structures have been proposed to improve LED efficiency.[11–15)] It is also important to use high-purity materials because some impurities, such as oxygen, act as non-radiative recombination centers.[16)] In addition, an InGaN/GaN multiple quantum well (MQW) layer exhibits a specific deep emission similar to the yellow photoluminescence (PL) observed in GaN.[17,18)] Meanwhile, we previously quantitatively investigated the effect of an oxygen-containing impurity on LED performance by intentionally adding H_2O to NH_3.[19)] It was found that the oxygen concentration in the MQWs increased with increasing H_2O concentration in NH_3 and that the output power of the LED decreased with increasing oxygen concentration in the active layer. Thus, the oxygen concentration is one of the critical issues affecting LED performance. We also revealed that oxygen is easily incorporated in the InGaN layer. It is well known that the EQE of LEDs decreases with increasing emission wavelength from the green to red regions.[20)] Thus, reducing the oxygen concentration is important for LEDs consisting of InGaN MQWs with a high In composition. On the other hand, Si doping into the barrier and/or well layers improves the optical properties and LED performance.[21–25)] These phenomena are attributed to the suppression of the internal electric field, which can enhance the carrier recombination process in MQWs. Similarly to the effect of Si doping, oxygen doping can also improve the light output power of LEDs since oxygen acts as a donor in nitride-based materials.[26,27)] Thus, oxygen could not only act as a non-radiative recombination center but also enhance the carrier recombination process, which has a trade-off relationship with the efficiency. Although we investigated the effect of intentionally adding H_2O to NH_3 gas on the performance of LEDs, the effect of other impurities containing oxygen should be investigated because H_2O is not only involved in the oxygen-containing impurity. In this paper, we focused on impurity gases containing oxygen such as O_2 and CO and investigated their effect on the performance of InGaN/GaN LEDs.

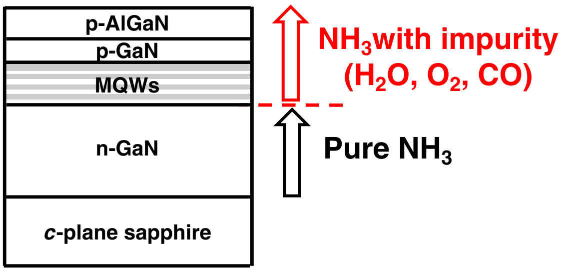


Fig. 1. (Color online) Schematic diagram of LED structure. NH_3 gas with an impurity was used in the growth of the InGaN/GaN MQW layer, the p-type AlGaN electron-blocking layer, and the p-type GaN contact layer.

2. Experimental procedure

A schematic diagram of the LED structure used in this study is shown in Fig. 1. We prepared an LED composed of a 25-nm-thick low-temperature GaN buffer layer, a 5.5-µm-thick n-type GaN:Si layer, six-period MQWs of $In_{0.1}Ga_{0.9}N$ (1.35 nm)/GaN (9.5 nm) pairs, a 12-nm-thick p-type AlGaN:Mg electron-blocking layer, and a 126-nm-thick p-type GaN:Mg layer on a *c*-plane sapphire substrate via metalorganic vapor phase epitaxy (MOVPE). Here, note that Si was not doped into the barrier and/or well layers, meaning that there is room to improve the device performance using a donor impurity such as oxygen. The growth temperatures of the MQWs and the p-type layers were 740 and 1050 °C, respectively. The reactor pressure was maintained at atmospheric pressure during growth. Trimethylgallium (TMGa), trimethylaluminum (TMAl), and trimethylindium (TMIn) were used as precursors. High-purity NH_3 (99.999%) was used as the nitrogen source. NH_3 gas with added O_2 or CO was used after the growth of n-type GaN, i.e., from the start of the growth of the MQWs, as shown in Fig. 1. The O_2 or CO concentration in NH_3 was varied from 12.5 to 4000 ppb.

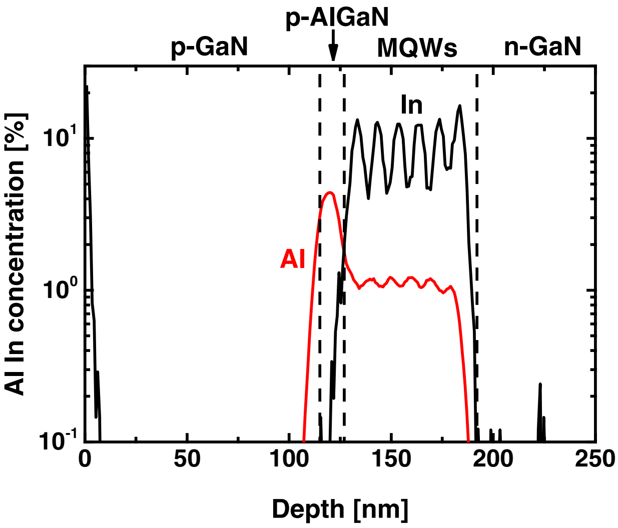


Fig. 2. (Color online) Concentrations of Al and In in LED.

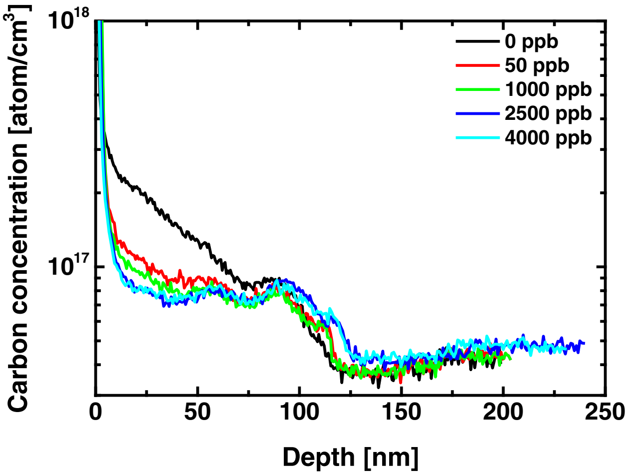


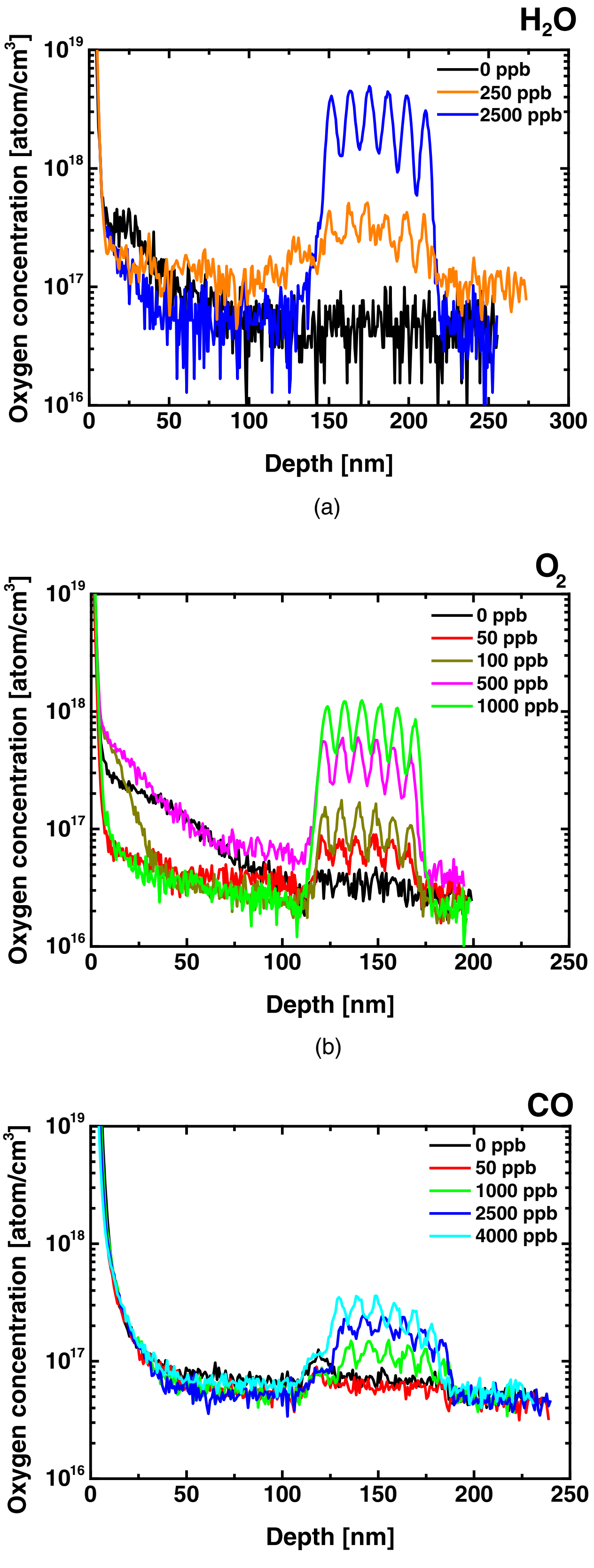
Fig. 3. (Color online) SIMS depth profiles of carbon concentration in LEDs grown using NH_3 gas containing CO.

Here, O_2 or CO was added to NH_3 gas using an O_2 or CO addition system, respectively, and the O_2 or CO concentration in NH_3 gas was measured using an optical analyzing system. The results obtained in a previous study using NH_3 with H_2O are also shown.

3. Results and discussion

First, secondary ion mass spectroscopy (SIMS) was performed. The SIMS depth profiles of Al and In are shown in Fig. 2, which were used to identify the region in which each nitride alloy was grown. To reveal the effect of the H_2O, O_2, and CO concentrations in NH_3 gas, the impurity concentrations in the epilayer were analyzed. The impurities detected were oxygen, carbon, silicon, and hydrogen. Only the oxygen concentration changed with changing H_2O, O_2, and CO concentrations. Figure 3 shows SIMS depth profiles of the carbon concentration for the LEDs grown using NH_3 containing CO. No significant difference in the carbon concentration was detected among all samples, which indicated that carbon does not affect the device performance and that it is not incorporated easily in the epilayer. Only the profile of 0 ppb showed a tale figure from the surface; we believe that this tale can be attributed to unexpected measurement results due to, for example, the rough surface morphology, and that it is unrelated to the actual carbon concentration. This result was consistent with the case of using methyl groups in metal organic sources under typical growth conditions of GaN with atmospheric pressure, a V/III ratio of the order of 10^3, and a high growth temperature, which is similar to our growth conditions of the p-type layers. Generally, a high V/III ratio, high-pressure, and high growth temperature suppress the incorporation of carbon.[28–30] Figure 4 shows the SIMS depth profiles of the oxygen concentration for the LEDs grown using H_2O, O_2, or CO with different impurity concentrations in NH_3. The H_2O, O_2, and CO concentrations in NH_3 were in the ranges of 0–2500, 0–1000, and 0–4000 ppb, respectively. The oxygen concentration increases with increasing concentration of each impurity; however, at the same impurity concentration the oxygen concentration differs with the impurity. As can be seen in Fig. 4(b), the profiles for 0, 100, and 500 ppb showed the tale figures from the surface, which is similar to the result for the carbon concentration profile of 0 ppb shown in Fig. 3. Figure 5 shows a summary of the relation between the oxygen concentration in the InGaN well layer and the impurity concentration for each impurity. Under the impurity concentration of 100 ppb, the highest oxygen concentration was achieved when H_2O was added. The oxygen concentration depends on the binding energy of the impurity; those of H_2O, O_2, and CO are 463, 494, and 615 kJ/mol, respectively.[31] With decreasing binding energy of the impurity, the oxygen concentration in the InGaN well layer increased. These results demonstrate that H_2O has the greatest effect on the oxygen concentration among the three impurities. A detailed explanation of the difference in the oxygen incorporation between the InGaN well and GaN barrier layers based on the consideration of stoichiometry was given in Ref. 7. When MQWs are grown under a nonstoichiometric condition, oxygen can be incorporated into the MQWs. In particular, oxygen from H_2O, CO, or O_2 can be incorporated easily into MQWs composed of InGaN with a high In composition grown at a lower temperature. Oxygen-containing impurities strongly affect the light output power of green LEDs.

Figures 6(a) and 6(b) show the EL intensity as functions of the oxygen concentration in InGaN well and the impurity concentration in NH_3, respectively, at an injection current of 20 mA. From here, the standard is defined as the LED fabricated with pure NH_3 gas. As shown in Fig. 6(a), the EL intensity markedly decreased with increasing oxygen concentration at high oxygen concentrations. However, the EL intensity was improved when a small amount of oxygen was included in the active layer. The samples consist of a non-Si-doped active layer. There are many reports on improving the PL or EL light output power by doping Si in the active layer. The improvement in EL intensity by the doping of a small amount of oxygen, with a concentration of approximately $1 \times 10^{17}/cm^3$ is due to its similar effect to Si doping. We measured the internal quantum efficiency (IQE) of the LEDs grown using NH_3 containing O_2 or CO as shown in Fig. 7. The IQE was evaluated by comparing the PL intensity at room temperature with that at a cryogenic temperature using a He–Cd laser with a 325 nm wavelength. It was found that



(a)

(b)

(c)

Fig. 4. (Color online) SIMS depth profiles of oxygen concentration in LEDs grown using NH_3 gas containing (a) H_2O, (b) O_2, and (c) CO.

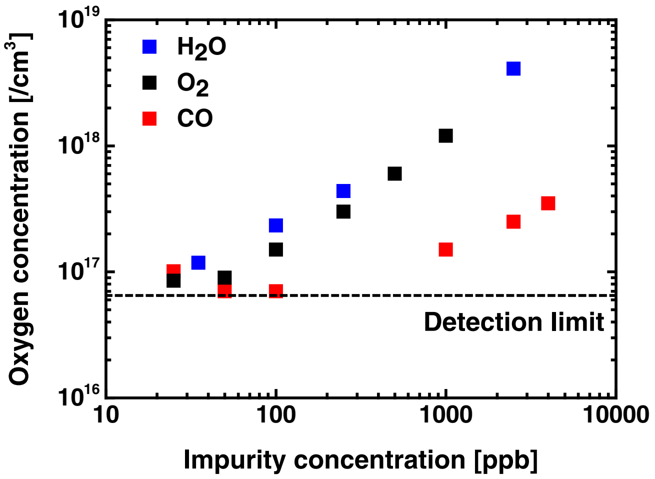
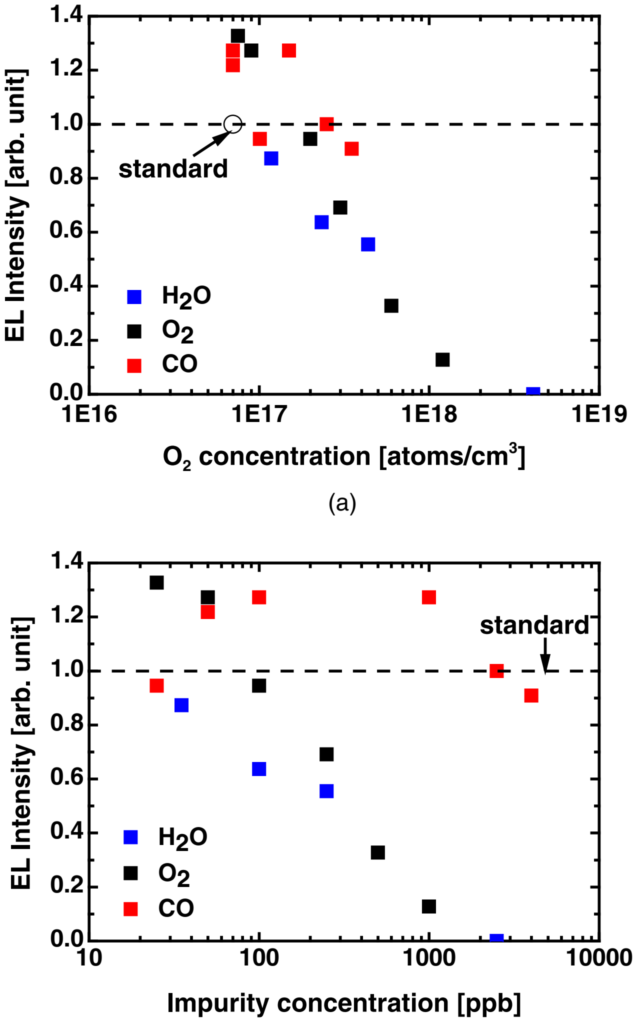


Fig. 5. (Color online) Oxygen concentration in InGaN well layer as a function of the impurity concentration in NH_3 gas for H_2O, O_2, and CO impurities.



(a)

(b)

Fig. 6. (Color online) EL intensity as functions of (a) oxygen concentration in InGaN well and (b) impurity concentration in NH_3 gas.

the EL intensity was strongly related to the IQE, which revealed that the optical properties of the LEDs are affected by the oxygen concentration in the active layer. Finally, the current–voltage (*I*–*V*) characteristics of LEDs grown using NH_3 containing O_2 or CO under reverse bias were investigated, as shown in Fig. 8. The leakage current slightly

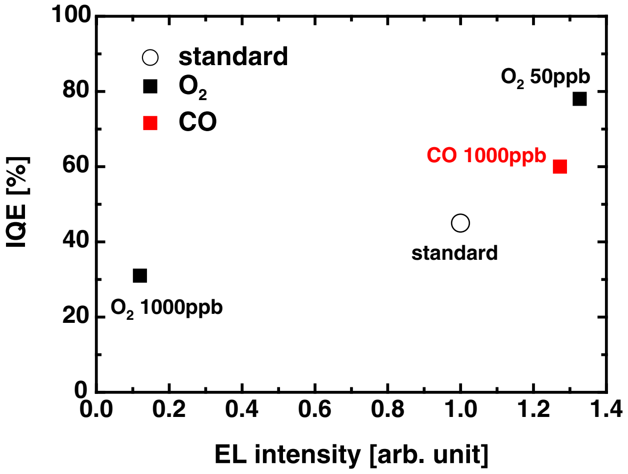


Fig. 7. (Color online) Relationship between IQE and EL intensity.

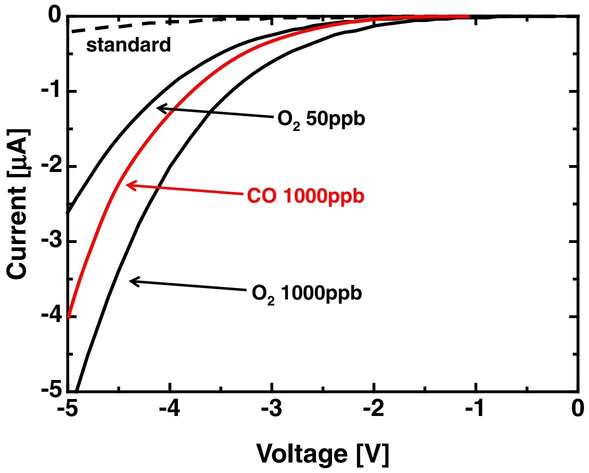


Fig. 8. (Color online) *I–V* characteristics under reverse bias.

increased with increasing oxygen concentration in the active layer. It was thus determined that the oxygen in the InGaN/GaN MQWs was the cause of the leakage current. As shown in Fig. 7, the IQE also decreased when a high concentration of oxygen was doped. Thus, the light output power of the device deteriorated due to an increase in the leakage current and the deterioration of the IQEs. On the other hand, although the EL intensity was improved in the low-oxygen-concentration region, the leakage current was increased. As compared with an optimum Si doping concentration of the order of $10^{18}/cm^3$[32,33] the highest EL intensity was obtained at a lower oxygen concentration of around $1 \times 10^{17}/cm^3$. To clarify the reason for the difference between the optimum impurity concentrations of oxygen and Si of one order of magnitude, we take into account the Si doping in both the barrier and well layers. Oxygen more efficiently acts as non-radiative recombination centers than Si.[16] Thus, when oxygen is doped in both the barrier and well layers, the optimum oxygen concentration is expected to be smaller than that for Si. Moreover, considering a co-doping of oxygen and Si, only Si doping could be effective for improving the LED efficiency. In this study, Si was not doped into the MQWs; the study of the effect of an oxygen-related impurity in Si-doped MQWs on the light output power of LEDs is a future task.

The LED structure is fabricated using various gases and materials such as carrier and doping gases, and metal–organics. The componential analysis of impurities is typically evaluated at the order of ppm. However, oxygen-containing impurities with a concentration of less than 100 ppb were found to affect the light output power of LEDs as shown in Fig. 6(b). Furthermore, the concentration of each impurity must be regulated. To maintain the purity of NH_3, we introduced an NH_3 purifier system that guarantees an impurity concentration of less than 10 ppb in NH_3. Here, the NH_3 purifier system was used for all the layers including the low-temperature GaN buffer layer and n-type GaN layer. Using the NH_3 purifier, we confirmed that the EL intensity of an LED using NH_3 grown with various impurities recovered to the same level as that of an LED grown using pure NH_3.

4. Summary

We quantitatively investigated the influence of oxygen-containing impurities, such as H_2O, CO, and O_2, in NH_3 on the light output power of InGaN/GaN LEDs. The oxygen concentration in the active layer differed with the impurity, which is related to the different binding energies of the impurities. The light output power of the LED was strongly affected by the oxygen concentration in the active layer. When a small amount of oxygen, with a concentration from 7×10^{16} to $1 \times 10^{17}/cm^3$ was incorporated in the InGaN active layer without Si doping through an oxygen-containing impurity, the light output power of the LED was improved, whereas the light output power of the LED gradually deteriorated with increasing oxygen concentration above $2 \times 10^{17}/cm^3$. These phenomena are attributed to both the advantageous and disadvantageous effects of oxygen on the light output power. When NH_3 with any oxygen-containing impurity was purified using a purification system giving a guaranteed impurity concentration of less than 10 ppb, the light output power of the LED was recovered to that of the LED fabricated with pure NH_3.

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