Improving the Performance of Green LEDs by Low-Temperature Annealing of p-GaN with PdZn

Ja-Yeon Kim, a,c Min-Ki Kwon, a,c Seong-Ju Park, a,c Sunwoon Kim, b Je Won Kim, b and Yong Chun Kim b

a Department of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Korea
b Samsung Electronics Company, Limited, Suwon 443-743, Korea

This article reports the electrical properties of p-GaN annealed at low activation temperature by using a PdZn film in green InGaN/GaN multiquantum well (MQW) light-emitting diodes (LEDs). Electroluminescence (EL) intensity of green MQW LED annealed at 600 °C using PdZn was improved by 35% at 20 mA compared to that annealed at 800 °C without PdZn. These results are attributed to an increase of the hole concentration of p-GaN due to removal of hydrogen in p-GaN by PdZn and a decrease in thermal damage of MQW at low activation temperature. © 2009 The Electrochemical Society. [DOI: 10.1149/1.3093094] All rights reserved.

Manuscript submitted November 3, 2008; revised manuscript received February 11, 2009. Published March 10, 2009.

For application to displays, traffic signals, and solid-state lighting, InGaN/GaN multiquantum well (MQW) blue and green light-emitting diodes (LEDs) have recently been extensively used as highly efficient light sources. In particular, the longer wavelength pure green, yellow-green, and yellow LEDs are essential for producing full color displays. However, it has been reported that the internal quantum efficiency of green LEDs is only 5–10% due to the low crystal quality of InGaN layers with a high indium content over 20% and the high piezoelectric field in InGaN/GaN green MQW LEDs. Because of the high volatility of indium, green MQW LEDs with indium contents over 20% are easily damaged by the high-temperature annealing process required for dopant activation.

To enhance the efficiency of the LED, p-GaN with a high hole concentration is also required to eliminate high parasitic resistance and imbalance between the electron and hole concentration in the active layer. One of the major reasons for a low hole concentration in the p-GaN layer is the presence of Mg–H complexes which hinder the activation of Mg dopants. To obtain p-GaN by breaking the Mg–H complex, as-grown Mg-doped GaN films should be annealed at a temperature above 700 °C in an inert gas ambient.

Recently, it was reported that a Ni film deposited on top of the p-GaN layer increases the hole concentration of p-GaN by acting as a hydrogen desorber. The hole concentration of p-GaN annealed with a Ni film was significantly increased over that of p-GaN without a film when the annealing was performed at temperatures lower than 700 °C.

In this study, we employed a PdZn film during the low-temperature annealing of p-GaN layers for the fabrication of high-efficiency InGaN/GaN green MQW LEDs. Pd is believed to act as a hydrogen desorber like Ni in Mg-doped p-GaN layers because Pd can remove thermally activated H ions out of p-GaN, resulting in an increase of hole concentration in p-GaN. Moreover, Pd-based alloys such as Pd–Cu, Pd–Ni, and Pd–Zn have been reported to enhance the separation selectivity of production of H2 and CO2 during reforming the methanol (CH3OH + H2O → CO2 + 3H2) compared to parent Pd metal.

In this work, we found that a PdZn alloy on the Mg-doped p-GaN surface enhances the removal of hydrogen from p-GaN and as a consequence, the hole concentration of p-GaN is remarkably increased at low temperatures and the performance of green LED is improved.

The InGaN/GaN green MQW LEDs with a green emission at 530 nm were grown on a c-plane sapphire substrate by metalorganic chemical vapor deposition (MOCVD). The green LEDs consisted of the following layers: a 2 μm thick Si-doped GaN layer; undoped InGaN/GaN MQWs consisting of 5 periods of 8 nm GaN barriers and 2 nm InGaN wells; and a Mg-doped GaN layer with a thickness of 0.1 μm. The Mg-doped GaN was activated at 600 °C by using a 10-nm-thick PdZn film deposited on it by E-beam evaporation. After the annealing process, the PdZn film was removed by dipping in HNO3 for 30 min at room temperature, rinsing in deionized water for 1 min, and drying using a stream of N2 blower. For comparative study, the Mg-doped GaN without PdZn was activated at 800 °C. To investigate the electrical and optical characteristics of green LEDs with and without the PdZn film, green LEDs were fabricated as follows. For the electrode formation, mesa patterns were formed by an inductively coupled plasma etching process using Cl2/CH3H2/Ar gases. An Ag/indium tin oxide (ITO) layer was used as a transparent contact layer and a Cr/Au layer (50/350 nm) was deposited by electron-beam evaporation onto both exposed transparent ITO and n-GaN layers to serve as the p- and n-bonding pads.

The effect of thermal annealing on the optical properties of MQWs in green LEDs was studied using photoluminescence (PL) measurement. Figure 1 shows PL spectra of green LEDs annealed for 5 min at various annealing temperatures. The integrated PL intensity of a green LED annealed at 600 °C was decreased...
by only 2% compared to that without annealing. However, the integrated PL intensities of green LEDs annealed at 800 and 900°C were dramatically decreased by 48 and 91%, respectively. It was recently reported that indium contents of over 20% induce a dramatic degradation of luminescence in InGaN/GaN MQW LEDs due to thermodynamically unstable characteristics of indium.\textsuperscript{7,12,16} Annealing of MQW at high temperature increases the interdiffusion and volatility of indium, resulting in the formation of defects in green MQWs and deteriorated PL intensity as shown in Fig. 1. To obtain high-efficiency green LEDs, it is therefore desirable to anneal green LEDs with Mg-doped GaN at low temperature.

Figure 2 shows the hole concentration and hole mobility in p-GaN as a function of annealing temperature. The Mg-doped p-GaN (1 μm thick) grown on an undoped GaN (1 μm)/sapphire (0001) substrate by MOCVD. The hole concentrations of p-GaN, with and without PdZn, were measured with increasing annealing temperature from 500 to 800°C for 3 min. The hole mobility decreased with increasing hole concentration due to carrier–carrier scattering, as shown in Fig. 2. It has been reported that thermal annealing above 700°C is needed to break the Mg–H bond of Mg–H complex in Mg-doped GaN.\textsuperscript{10,11} The hole concentration and hole mobility of p-GaN annealed at 800°C without PdZn were $1.4 \times 10^{17}$ cm\textsuperscript{-3} and 9.1 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, respectively. However, a hole concentration of $3.0 \times 10^{17}$ cm\textsuperscript{-3} was achieved by annealing Mg-doped GaN with a PdZn film at 500°C. Furthermore, the highest hole concentration of $5.0 \times 10^{17}$ cm\textsuperscript{-3} with a hole mobility of 7.5 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} was obtained at an annealing temperature of 600°C. This hole concentration is 28 times larger than that of p-GaN without a PdZn film annealed at 600°C. Above 700°C, however, the hole concentrations of p-GaN annealed with PdZn film were decreased because of increase in nitrogen vacancy in p-GaN with increasing annealing temperature.\textsuperscript{18}

In order to understand the effect of PdZn film on hydrogen removal at low temperatures, the hydrogen concentration in the Mg-doped GaN was measured using secondary ion mass spectrometry (SIMS). Figure 3 depicts the hydrogen depth profiles of Mg-doped GaN annealed at 600°C with and without PdZn film. This result shows that the hydrogen concentration of Mg-doped GaN with a PdZn film was much lower near the surface region and by a factor of 2 in the bulk p-GaN layer compared to those without PdZn. The removal of hydrogen dissociated from Mg–H by thermal energy in p-GaN can be attributed to a low diffusion barrier for thermally activated H\textsuperscript{+} ion in p-GaN film\textsuperscript{17} and a desorption of hydrogen on the p-GaN surface by PdZn. These results indicate that a removal of hydrogen from p-GaN by PdZn film at low temperature can lead to an increase of hole concentration in p-GaN. Zn in PdZn alloy, which is known as p-dopant for GaN,\textsuperscript{19} may also increase the hole concentration, even though Zn profiles were difficult to measure in p-GaN by SIMS analysis.

To further investigate the effect of annealing temperature with and without PdZn film on the performance of MQW in green LEDs, two kinds of green LEDs annealed at 600°C for 3 min with PdZn (WPZ600) and annealed at 800°C for 3 min without PdZn (WOPZ800) were fabricated. The current–voltage (I–V) characteristics of WPZ600 and WOPZ800 were measured using a parameter analyzer (HP 4155A). As shown in the I–V curves in Fig. 4, the forward voltage of WPZ600 and WOPZ800 was 3.4 and 4.1 V, respectively, at an input current of 20 mA. The series resistance of WPZ600 was estimated to be 15 Ω and the resistance of WOPZ800 was approximately 16 Ω, as shown in Fig. 4a. The slightly lower series resistance of WPZ600 is attributed to a slightly higher hole concentration of p-GaN with a PdZn film. Figure 4b and c shows the forward and reverse leakage currents of WPZ600 and WOPZ800. The forward leakage current of WPZ600 is lower in the forward current region in log scale, and the reverse leakage current in linear scale.

---

Figure 2. (Color online) Hole concentration and mobility of Mg-doped GaN as a function of annealing temperature.

Figure 3. (Color online) Hydrogen concentration of Mg-doped GaN annealed at 600°C with and without PdZn film.

Figure 4. (Color online) I–V curves for WPZ600 and WOPZ800: (a) linear scale, (b) forward-current region in log scale, and (c) reverse-current region in linear scale.
and high volatility of indium in MQW at high annealing temperature. The forward and reverse leakage currents of WPZ600 were much lower, suggesting that the carrier trap centers in the MQW layers were decreased due to the low annealing temperature used when employing the PdZn film.

Figure 5 shows the typical output power-current (I-L) characteristics of WPZ600 and WOPZ800 as a function of input current. The electroluminescence (EL) intensity of green LEDs was measured using a 2 cm diameter, calibrated Si photodiode connected to an optical power meter, and placed on top of the LEDs. The enhancement of the EL intensity of WPZ600 was 33% at 20 mA and 34% at 100 mA. These results can be attributed to a decrease of thermal defects in the green MQW layers and a high hole concentration in the p-GaN by low-temperature annealing using a PdZn film. These results clearly demonstrate that the low-temperature annealing of green MQW using a PdZn film is a promising way to increase the efficiency of MQW LEDs.

In summary, the hole concentration of p-GaN annealed at 600°C with a PdZn film was almost 28 times higher than that of p-GaN without PdZn film annealed at the same temperature. SIMS analysis revealed that the hydrogen concentration in p-GaN annealed with a PdZn film was lower, especially near the surface region of p-GaN, because the PdZn film enhanced hydrogen desorption. The forward and reverse leakage currents of WPZ600 were greatly lowered in comparison to WOPZ800 due to fewer defects in the MQW of WPZ600. In addition, compared to WOPZ800, WPZ600 exhibited a lower forward voltage and a 33% enhancement of EL intensity at 20 mA.

Acknowledgments

This work was supported by a BK 21 Program, wide-bandgap optoelectronic device research laboratory of the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (no. R17-2007-078-01000-0), and Samsung Electro-Mechanics Co., Ltd., in Korea.

Gwangju Institute of Science and Technology assisted in meeting the publication costs of this article.

References