Electroluminescence emission from light-emitting diode of p-ZnO/(InGaN/GaN) multiquantum well/n-GaN

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We report on the fabrication and characteristics of light-emitting diodes (LEDs) which consist of antimony (Sb) doped p-ZnO, (InGaN/GaN) multiquantum well (MQW), and n-GaN. An electroluminescence (EL) emission at a wavelength of 468 nm is observed from the hybrid LEDs after thermal annealing at 750 °C, showing that Sb-doped p-ZnO can be used as a hole supplying layer in hybrid LEDs. Furthermore, the EL peaks are redshifted as the injection current is increased, indicating that the compressive strain in MQW layers is relaxed due to Sb-doped p-ZnO layer.


Gallium nitride (GaN) is a very promising material for light-emitting devices in the UV-visible range due to its wide band gap (3.4 eV), high thermal conductivity (1.31 W/cm K),1 high breakdown electric field, high chemical stability, and high electron saturation velocity.2 Although enormous efforts have been devoted to growing high quality p-GaN with a high hole concentration, the typical resistivity of p-GaN is ~1 Ω cm and it is much higher than that of n-GaN with a resistivity of ~0.01 Ω cm,3 resulting in a delay to realize high efficiency GaN light-emitting diodes (LEDs). Therefore, it is necessary to replace p-GaN layer with a p-type semiconductor layer which has high hole concentration, as well as appropriate structural and optical properties. Recently, Zeng et al.6 reported on N-doped p-ZnO layers with a resistivity of 1.7 Ω cm. It was also reported that the resistivity of Sb-doped p-ZnO layers can be lowered to 0.1 Ω cm.7 Furthermore, it is known that ZnO films grown by metalorganic chemical vapor deposition (MOCVD) are oriented along c-axis with a wurtzite structure and there is very small in-plane lattice mismatch of 1.8% between ZnO and GaN.8 In addition, thermal expansion coefficient of 6.51×10−6/K of ZnO is similar to that of GaN with 5.59×10−6/K.9 These facts indicate that p-ZnO can be used as a hole supplying layer by replacing the p-GaN in GaN LEDs. Hybrid LEDs of p-ZnO on InGaN/GaN MQW are expected to have several advantages in electrical and optical properties over the conventional GaN LEDs. For example, the electron affinity of ZnO is lower than that of GaN by 0.15 eV,10 leading to a decrease in hole injection barrier. Furthermore, the ZnO refractive index reative index of 2.0 is smaller than GaN of 2.4,11 allowing an increase in the probability of photon escape in the hybrid LEDs.

In this letter, hybrid LEDs were demonstrated by depositing Sb-doped p-ZnO layers on InGaN/GaN multiquantum well (MQW) LED. The forward voltage and series resistance of hybrid LEDs were measured as 2.9 V and 11.8 Ω, respectively. A blue electroluminescence (EL) at a wavelength of 468 nm was observed from the hybrid LEDs.

The sapphire substrate was cleaned in H2 at 1070 °C, followed by the low temperature growth of a GaN buffer layer (30 nm) at 570 °C. After high temperature annealing of the buffer layer, undoped GaN (5 μm) and Si-doped n-GaN layer (2 μm) were grown at a temperature of 1150 °C. InGaN/GaN MQWs with five pairs of undoped InGaN wells (3 nm) grown at 820 °C and undoped GaN barriers (7 nm) grown at 900 °C were grown on an n-GaN layer. After the growth of InGaN/GaN MQWs, the sample was loaded into a ZnO MOCVD reactor for the growth of Sb-doped ZnO layer. The growth temperature, pressure, and growth rate of Sb-doped ZnO layer were 750 °C, 50 Torr, and 0.67 μm/h, respectively. Diethylzinc, trimethylantimony, and oxygen were used as Zn source, p-type doping source, and oxidizer, respectively. After the growth of Sb-doped ZnO on InGaN/GaN MQWs, a rapid thermal annealing (RTA) was carried out in an N2 ambient for 1 min to activate Sb-doped ZnO. To fabricate a hybrid LED with a size of 300×300 μm2, the Sb-doped p-ZnO layers was partially etched in a diluted HCl solution, and then the LEDs were etched until n-GaN layer was exposed by using an inductively coupled plasma with CH4/Cl2/H2/Ar sources. Cr (30 nm)/Au (80 nm) were used as a p- and n-type electrode for the hybrid LEDs. NiO or oxidized Ni/Au which has been frequently used as p-ZnO ohmic contact metal was not used in this letter to eliminate a controversy of hole injection from the NiO or oxidized Ni/Au alloy which is known as a p-type semiconductor.12,13 For a comparative study of electrical and optical properties, reference GaN LEDs without a current spreading layer were also fabricated using a p-GaN layer with a thickness of 200 nm. The p- and n-type electrodes in the reference LEDs were same as those of hybrid LEDs.

In order to measure the conductivity of Sb-doped ZnO, Hall measurement was conducted in a van der Pauw configuration on Sb-doped ZnO films with a thickness of ~1 μm grown on c-sapphire. The Sb-doped ZnO films were annealed in N2 ambient for 1 min by using RTA process. The p-type conductivity was observed for Sb-doped ZnO layers which were annealed at a temperature range of 700–850 °C.
The hole concentration of Sb-doped ZnO was continuously increased from $8 \times 10^{17}$ cm$^{-3}$ to $2 \times 10^{18}$ cm$^{-3}$ and a hole mobility was decreased from 1–0.1 cm$^2$ V$^{-1}$ s$^{-1}$ by increasing annealing temperature from 700–850 °C. A further increase in annealing temperature up to 900 °C led to a decrease in hole concentration. The decrease in hole concentration at higher temperature is believed due to point defects of O vacancies which compensate the hole carriers produced by Sb dopants.$^{14}$

In order to investigate the optical properties of Sb-doped ZnO, photoluminescence (PL) measurement was conducted at 12 K on the undoped ZnO and Sb-doped ZnO films which were annealed at a temperature of 750 °C. The excitation wavelength and power of He-Cd laser for PL measurement were 325 nm and 30 mW, respectively. As shown in Fig. 1, a neutral donor-bound exciton (D°X) emission at 3.367 eV (Ref. 15) was observed dominantly on the PL spectra of undoped ZnO layers (square dot line). However, neutral acceptor-bound exciton (A°X) emission at 3.316 eV (Ref. 15) and their phonon replica peaks were dominant on the spectrum of the Sb-doped ZnO layers (solid line) while D°X emission was significantly suppressed. The peak of A°X has been observed from p-ZnO doped with As or Sb, and D°X emission was observed from n-ZnO.$^{16,17}$ These results are well agreed with a p-type conductivity of Sb-doped ZnO layers, which is shown after the post-thermal annealing process.

Figures 2(a) and 2(b) show that the typical Sb-doped p-ZnO films grown by MOCVD, which consist of columnar structures with a height of ~500 nm and diameter of 100–300 nm. The film structure are analogous to ZnO films grown in a film-to-nanorod transition mode on a sapphire substrate.$^{18}$ Recent letters have found that p-type behavior in ZnO materials is related to the localized acceptor states induced by p-type dopants and other native defects at the interface, such as grain boundary in the ZnO film.$^{19,20}$ These results indicate that Sb-doped ZnO films may also have p-type conductivity at the grain boundary interface or on the surface of columnar structures.

The Sb-doped ZnO films with a hole concentration of $1.18 \times 10^{18}$/cm$^3$ and mobility of 0.71 cm$^2$/V s were deposited on InGaN/GaN MQW to fabricate hybrid LEDs of p-ZnO:Sb/(InGa/N/GaN) MQW/n-GaN. Figures 3(a) and 3(b) show the current-voltage (I-V) curves of hybrid and reference LEDs which do not have a current spreading layer. The forward voltage and series resistance of the hybrid LEDs are measured as 2.9 V at 20 mA and 11.8 Ω, while those of a reference LED are 4.1 V at 20 mA and 18.1 Ω. The forward voltage of hybrid LEDs with Sb-doped p-ZnO is expected to be lower than the reference LED with p-GaN, because the electron affinity of ZnO is lower than that of GaN by 0.15 eV (Ref. 10) and the hole concentration of the Sb-doped p-ZnO films of $1.18 \times 10^{18}$/cm$^3$ is higher than $2.73 \times 10^{17}$/cm$^3$ of p-GaN used in the reference LED. However, the forward and reverse leakage currents of hybrid LEDs were significantly larger than those of reference LEDs, presumably due to the scattering of carrier with the columnar structures in Sb-doped p-ZnO films.

Figure 4(a) shows the EL spectra with a blue 468 nm as a function of injection current and the inset of Fig. 4(a) shows the emission image of hybrid LEDs at an injection current of 20 mA at room temperature. As shown in Fig. 4(a), EL intensity of hybrid LEDs increases as injection current increases, showing that the Sb-doped p-ZnO layer acts as a hole supplying layer in the hybrid LEDs. In addition, the EL emission peak position is redshifted as injection current increases as shown in Fig. 4(a). In the conventional GaN-based LEDs, the EL emission peak of InGaN/GaN MQW LEDs is blueshifted as the current increases due to the suppression of quantum confined Stark effect by electrical current,$^{21}$ and then the EL peak position is redshifted due to...
self-heating as the injection current further increases.\textsuperscript{22} However, the EL peak position of hybrid LEDs is redshifted toward long wavelength side as shown in Fig. 4(a). This result can be explained by the decrease in strain-induced piezoelectric field in the InGaN well by Sb-doped \( p \)-ZnO and Joule heating. In order to verify the strain relaxation of InGaN well, micro-Raman measurement were performed at room temperature. The Ar\textsuperscript{+} laser line of Raman excitation was 514.5 nm and a power of 2.4 mW was used for Raman measurement. The resolution of the Raman spectrometer (Jobin-Yvon LabRam HR) used in this experiment was 0.3 cm\(^{-1}\).

As shown in Fig. 4(b), the peak \( E_2^\text{H} \) mode of InGaN in the hybrid LEDs shows a low-frequency shift of 1 cm\(^{-1}\) compared to that of InGaN of reference LEDs and FWHM of InGaN, indicating that the compressive strain of InGaN well in the reference LEDs is relaxed by Sb-doped \( p \)-ZnO. It is reported that ZnO is relaxed in-plane tensile stress between ZnO and sapphire substrates when the diameter of ZnO nanorods on sapphire is larger than 30 nm,\textsuperscript{18} and InGaN layer of InGaN/GaN MQW on sapphire substrate is under compressive strain.\textsuperscript{23} Therefore, the tensile strain of ZnO nanorods in \( p \)-ZnO: \( p \)-ZnO layer is expected to compensate the compressive strain of InGaN well, reducing the strain induced piezoelectric field in the InGaN wells. However, it was reported that strain still remained in InGaN layer even though \( E_2 \) mode of InGaN was shifted as much as \( \sim 3 \) cm\(^{-1}\).\textsuperscript{24} Therefore, the redshift of EL peak can be attributed to the combined effects of strain relaxation and Joule heating.

Figure 5 shows the light output power of hybrid LEDs and reference LEDs as a function of injection current. A strong EL emission is observed from the hybrid LEDs, but the light output power is lower by 3.8 times at 100 mA than reference LEDs. The decrease in optical power is attributed to the poor current spreading in Sb-doped \( p \)-ZnO layers with columnar structure and an absorption in the thick layer of Sb-doped \( p \)-ZnO. The light output power of hybrid LEDs may be further increased by optimizing the film thickness, film structure, hole mobility of Sb-doped \( p \)-ZnO, and ohmic contact to Sb-doped \( p \)-ZnO.

In summary, the Sb-doped ZnO layers grown by MOCVD showed \( p \)-type conductivity after thermal annealing at 750 °C in N\(_2\) ambient. The hybrid LEDs of \( p \)-ZnO:Sb/(InGaN/GaN) MQW/\( p \)-ZnO showed a low forward voltage of 2.9 V at 20 mA and a low series resistance of 11.8 Ω, respectively. EL emission from the hybrid LEDs was observed at 468 nm at room temperature. Furthermore, EL peak position was shifted toward long wavelength side, indicating that the strain in the MQW was relaxed by Sb-doped \( p \)-ZnO. These results show that Sb-doped \( p \)-ZnO layer can be used as a hole supplying layer in the hybrid LEDs.

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