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Effect of a p-type ZnO insertion layer on the external quantum efficiency of GaInN light-emitting diodes

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The external quantum efficiency (EQE) of a GaInN green light-emitting diode (LED) is improved by inserting a p-type ZnO layer between the indium tin oxide electrode and the p-type GaN layer. Several hypotheses are discussed to explain the EQE improvement in the LED with the ZnO layer. It is concluded that higher hole injection efficiency and better electron confinement explain the EQE improvement, which is supported by the results of device simulations showing that the EQE is sensitive to the polarization sheet charge density at the interface between the last quantum barrier and electron-blocking layer.

Although the external quantum efficiency (EQE) of GaInN light-emitting diodes (LEDs) has markedly improved over the last two decades, it remains the most important figure-of-merit for LEDs since the LED cost per luminous-flux output ($/lm), which is a limitation to further market penetration of LEDs, can be lowered by improving EQE, thereby allowing devices to operate at higher current densities.[1–4] Recently, ZnO-based transparent conducting oxides have received considerable attention as an alternative to indium tin oxide (ITO) for a p-type GaN ohmic contact layer because ZnO is abundant in nature, is nontoxic, has high transparency due to a wide band gap, and has electrical properties similar to ITO.[5] Accordingly, many studies have been published showing an improved EQE when ZnO layers are utilized in GaInN LEDs.[5–15] The reason for the efficiency improvement caused by the inclusion of a ZnO layer has not yet been fully understood, although several hypotheses, such as better refractive index matching than conventional metal oxide electrodes,[10,12] better current spreading than ITO,[13] better transparency than ITO,[9,15] and improved hole injection efficiency,[14] have been published. In this study, we investigate an LED structure with a p-type ZnO layer between the ITO electrode and the p-type GaN layer. Inserting a p-type ZnO layer provides a distinct EQE improvement in the LEDs, which causes us to review the reasons that have been proposed so far to explain the effect of the ZnO layer. We conclude that the strain exerted on the electron-blocking layer (EBL) and multiple-quantum wells (MQWs), as a result of ZnO deposition, can be the root cause for the improvement in quantum efficiency and/or injection efficiency. We employ the $ABC + f(n)$ model,[16] which has proven to be effective in studying recombination mechanisms in GaInN LEDs, to support our analysis of the enhanced EQE in the GaInN LED with a p-type ZnO insertion layer.

A commercial GaInN LED wafer emitting approximately 530 nm was used in our study. The epitaxial structure includes a buffer layer, an undoped GaN layer, an n-type GaN layer, light-emitting GaInN/GaN MQWs, a p-type AlGaN EBL, and a top p-type GaN layer, all of which were sequentially grown on a sapphire substrate. The hole concentration of the p-type GaN layer is in the low-to-mid 10^{17} cm^{-3} range. First, the wafer was cut into two pieces. One piece of the wafer was loaded into the vacuum chamber for the p-type ZnO growth. A hybrid beam deposition (HBD) method was used to deposit the single-crystal arsenic-doped p-type ZnO layer on the p-type GaN surface. The HBD method is described in detail elsewhere.[7,14] The thickness of the p-type ZnO films is about 150 nm. After the ZnO deposition, both of the wafer pieces were loaded into an evaporator in order to simultaneously deposit the p-type electrode, i.e., the ITO layer. The thickness of the ITO layer is about 200 nm, which provides good current spreading during operation. The LED chips were fabricated using a conventional method, i.e., defining a mesa structure through reactive ion etching using a mixture of BCl_3 and Ar gases, and depositing an n-contact made of Ti/Au (20 nm/300 nm). The chip size is 500 × 500 μm^2. A schematic diagram of the two LED structures is shown in Fig. 1. The reference LED with a conventional structure is referred to as the "ITO LED", and the other LED with a ZnO insertion layer is referred to as the "ZnO/ITO LED", as shown in Fig. 1. It is notable that the two LEDs are identical in both epitaxial structure and fabrication process, except that the p-type ZnO layer is inserted between the ITO layer and the p-type GaN layer for the ZnO/ITO LED. The optical output power of the chips before packaging was measured with a Si photodetector not only from the front side of the chip but also from the inner side of an integrating sphere. The APSYS device simulation and LightTools® ray-tracing simulation were used to support our analysis.

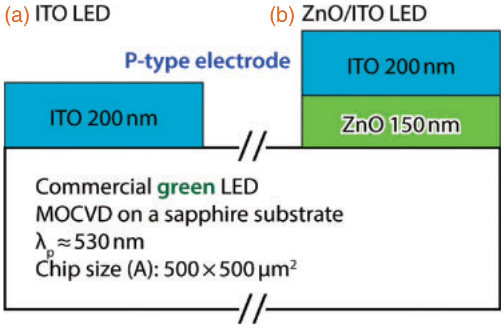

Fig. 1. Schematic layer sequences of the conventional LED ("ITO LED") and the LED with a ZnO insertion layer ("ZnO/ITO LED").

Figure 2 shows the EQEs of the two LEDs (i.e., ZnO/ITO and ITO LEDs) as a function of current, measured with an

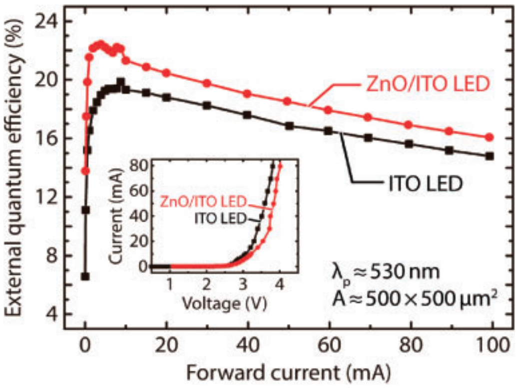

Fig. 2. External quantum efficiencies of the ITO and ZnO/ITO LEDs as functions of current. The inset shows a current–voltage characteristic of the two LEDs.

integrating sphere setup. The inset of Fig. 2 shows a current–voltage characteristic of the two LEDs. We find that the operating voltage for the ZnO/ITO LED is higher than that for the ITO LED. We believe that this is caused mainly by the deterioration of the contact property between the p-type ZnO and p-type GaN layers, and partially by the thickness increase of the p-type electrode for the ZnO/ITO LED. Further optimization of the p-type ZnO layer will resolve the higher operating voltage observed here, resulting in the definite benefit for efficiency. Note that Fig. 2 shows EQE not wall-plug efficiency (or power efficiency) that includes the effect of operating voltage. One distinct characteristic of the ZnO/ITO LED is the higher EQE for all current densities relative to the ITO LED, as shown in Fig. 2. The peak EQEs of the ZnO/ITO and ITO LEDs are approximately 23 and 19.5%, respectively, showing an 18% higher EQE for the ZnO/ITO LED. The improvement of the EQE of the ZnO/ITO LED is quite apparent. However, it is even more extraordinary when considering that only a p-type ZnO layer was inserted between the as-grown wafer and ITO. The results triggered our curiosity as to the effect that inserting the ZnO layer could have on the performance of the LED, particularly with respect to EQE. Therefore, we have considered a number of possible hypotheses, one by one, as described below.

First, we consider the difference in optical transmittance between the ITO and ZnO layers. The ZnO layer may have a higher transmittance than the ITO layer, particularly in the short-wavelength region.[9,15)] However, as shown in Fig. 1, the ZnO layer does not replace the ITO layer but is inserted as an additional layer between the ITO and p-type GaN layers. As a result, this hypothesis can be readily excluded.

Second, we consider possible changes in light extraction efficiency due to the ZnO layer. Generally, the light-escape cone from GaN to air is narrow owing to the large refractive index difference between GaN and air. Incorporating a material with an intermediate refractive index between GaN and air reduces Fresnel reflection and can help increase the extraction efficiency. At a wavelength of 500 nm, the refractive indices of GaN, ZnO, and ITO are 2.43, 2.03, and 1.95, respectively.[17)] Therefore, we can expect to have better refractive index matching by inserting a ZnO layer between GaN and ITO. However, the difference in refractive index between ZnO and ITO is small; thus, the index matching effect is quite limited. In addition, since the thicknesses of ZnO and ITO are about 150 and 200 nm, respectively, they are too thin to allow for an increase in the size of the light-escape cone from GaN to air unless micrometer-sized patterns are formed in the layers.[18)] Indeed, a ray-tracing simulation using the LightTools® simulator indicates that the improvement of light extraction due to the 150-nm-thick ZnO insertion layer is less than 1% (the result is not shown here). Furthermore, the light output power ratio between the ITO LED and the ZnO/ITO LED should be independent of current if the EQE improvement is caused purely by the improvement of light extraction. However, Fig. 2 shows that this is not the case.

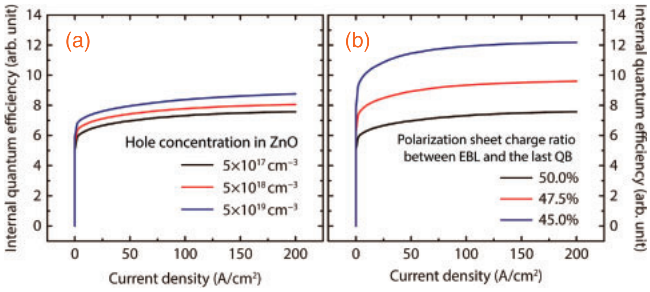

Fig. 3. Internal quantum efficiency obtained from device simulation for variations in (a) hole concentration in the ZnO insertion layer and (b) polarization sheet charge ratio at the QB/EBL interface.

Third, the hole injection efficiency will be higher when a highly conductive p-type ZnO layer is deposited on the p-type GaN layer. The arsenic (As)-doped ZnO layer (~ high 10^{17} cm^{-3} hole concentration) can be more conductive than the Mg-doped p-type GaN.[9,19)] In this hypothesis, the ZnO layer is believed to act as a hole-supply layer, increasing the hole concentration in the active region of the LEDs. It has long been known in the art of fabricating GaInN LEDs that an improvement in p-type contacts will not only reduce the forward voltage but also improve the EQE.[20)] This well-established experimental fact is not fully understood and cannot be easily reproduced by simulations (simulations do not reveal an increase in hole injection efficiency upon decreasing contact resistance). This empirical fact shows that improved p-type contact properties can result in a higher hole injection efficiency. Indeed, we can expect a decrease in contact resistance between the electrode (ITO) and ZnO due to the higher doping concentration in ZnO (compared with p-type GaN). One may argue that the beneficial effects of a better p-type contact structure are unlikely to affect the active region. However, experimental results contradict such reasoning. In order to investigate further the effect of a layer with high hole concentration, we simulate the structure shown in Fig. 1(b) using the APSYS simulator for a ZnO hole concentration ranging from 5×10^{17} to $5 \times 10^{19}\,\mathrm{cm}^{-3}$ (an intentional difference of two orders of magnitude). The simulated results shown in Fig. 3(a) indicate that the effect of the high hole concentration in the ZnO layer is limited, resulting in only a 10% increase in the internal quantum efficiency of the LEDs in spite of the significant increase in hole concentration. Therefore, the possibility that a high hole injection efficiency could be attributed to the high hole concentration in the ZnO layer is a possible explanation for the experimental finding.

Fourth, a p-type ZnO layer could change the strain state in the upper epitaxial layers of the LEDs, which induces a change in the carrier confinement capability of the LED's active region. The dielectric-material-induced strain was studied with GaN electronic devices (i.e., high-electron-mobility transistors), in which an enhanced lateral carrier transport was reported.[21–24] For example, an AlGaN/GaN layer with a compressive strain induced by a SiO_2 top layer exhibited an increase in polarization sheet charge density between the AlGaN and GaN interface.[22] It was reported that a few-hundred-nanometer-thick SiO_2 layer could easily change the polarization sheet charge density by up to 10%. In contrast to SiO_2, a ZnO layer on top of the p-type GaN layer may induce tensile strain onto the AlGaN EBL; consequently, the (positive) polarization sheet charge density between the last GaN quantum barrier (QB) and the EBL is reduced, thereby reducing the electric field that pulls electrons out from the active region. Because the ZnO layer deposited via HBD is denser than those produced through other techniques (including e-beam evaporation and sputtering), it is believed to cause significant stress for the layers underneath. The small-angle X-ray scattering is likely to be useful for estimating such a strain change at the interface between GaN and AlGaN because of its high sensitivity to properties in localized areas. Instead, in order to quantitatively analyze the effect of the polarization sheet charge between the last QB and the EBL of the LED, three interface sheet-charge conditions are simulated using the APSYS simulator: (i) 50% of the theoretical polarization charge between the last QB and the EBL,[25,26] (ii) 47.5% of the theoretical polarization charge, and (iii) 45% of the theoretical polarization charge. Figure 3(b) shows that more than 50% improvement is achieved for the internal quantum efficiency (i.e., the product of the radiative efficiency and current injection efficiency) through a 5% decrease in polarization sheet charge from 50 to 45%. The reduction in polarization sheet charge at the last QB/EBL interface reduces the electrostatic attraction for the electrons in the active region to the p-side region, thereby reducing electron leakage from the active region. As a result, the EQE of the LEDs can be improved. Note that the polarization sheet charge at the QB/EBL interface, which can be strained or relaxed by an external force, has a large effect on the EQE. Xu et al. introduced strain in blue LEDs by mechanically bending an LED wafer and observed an improvement in the optical performance (less efficiency droop) of the LEDs.[27] The density of polarization sheet charges at the QW/QB interface increased, but that of polarization sheet charges at the last QB/EBL interface decreased as the bending level increased.[27] Another implementation that showed similar results was presented by Son and Lee.[28] By mounting thin-film LED chips on an electroplated Ni metal substrate, they found that the stress exerted on the LED could be adjusted as a result of the thickness of the Ni metal. Remarkably, the larger stress on the LED showed less efficiency droop (due to the fewer polarization sheet charges at the QB/EBL interface).

As an in-depth analysis tool for the change in EQE that occurred in the ZnO/ITO LED, we utilize the $ABC + f(n)$ model, which is effective in investigating each recombination channel in an LED, and thus helps to identify the underlying recombination mechanisms of LEDs.[16] In the $ABC + f(n)$ model, the recombination rate (R) is described by using a polynomial series for the carrier concentration (n), i.e., $R = An + Bn^2 + Cn^3 + f(n) = An + Bn^2 + Cn^3 + (C^2/B)n^4$.[16] Figure 4 shows the calculated EQE of two LEDs versus current (I) and carrier concentration. The carrier concentration n in Fig. 4 is calculated using the following equations:

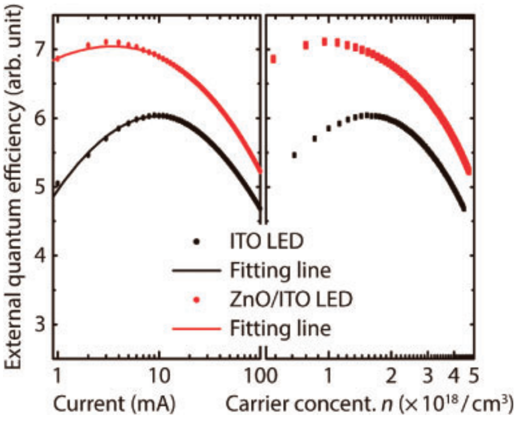

Fig. 4. External quantum efficiencies (red and black circles) of the ITO and ZnO/ITO LEDs as functions of current and carrier concentration in the active region. The solid lines are the theoretical curves fitted to the experimental points by using the $ABC + f(n)$ model.

Table I. Fitting parameters used for the ITO and ZnO/ITO LEDs in the $ABC + f(n)$ model.

Sample	A (s^{-1})	B ($cm^3\,s^{-1}$)	C ($cm^6\,s^{-1}$)	Goodness of fit
ITO LED	7.809×10^7	5.0×10^{-11}	2.976×10^{-29}	0.9993
ZnO/ITO LED	6.237×10^7	5.0×10^{-11}	2.702×10^{-29}	0.9995

$$IQE = RE \times IE = Bn^2/R, R = I/qV_{\mathrm{active}}, \quad (1)$$

$$n = \sqrt{IQE \times I/BqV_{\mathrm{active}}}, \quad (2)$$

where RE, IE, q, V_{active}, and B, are the radiative efficiency, the injection efficiency, the elementary charge, the active region volume, and the bimolecular radiative recombination coefficient, respectively. The $f(n)$ term in the $ABC + f(n)$ model represents how many carriers recombine outside or flow out of the active region. The solid lines in Fig. 4 are the polynomial fitting curves of the scattered data (i.e., experimental data), showing that the theoretical model can produce a reasonable fit. The parameters extracted from those two efficiency curves are summarized in Table I. The fitting results indicate that the first-order fitting coefficient A decreases in the "ZnO/ITO LED" ($6.237 \times 10^7\,s^{-1}$) relative to the "ITO LED" ($7.809 \times 10^7\,s^{-1}$). The A coefficient reflects the Shockley–Read–Hall (SRH) recombination of an LED. Since the active region in the two LEDs has identical growth conditions and remains untouched during processing, the lower SRH recombination that is found for the ZnO/ITO LED can be caused by the strain-relaxed EBL, which results in the higher radiative recombination rate in the active region. In Table I, the higher-order coefficient C is also slightly reduced in the ZnO/ITO LED relative to the ITO LED implying a better carrier confinement as well as a higher carrier concentration in the active region, which is consistent with the higher EQE and smaller efficiency droop found in the ZnO/ITO LED.

In conclusion, we investigate GaInN green LEDs with a p-type ZnO layer inserted between the ITO p-type electrode and the top p-type GaN layer. We find that the EQE of a GaInN green LED is improved by the p-type ZnO insertion layer. Experimentally, we observe an 18% improvement of EQE when a ZnO layer is deposited on the as-grown LED wafer. Several hypotheses to explain the EQE improvement in the LED with a ZnO layer are reviewed and discussed. We find that the p-type ZnO layer has a higher hole injection efficiency and a better electron confinement. There is good agreement between the APSYS simulation, $ABC + f(n)$ analysis, and experimental results. In the APSYS simulation, we find that the quantum efficiency of an LED is sensitive to the polarization sheet charge density at the last QB/EBL interface. The polarization sheet charge at the interface is believed to be modified by the strain induced by the ZnO layer. From the $ABC + f(n)$ model, we find that the first-order and high-order nonradiative coefficients are reduced in the ZnO/ITO LED, implying a better confinement and a higher carrier concentration in the QWs of the active region. The results suggest that an internal and/or external control of the strain in LEDs has the potential to improve the LED efficiency.

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