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Emission Pattern Control of GaN-Based Light-Emitting Diodes with ZnO Nanostructures

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We report a controllable way of changing the emission patterns of GaN-based blue light-emitting diodes (LEDs) using ZnO nanorods (NRs) grown hydrothermally. The shape of the ZnO NRs was controlled using seed layers for flower, askance, and vertical structures. The electrical properties of the LEDs with the ZnO NRs did not degrade, while the integrated electroluminescence intensity increased compared with that of the bare LEDs. The emission patterns of the LEDs were broadened as the inclination angle of the ZnO NRs increased. These are attributed to the ZnO NRs acting a role in scattering and guiding the light wave efficiently.

Light-emitting diodes (LEDs) based on group III–nitride semiconductors have generated much attention for applications, such as solid-state lighting, displays, and automobiles due to their inherent advantages of low energy consumption, long lifetime, short response time, and small device capability.[1)] However, the still low external quantum efficiency of LEDs caused by their inherently limited internal and extraction efficiencies leads to much research focusing on overcoming these problems. In particular, the light extraction problem of LEDs originates from the low critical angle at the GaN–air interface resulting in $\sim 23^\circ$ estimated by using Snell's law. Several approaches, such as roughening the p-GaN or indium tin oxide (ITO) transparent electrodes, conductive omnidirectional reflectors, and photonic crystal structures, have been investigated intensively to solve these problems.[2–5)] ZnO nanostructures grown by the hydrothermal method have been investigated widely to enhance the light extraction efficiency of the GaN-based LEDs, because this process is favorable to integrate with the LED process.[6–9)] In this structure, the ZnO nanostructures enhance the extraction efficiency of LEDs acting as a light wave guide or antireflection films reducing the Fresnel reflection problem.[7,8)] As described above, most research based on ZnO nanostructures for LEDs have focused on enhancing the extraction efficiency of the LEDs. However, the light emission from LEDs should be controlled for highly directional or broad spread-type patterns for the diverse applications of the LEDs. In this study, we report on a controllable way of tuning the light emission pattern of the GaN-based blue LEDs using the shape of ZnO nanorods (NRs).

The ZnO NRs with three different inclination angles, termed vertical, askance, and flower, were fabricated by the two-step hydrothermal method: forming seed and main ZnO NRs. The shape of the ZnO NRs was controlled using the seed layers. The seed layer was formed by spin coating the mixed solution of 40 mM zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] and hexamine [$(CH_2)_6N_4$] dissolved in ethanol with a spin speed at 1000 rpm for 30 s followed by annealing at 100 °C for 2 min to make ZnO NR with a flower structure. In contrast, seed layers for askance and vertical ZnO NRs were formed by dipping the substrate into zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] dissolved in an ethanol solution followed by annealing at 100 °C for 3 min. After forming the ZnO seed layers, the main growth for the ZnO NRs was carried out in solutions of zinc nitrate hexahydrate and hexamine dissolved in deionized (DI) water at 95 °C for 3 h. The molar contents of zinc nitrate hexahydrate and hexamine were 25, 40, and 80 mM for the flower, askance, and vertical ZnO NRs, respectively. Figure 1 shows the schematic of the LED device structure with the ZnO NRs. The blue LEDs with a dominant emission peak at 450 nm were grown on a c-Al_2O_3 by metal organic chemical vapor deposition. The p-GaN layer was etched using inductively coupled $Cl_2/CH_4/H_2/Ar$ plasma until the n-GaN layer was exposed for n-type Ohmic contact formation to fabricate lateral-type LEDs. A 200-nm-thick ITO film was deposited on top of p-GaN followed by the deposition of Ti/Au (50/200 nm) and Cr/Au (50/200 nm) layers as n- and p-type electrodes, respectively, to make a transparent conducting layer. The ZnO NRs were grown by dipping the LED chip with the full structure in each solution to grow the ZnO NRs with different inclination angles.

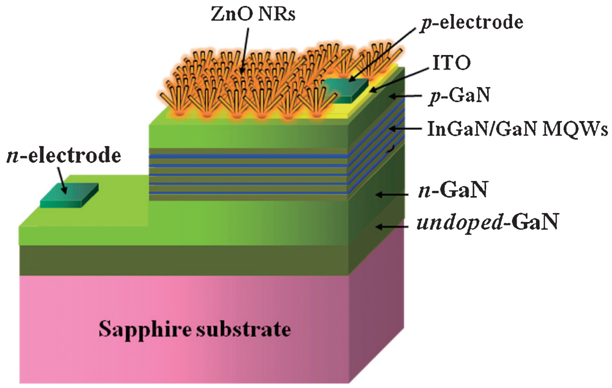

Fig. 1. Schematic view of LED device structure with various shapes of ZnO NRs.

Figure 2 shows the scanning electron microscopy (SEM) surface morphology and cross-sectional images of the ZnO NRs with flower, askance, and vertical shapes. The shape of the ZnO NRs changes from flower to askance and vertical, as the density of the ZnO seed grain increases. The seeds for askance and vertical ZnO NRs are denser and smaller than those for the flower structure, as shown in the insets of Figs. 2(a) and 2(c). The average inclination angles of the ZnO NRs measured from the substrate normal axis were about 3, 15, and 35° for the vertical, askance, and flower shapes, respectively.

The ZnO NRs with three different shapes were grown on the ITO top contact of GaN-based blue LEDs. Table I summarizes the electrical and optical properties of the

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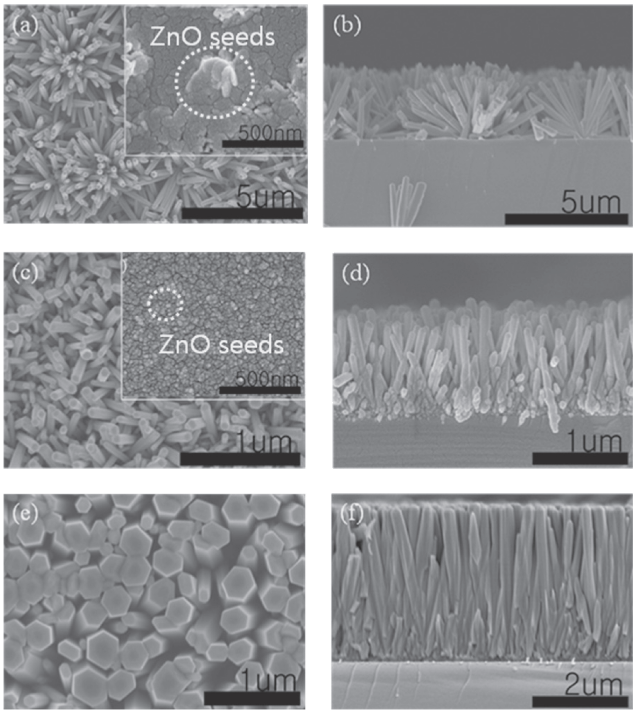

Fig. 2. SEM images of surface and cross-sectional morphologies of ZnO NRs; (a, b) flower shape, (c, d) askance shape, and (e, f) vertical shape. The inset shows SEM images of morphologies of ZnO seed for (a) flower-shaped NRs, (c) vertical and askance-shaped NRs, respectively.

Table I. Summary of the characteristics of LEDs.

Characteristics of LEDs		Bare	Flower	Askance	Vertical
Current–voltage characteristics	V_f (at 20 mA) (V)	2.78	2.75	2.75	2.78
	R_s (Ω)	2.89	3.53	3.39	3.85
EL characteristics	Peak wavelength (nm)	443	450	446	445
	Relative integrated intensity (arb. unit)	1.00	1.06	1.34	1.17
Angular-dependent EL	FWHM (deg)	122	129	119	115

LEDs. A bare LED means a conventional LED without ZnO NRs. Figure 3 shows current–voltage (I–V) characteristics of the LEDs with ZnO NRs of different shapes. The forward voltages at 20 mA for the LEDs with ZnO NRs are varied in the range of 2.75–2.78 V, similar to that of the bare LED with 2.78 V. The series resistances of the LEDs were 3.53, 3.39, and 3.85 Ω for the LEDs with flower, askance, and vertical ZnO NRs, respectively. These are slightly higher than that of the bare LED with 2.89 Ω. The forward leakage current of the LEDs with ZnO NRs was larger than that of the bare LED by more than one order of magnitude, as shown in the inset of Fig. 3. This would be attributed to the leakage paths formed during the growth of the ZnO NRs and could be removed by the well-optimized selective-area growth of ZnO NRs on ITO. The electrical properties of the LEDs did not degrade significantly, even though the ZnO NRs are formed on the ITO contacts of the LEDs.

Figure 4 shows electroluminescence (EL) spectra of the LEDs with ZnO NRs measured at an input current of 20 mA. The EL peak wavelengths of the LEDs were in the range of

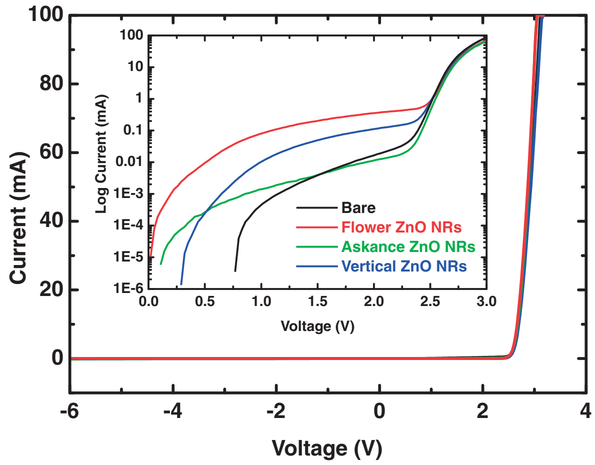

Fig. 3. I–V characteristics of LEDs with various shapes of ZnO NRs. The inset shows I–V characteristics on a log scale.

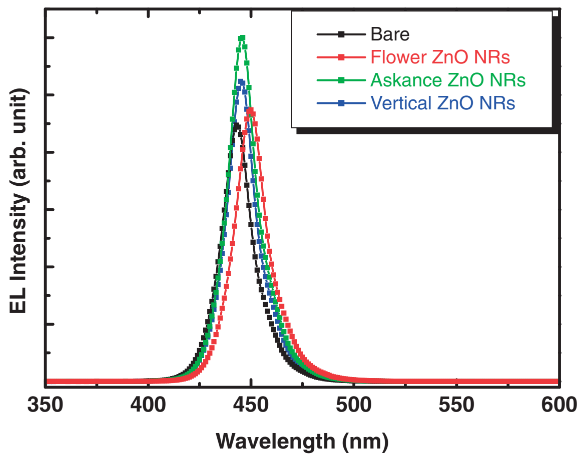

Fig. 4. EL spectra of LEDs with various shapes of ZnO NRs measured on top of LEDs.

443–450 nm. The slight variation of the peak wavelength originated from the spatial variation of composition or thickness of the InGaN quantum wells in the LED epi-layers. The integrated EL intensity of the LEDs with ZnO NRs, compared with that of the bare LED, increased by 1.06, 1.34, and 1.17 times for the LEDs with flower, askance, and vertical ZnO NRs, respectively. This result is similar to the previous work showing improved LED performance by integrating the ZnO nanostructures on the top of LEDs.[6–8] The critical angle for light extraction can be calculated based on Snell's law $\theta_{crit} = \sin^{-1}(n_1/n_2)$, where n_1 and n_2 are refractive indices of more and less optically dense materials, respectively. Incident photons beyond this angle can be reflected from the interface and internally confined or reabsorbed in the active layers or surface of the LED. The critical angle for light extraction at the ITO/air interface is 31.8°, considering that the refractive indices of ITO and air are 1.9 and 1.0, respectively. The light extraction efficiency of the bare LED is determined at the interface between the flat ITO and air. To circumvent this problem, an intentionally roughened ITO surface is known to be effective in reducing internal reflection, and finally improving the

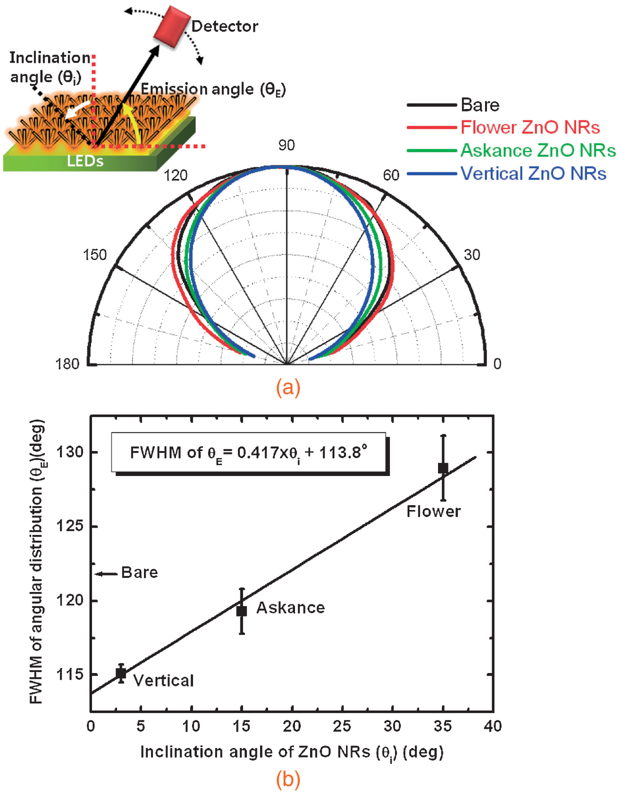

Fig. 5. (a) Angular dependence of EL emission intensity for LEDs with various shapes of ZnO NRs. The inset shows a schematic view of sample geometry for the measurement. (b) Plot of FWHM of the angular-dependent EL intensity, as a function of the inclination angle of ZnO NRs.

extraction efficiency of the LEDs.[3,10,11] However, if the ZnO NRs are formed on the ITO surface of the LEDs, the light extraction efficiency of the LED is determined at the interface between the ZnO NRs and air because the refractive index difference between ZnO ($n \approx 2.0$) and ITO ($n \approx 1.9$) is negligibly small. The incident light in the ZnO NRs can be guided and extracted easily to multiple facets of the ZnO NRs, which finally result in improved extraction efficiency of LEDs.[7]

Figure 5(a) shows normalized angular-dependent EL emission intensity of the LEDs with ZnO NRs, which was measured with a photodetector attached to a goniometer, as shown in the inset of Fig. 5(a). The emission pattern is most narrow for the LED with vertical ZnO NRs and becomes broader for that of LEDs with askance and flower-shaped ZnO NRs. Because the contact area to the top of LEDs with the flower shaped ZnO NRs is much smaller than that with the vertical and askance shaped ZnO NRs, the broader emission pattern from the LED with flower shaped ZnO NRs would be due to combined effect of light wave guiding and scattering effects of the inclined ZnO NRs. The full width at half maximum of the angular-dependent EL intensity (FWHM of θ_E) was plotted versus inclination angle of ZnO NRs (θ_i) as shown in Fig. 5(b) to investigate the effect of the ZnO NR shape on the emission pattern of the LEDs. The FWHM of θ_E increased linearly, indicating that the emission patterns become broader with increasing θ_i. The FWHM of θ_E as a function of θ_i can be linearly fitted by

$$\text{FWHM of } \theta_E = 0.417(\theta_i) + 113.8°.$$

The y-axis intercept value of 113.8° indicates that the FWHM of θ_E for the LED with ZnO NRs aligned perfectly normal to the top surface. The y-axis intercept value is smaller by 9.8° for the LED with ZnO NRs compared with the LED with a flat ITO top surface. It should be noted that this is a large difference, considering that the refractive indices of ITO and ZnO are almost the same. This implies that the ZnO NRs play role in guiding the light wave efficiently. Therefore, the light emission pattern of the LEDs could be systematically controlled using the shape of the ZnO NRs.

In summary, a controllable way of changing the emission patterns of GaN-based LEDs was demonstrated using various shapes of ZnO NRs that had different inclination angles. The shape of the ZnO NRs with flower, askance, and vertical structures was controlled using seed layers. As the density of the ZnO seed grain increases, the shape of ZnO NRs changes from flower to askance and vertical shapes. The electrical properties of the LEDs with the ZnO NRs were degraded slightly after forming the ZnO NRs on top of the ITO layer of LEDs. The integrated EL intensity, however, increased by 1.06, 1.34, and 1.17 times for the LEDs with flower, askance, and vertical ZnO NRs, respectively. The broadness of the emission patterns of LEDs increased linearly, as the inclination angle of the ZnO NRs increased. These are attributed to the ZnO NRs scattering and guiding the light wave efficiently and making it easier for light to be extracted through the ZnO NRs.

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