Enhanced optical output power of InGaN/GaN vertical light-emitting diodes by ZnO nanorods on plasma-treated N-face GaN†

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Light-emitting diodes (LEDs) play an important role as a formidable contender for next-generation lighting sources and rapidly replace conventional lighting sources. In this report, the growth of high density inclined ZnO nanorods (NRs) on the N-face n-GaN surface for high efficiency vertical light-emitting diodes (VLEDs) is demonstrated based on oxygen plasma pretreatment and hydrothermal growth. Surface modification by oxygen plasma pretreatment efficiently produces GaOx nanoparticles on the N-face n-GaN surface and they play an important role in the hydrothermal growth of dense and inclined ZnO NRs. The optical output power of ZnO NR VLEDs following oxygen plasma pretreatment is strongly enhanced by a factor of 3.25 at an injection current of 350 mA, compared to that of planar VLEDs. The large enhancement of optical power is attributed to the dense ZnO NR layer which efficiently reduces the total internal reflection and enhances the waveguide effect in ZnO NRs.

1. Introduction

III-Nitride semiconductors have been widely used to develop high-power and high-efficiency light-emitting diodes (LEDs) in solid-state lighting, display, and automobile applications.1–5 Recently, GaN-based vertical LEDs (VLEDs), fabricated by laser lift-off (LLO) and wafer bonding processes, have received much interest because they have many advantages, such as excellent heat dissipation capability and uniform current spreading, without the use of a transparent contact layer.6–8 Therefore, VLEDs can be used as high-power LEDs and replace conventional top-emitting lateral LEDs which show some problems, such as low heat dissipation and severe current crowding, under high current conditions. Although the internal quantum efficiency (IQE) of blue LEDs typically exceeds 70%, the light extraction efficiency (LEE) on a flat GaN surface is only ~4% owing to the total internal reflection (TIR) of light, which is caused by the large difference in refractive indices between GaN (n = 2.5) and air (n = 1). To enhance the LEE, several methods such as surface texturing,9–11 antireflection coating,14–17 omnidirectional reflection,18,19 and photonic crystal structuring20–23 have been suggested. In particular, surface texturing processes including surface roughening by alkaline-solution based wet etching24–26 and micrometer-scale arrays using photolithography followed by the plasma etching process22,23 are practical methods for achieving highly enhanced light extraction with low cost over a large area. However, the alkaline-solution, typically KOH and NaOH, can not only selectively etch GaN for fabricating hexagonal pyramid structures bound by the stable {1011} planes but also completely remove some important metals such as Al which acts as the most conventional n-electrodes in lateral LEDs.24 In addition, the wet etching methods degrade the electrical properties in VLEDs owing to the defect states exposed by the wet etching process at the threading dislocation of the GaN epilayer and the reduction of the n-GaN layer thickness which increases the resistance of the current channel.25 Micrometer-scale arrays of texture are also known as an efficient structure which increases the LEE with higher process stability than the wet etching methods. However, these structures have a lower pattern density and require higher process complexity compared to the wet etching process. Recently, ZnO nanowires (NWs) or nanorods (NRs) grown by the hydrothermal method have been actively studied because they can enhance the LEE and are favorable to be integrated into top-emitting lateral LEDs without damage to the GaN epilayer.26–29 However, it is difficult to grow ZnO NRs on the N-face GaN surface of VLEDs by the hydrothermal method without using the ZnO seed layer owing to the strong surface polarity dependence, compared to the Ga-face GaN surface of top-emitting lateral LEDs.26–28 In the previous studies, ZnO seed layers were deposited on the GaN epilayer of LEDs to grow high-density ZnO NRs to decrease the effect of surface polarity. However, TIR

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4nr01503g
occurs at the interface between the ZnO seed layer and the GaN epilayer owing to an abrupt change in refractive indices and the enhancement of optical output power in ZnO NR LEDs with the ZnO seed layer is limited. Therefore, the growth of high-density ZnO NRs on the N-face n-GaN surface of VLEDs without using the ZnO seed layer is required to eliminate the extra interface and reduce the TIR for high LEE and high-power VLEDs. The N-face GaN surface exposed to air and reduce the TIR for high LEE and high-power using the ZnO seed layer is required to eliminate the extra density ZnO NRs on the N-face n-GaN surface of VLEDs without compared to Ga-face GaN.

Furthermore, although many investigations of LEDs with ZnO NRs have focused on the enhancement of the LEE of LEDs, it is also necessary to obtain the broad emission pattern required for various LED applications. In this work, we increase the density of nucleation sites for the growth of high-density ZnO NRs on the N-face n-GaN surface of VLEDs. We then demonstrate that the ZnO NR VLEDs provide a high LEE and a broad emission pattern.

2. Results and discussion

Fig. 1a illustrates the schematic diagram of a blue VLED with inclined ZnO NRs. The blue VLEDs with a dominant emission peak at 438 nm were grown on c-plane sapphire substrates by metalorganic chemical vapor deposition (MOCVD). After the growth of a 25 nm-thick GaN buffer layer at 550 °C, a 5 μm-thick undoped GaN and a Si-doped n-GaN layer were grown at 1010 °C. Then, five pairs of InGaN/GaN MQW were grown, followed by a p-type GaN layer, to fabricate VLEDs. The p-GaN and MQW layers were partially etched by an ICP etching process until the n-GaN layer was exposed and Cr/Au-based n-pad electrodes were deposited by electron beam evaporation.

Next, the VLEDs with a size of 1 mm × 1 mm were fabricated by depositing a Ag based p-pad electrode on the p-GaN layer by electron beam evaporation. A SiAl substrate was bonded on the p-pads as a platform and then the LLO process was performed to separate the sapphire wafer. The Ti/Au metal layers were deposited by electron beam evaporation as n-pad electrodes after the u-GaN layer was fully etched. The patterned SiO2 mask was used to prevent the growth of ZnO NRs on the p-contact electrodes and the mesa sidewalls of VLEDs. Details of the fabrication method have been described elsewhere.

To modify the surface structure of the N-face n-GaN surface prior to the hydrothermal growth of ZnO NRs, the VLEDs were transferred to the inductively coupled plasma (ICP) system for oxygen plasma pretreatment at room temperature for 5 min. The working pressure of the ICP system was 2.0 × 10⁻² Torr and the input power was 150 W. The VLEDs with oxygen plasma pretreatment were dipped in an aqueous solution of 20 mM zinc nitrate hydrate (Zn(NO3)2·6H2O) and 20 mM hexamethylenetetramine (HMTA, C6H12N4) at 90 °C for 1 h for the growth of crystalline ZnO NRs on the N-face n-GaN layer of VLEDs. Results of the AFM analysis were performed on the N-face n-GaN surface before and after oxygen plasma pretreatment on the N-face n-GaN layer, respectively.

As shown in Fig. 1b, the density of ZnO NRs on the N-face layer without oxygen plasma pretreatment is 3.7 × 10⁶ cm⁻². However, the density of ZnO NRs is drastically increased up to 1.4 × 10⁹ cm⁻² after oxygen plasma pretreatment (Fig. 1c). The average diameter and height of ZnO NRs on the oxygen plasma treated N-face n-GaN surface are approximately 165 and 910 nm, respectively, and the ZnO NRs are inclined at arbitrary angles.

To investigate the chemical composition and structure of the N-face n-GaN surface after oxygen plasma treatment, X-ray photoelectron spectroscopy (XPS) analysis and atomic force microscopy (AFM) analysis were performed on the N-face n-GaN surface. Results of the XPS Ga 3d core level spectra observed from the N-face n-GaN surface before and after oxygen plasma treatment, respectively. The binding energy of the Ga 3d XPS peak of the N-face n-GaN surface is shifted from 19.3 eV to 19.6 eV following oxygen plasma irradiation. The deconvoluted Ga 3d peaks, which correspond to Ga–N and Ga–O bonds, indicate that the number of Ga–N bonds is reduced whilst that of Ga–O bonds is increased following oxygen plasma irradiation. The large increase in the peak intensity of the Ga–O bond indicates that GaOx species are formed on the N-face n-GaN surface after oxygen plasma treatment. A possible reaction process on the N-face n-GaN surface during oxygen plasma treatment is that highly active oxygen plasma species, such as oxygen radicals, react with nitrogen atoms on the surface, forming the volatile NOX species. This leads to the formation of Ga or GaOx species at the topmost N-face GaN surface. It was
reported that the growth of ZnO NRs on N-face GaN is not favored because the Zn–N bonds on the N-face GaN surface are relatively weak and the Zn atoms can diffuse along the N-face GaN surface.\(^{30}\) However, the growth of high density ZnO NRs on the surface after oxygen plasma treatment in this study indicates that the GaO\(_x\) species contribute greatly to the growth of the dense ZnO NRs on the N-face n-GaN surface. Fig. 2c and d show the AFM images of the N-face n-GaN surface before and after the oxygen plasma treatment, respectively. The N-face n-GaN surface before the oxygen plasma treatment shows a rough surface with a root mean square (RMS) roughness of 3.81 nm, owing to the LLO process. But the surface roughness decreases to 2.88 nm after oxygen plasma treatment. In addition, a large number of particles with an average diameter of 9.6 nm were formed on the N-face n-GaN surface after oxygen plasma treatment, as shown in the inset of Fig. 2d. The density of the nanoparticles on the N-face n-GaN layer is \(2.5 \times 10^9\) cm\(^{-2}\) and this value is close to the density of ZnO NRs grown on the surface treated by the oxygen plasma. The XPS and AFM analysis results suggest that Ga atoms remain in an unstable state owing to the Ga–N bond deficiency during oxygen plasma treatment and then form Ga nanoparticles on the N-face GaN surface.\(^ {39,40}\) During the oxygen plasma treatment, the oxygen plasma provides the reactive oxygen radicals to the Ga nanoparticles and convert them into GaO\(_x\) species. Because the ZnO nuclei can grow on the GaO\(_x\) nanoparticles in any direction and the crystal orientation of the GaO\(_x\) nanoparticles may not be the same as that of the N-face GaN (0001) epilayer at a low temperature of plasma pretreatment, the vertically aligned ZnO NRs are not likely to be observed on the GaO\(_x\) nanoparticles (see Fig. S2, ESI†). Similar densities of ZnO NRs and GaO\(_x\) nanoparticles on the surface after oxygen plasma treatment indicate that GaO\(_x\) nanoparticles play an important role in the hydrothermal growth of dense and inclined ZnO NRs on the N-face n-GaN surface, as shown in Fig. 1c.

To demonstrate the advantages of ZnO NR VLEDs with oxygen plasma pretreatment, we measured the electrical and optical characteristics of VLEDs with surface textures fabricated by using the KOH wet etching process, which is a well known structure for high LEE of VLEDs. Details of the fabrication process for surface textures are described in Fig. S3 and S4 in the ESI.\(^ {†}\) The current–voltage (I–V) characteristics of the planar VLEDs, VLEDs with wet-etched surface, and ZnO NR VLEDs without and with oxygen plasma pretreatment are shown in Fig. 3a. The I–V characteristic curves of all VLEDs except for wet-etched VLEDs show that the forward voltage of 3.39–3.40 V is almost the same and the series resistance of 1.9–2.0 \(\Omega\) is very close. The reverse leakage currents of these three VLEDs are less than \(10^{-5}\) mA at –10 V, as shown in the inset of Fig. 3a. However, the forward voltage and series resistance of VLEDs with wet-etched surface are increased to 3.56 V and 3.0 \(\Omega\), respectively. Such electrical deterioration of VLEDs after the wet etching process can be attributed to the additional defect states, which cause not only electrical leakage current but also non-radiative recombination, at the threading dislocations in the GaN layer and the reduced film thickness of the n-GaN layer acting as a current channel.\(^ {34,25}\) Similar values of the forward voltage and reverse leakage currents for three VLEDs except for the VLED with wet etched surface as shown in Fig. 3a indicate that the oxygen plasma treatment does not produce any etch damage or defects on the N-face n-GaN surface. Fig. 3b shows the electroluminescence (EL) spectra of VLEDs with ZnO NRs measured at an injection current of 350 mA. The integrated EL intensity of the ZnO NR VLEDs with oxygen plasma pretreatment is increased by 11\%, compared to that of the VLEDs with wet-etched surface. As shown in Fig. 3b, the EL intensities of the
ZnO NR VLEDs increase with increasing density of NRs without showing any peak shift of the EL spectrum. These results indicate that the enhancement in EL intensity of ZnO NR VLEDs is owing to the increase of LEE by the ZnO NRs and the electrical characteristics of VLEDs are not deteriorated by the oxygen plasma pretreatment for the growth of dense ZnO NRs on the N-face n-GaN layer.

Fig. 4a shows the light output power–current characteristics of ZnO NR VLEDs. The light output power of the ZnO NR VLEDs without and with the oxygen plasma pretreatment is higher by a factor of 1.64 and 3.25 at an injection current of 350 mA, respectively, compared to the planar VLEDs. The large improvement in light output power of ZnO NR VLEDs is attributed to both the propagation of light waves along the ZnO NRs and the decrease of effective refractive indices of high density ZnO NRs on the N-face n-GaN surface. Light with fundamental mode can travel along the ZnO NR, when the NR waveguide satisfies the following condition:

$$\frac{\pi d}{\lambda}\left(\frac{n_{\text{ZnO}}^2 - n_{\text{air}}^2}{2}\right)^{1/2} < 2.405$$

where $\lambda$ is the wavelength of light and $d$ is the diameter of NRs. Because the critical diameter of ZnO NRs at a wavelength of 438 nm is 194 nm, the diameter of ZnO NRs in this study (165 nm) can satisfy the single mode waveguide condition. Therefore, a ZnO NR under the fundamental mode condition can guide light with excellent quality and higher output intensity compared with a ZnO NR with a large number of modes. However, the light which is not in the fundamental mode is unable to efficiently propagate along the ZnO NR and considers the NRs as a homogeneous film. Because the distance between ZnO NRs and the diameter of ZnO NRs are shorter than the emission wavelength of 438 nm, the ZnO NR layer can be considered as a medium composed of a disordered assembly of ZnO NRs and air. Thus, the effective refractive index of the ZnO NR layer can be estimated by the effective medium theory,

$$n_{\text{eff}} = \left[\frac{n_{\text{ZnO}}^2 V_{\text{ZnO}} + n_{\text{air}}^2 (1 - V_{\text{ZnO}})}{2}\right]^{1/2}$$

where $n_{\text{ZnO}}$ and $n_{\text{air}}$ are the refractive indices of ZnO and air, respectively, and $V_{\text{ZnO}}$ is the volume fraction of ZnO. The lower effective refractive index of the inclined ZnO NR layer than that of the ZnO film ($n = 2.0$) can lead to a gradual decrease of the refractive index at the interface between GaN and air, reducing the TIR and the Fresnel reflection. Therefore, the large increase in the optical output power of ZnO NR VLEDs with oxygen plasma pretreatment can be attributed to the NR waveguide effect and efficient reduction of TIR and Fresnel reflection in the ZnO NR layer. Fig. 4b shows the angle-dependent EL emission pattern of the ZnO NR VLEDs with 90° as the surface normal direction. The full-width at half-maximum (FWHM) of the far-field radiation patterns is 111.2, 104.6, and 124.5° for the planar VLEDs and the ZnO NR VLEDs without and with oxygen plasma pretreatment, respectively. The emission pattern for the ZnO NR VLEDs with inclined ZnO NRs is broader than the planar VLEDs and ZnO NR VLEDs without the surface pretreatment. These results can be explained by the propagation of light escaping from InGaN/GaN multiple-quantum-wells (MQWs) along the inclined ZnO NRs, since the light in the fundamental modes escapes along the axis of ZnO NRs. Thus, the emission patterns of the ZnO NR VLEDs can be determined by the tilt angles of ZnO NRs. In this work, the ZnO NR VLEDs without and with oxygen plasma pretreatment showed an increase of FWHM of the emission pattern from 104.6 to 124.5°, respectively, with the aid of the tilt angle of ZnO NRs, as shown in Fig. 1b and c.

To reveal the light propagation through the inclined ZnO NRs on the VLED, three-dimensional finite difference time domain (FDTD) simulation is performed. For the rudimentary consideration, we assume that the LED is composed of a single GaN layer on top of the reflection layer and employ ZnO NRs with different tilt angles from 40° to 90° on the GaN layer. The diameter and height of ZnO NRs on the GaN layer are 165 and 910 nm, respectively, as determined by the SEM images presented in Fig. 1c. The model structure is surrounded by a perfectly matched layer (PML), apart from the bottom layer, with a perfect electric conductor boundary (PEC). A monochromatic light source with an emission wavelength of 438 nm, matching with the emission peak in the EL spectra at an injection current of 350 mA, is located in the GaN layer. Fig. 4c presents the transverse electric field intensity within the
inclined ZnO NRs with different tilt angles on N-face n-GaN, showing that the light injected from the GaN layer propagates along the ZnO NRs. These results imply that the inclined ZnO NRs grown on N-face n-GaN with the oxygen plasma pretreatment are effective nanostructures for more intense and broader light emission, compared with the vertically aligned ZnO NRs on VLEDs without the plasma pretreatment.

3. Conclusions

In conclusion, we demonstrated the growth of high density inclined ZnO NRs on the N-face n-GaN surface of VLEDs via oxygen plasma pretreatment. The oxygen plasma pretreatment efficiently produced GaO nanoparticles which play an important role in the hydrothermal growth of dense and inclined ZnO NRs on the N-face n-GaN surface. The electrical properties of the VLEDs with ZnO NRs are not deteriorated by the oxygen plasma pretreatment on the N-face n-GaN surface. The light output power of the ZnO NR VLEDs with the oxygen plasma pretreatment shows a strong enhancement in intensity by a factor of 3.25 with respect to the planar VLEDs at an injection current of 350 mA. The large enhancement of the optical output power is attributed to the waveguide effect in ZnO NRs and the dense ZnO NR layer which gradually reduces the contrast in refractive indices at the interface between the GaN layer and air. Furthermore, the broad emission patterns of VLEDs with inclined ZnO NRs arise from the enhanced waveguide effect through the inclined ZnO NRs grown on the oxygen plasma pretreated N-face n-GaN surface.

Acknowledgements

This research was supported by Samsung Electronics Co. Ltd., the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (no. 2008-0062606, CELA-NCRC), and the Industrial Strategic Technology Development Program (Project no. 100411878) funded by the Ministry of Trade, Industry and Energy (MOTIE/KEIT, Korea).

Notes and references