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Improved Light Extraction of GaN-Based Green Light-Emitting Diodes with an Antireflection Layer of ZnO Nanorod Arrays

Jang-Won Kang,[a] Min-Suk Oh,[a] Yong-Seok Choi,[a] Chu-Young Cho,[a] Tae-Young Park,[a] C. W. Tu,[b,c] and Seong-Ju Park[a,b,z]

[a]Department of Materials Science and Engineering and [b]Department of Nanobio Materials and Electronics, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea

We investigate the effect of double ZnO nanorod layers on the light extraction of green light-emitting diodes (LEDs). The double ZnO nanorod layers with a step gradient of the refractive index are formed as antireflection layers on the transparent electrode of LEDs. The light output power of the green LEDs with ZnO nanorods is increased by 42.9% at an injection current of 20 mA compared to those without ZnO nanorods. The increase in light output power is mostly attributed to a reduction in Fresnel reflection by antireflection layers of ZnO nanorods on green LEDs.
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GaN-based light emitting diodes (LEDs) have attracted considerable attention for use in solid-state lighting and display applications.[1] The realization of super-bright emission requires an enhancement of quantum efficiency for LEDs that are based on InGaN/GaN multiple quantum wells (MQWs). The external quantum efficiency of LEDs is limited by the large difference of refractive indexes between GaN and air. The critical angle at the GaN-air interface, as calculated using Snell's law, is $\sim 23°$, and it determines the escape cone of light emitted from GaN-based LEDs. In addition, the light within the escape cone of GaN-based LEDs undergoes Fresnel reflection due to the difference of refractive indexes between the media. This is one of the limitations that reduces the external quantum efficiency of LEDs. Antireflection layers have been used to reduce the Fresnel reflection in a certain wavelength range for optical components, photovoltaic devices, or LEDs.[2-5] Conventionally, a single antireflection layer with a film thickness equal to one quarter of the wavelength of interest was used. Such single antireflection layer should have a refractive index, n_{AR}, given by

$$n_{AR} = \sqrt{n_{semiconductor} \times n_{air}}$$

It has been reported that the light extraction of GaN-based LEDs with an antireflection layer, which was composed of a single film with optimal refractive index at the interface of indium tin oxide (ITO)/air or GaN/air, can be enhanced by 15–17.8%.[6,7] These studies showed that the light extraction of the GaN-based LED is enhanced mostly by the reduction of Fresnel reflection because the antireflection layers are very flat and the light extraction due to surface roughening effect is negligibly small. However, the conventional technique has given rise to the material selection issue because the refractive index of the film layer is difficult to control. Alternatively, a subwavelength structure with sizes smaller than the light wavelength can solve the material selection issue due to the change in the refractive index profile by varying the volume fraction of the embedded nanostructures. Recently, it was reported that a nanostructured layer composed of a one-dimensional (1D) nanostructure, such as nanorods (NRs) and nanowires (NWs), may offer superior antireflection property due to the possibilities of fabricating porous layers that have a lower effective refractive index than the bottom layer.[8]

In the present work, we demonstrate that Fresnel reflection is reduced and the extraction efficiency of GaN-based green LEDs can be enhanced by including an antireflection layer that consists of ZnO NR double layers with different NR densities. A two-step growth method was used to grow ZnO NR double layers with different NR densities on an ITO transparent p-electrode, and Fresnel reflection could be decreased by the NR double layers at the interface between the ITO transparent p-electrode and air.

An antireflection layer that consists of a 1D ZnO nanostructure can be treated as a homogeneous film with a uniform refractive index by controlling the density of the NR. The light scattering of ZnO NRs can be described by Rayleigh scattering, which is the elastic scattering of light by particles that are much smaller than the wavelength. If the distances between individual ZnO NRs are much shorter than the green wavelength, the light intensity scattered by ZnO NRs is neglected ($\sim 10^{-3}$ order), and the layer can be considered a homogeneous film.[9] Thus, the ZnO NR layer can be viewed as a disordered, subwavelength assembly that consists of ZnO and air. Thus, the Bruggeman effective medium approximation (EMA) gives the effective refractive index of the ZnO NR layer as

$$n_{eff} = [n_{ZnO}^2 V_{ZnO} + n_{air}^2 (1 - V_{ZnO})]^{1/2}$$

where V_{ZnO} is the volume fraction of ZnO, and n_{ZnO} and n_{air} are the refractive indexes of ZnO and air, respectively.[5] The refractive index of ZnO is approximately 2.02 at the green wavelength, and the ZnO NR layer has an effective refractive index that is less than that of ZnO films.[10]

Figure 1a shows a schematic diagram of GaN-based green LEDs with ZnO NRs. The green LEDs with a dominant emission peak at 530 nm were grown on a (0001) sapphire substrate by metallorganic chemical vapor deposition (MOCVD). The LEDs had a mesa structure with an area of $300 \times 300\ \mu m^2$. To fabricate the LEDs with ZnO NRs, a 200 nm thick ITO film was deposited on the top of GaN based LEDs by E-beam evaporation. Cr/Au (50/150 nm) layers were deposited as the p- and n-contact electrodes. To prevent the growth of ZnO NRs on the p-ohmic contact electrode, the metal contacts were covered with a photoresist layer by using photolithography. A few nanometers thick ZnO thin films were deposited on an ITO layer by radio frequency (rf) magnetron sputtering at room temperature as a ZnO seed layer for the subsequent growth of ZnO NRs. It was reported that the ZnO seed layer influences the morphology of ZnO nanostructures that are grown by the solution method.[11,12] We developed a two-step growth process to deposit double layers of ZnO NRs with different refractive indexes in the range between ITO and air. First, the ZnO NRs were grown by immersing LEDs with a ZnO seed layer in an aqueous solution of reactants [20 mM zinc nitrate hydrate, 20 mM hexamethylenetetramine (HMT), and 5 mM polyethyleneimine (PEI)] at 90°C for 1 h.[13,14] After completion of the first ZnO NR layer with high NR density, the sample was again immersed in a solution of 10 mM zinc nitrate hydrate, 10 mM HMT, and 2.5 mM PEI at 90°C for 30 min to form a second ZnO NR layer with a lower NR density and refractive index than the first layer. As shown in Fig. 1b, a scanning

[c] Permanent address: Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, CA 92093-0407.
[z] E-mail: sjpark@gist.ac.kr

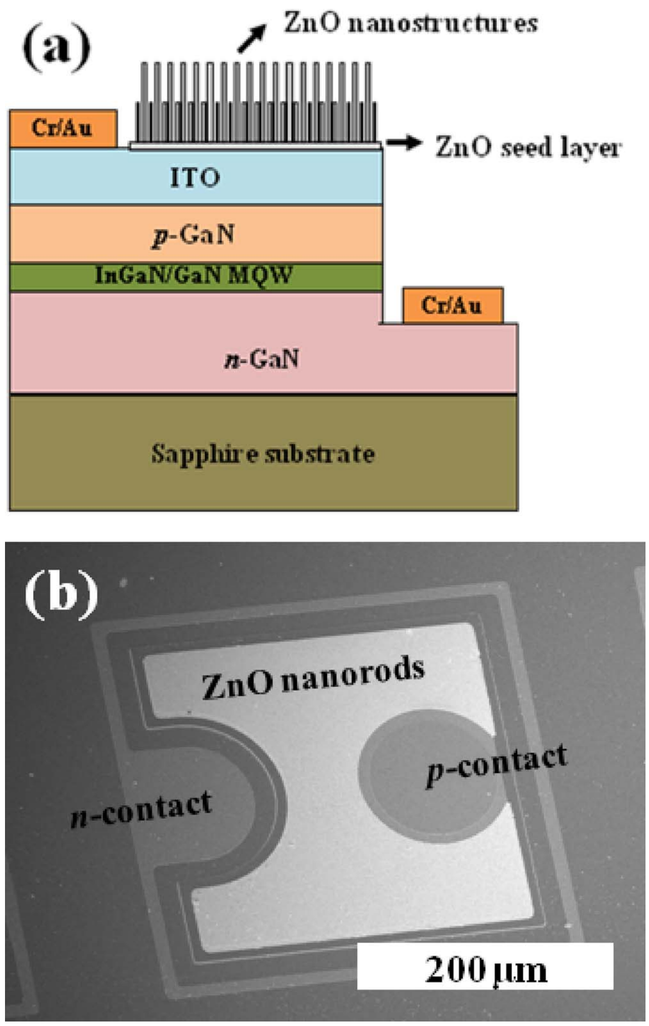

Figure 1. (Color online) (a) Schematic cross-sectional diagram of a green LED with ZnO NRs. (b) SEM image of a green LED with ZnO NRs.

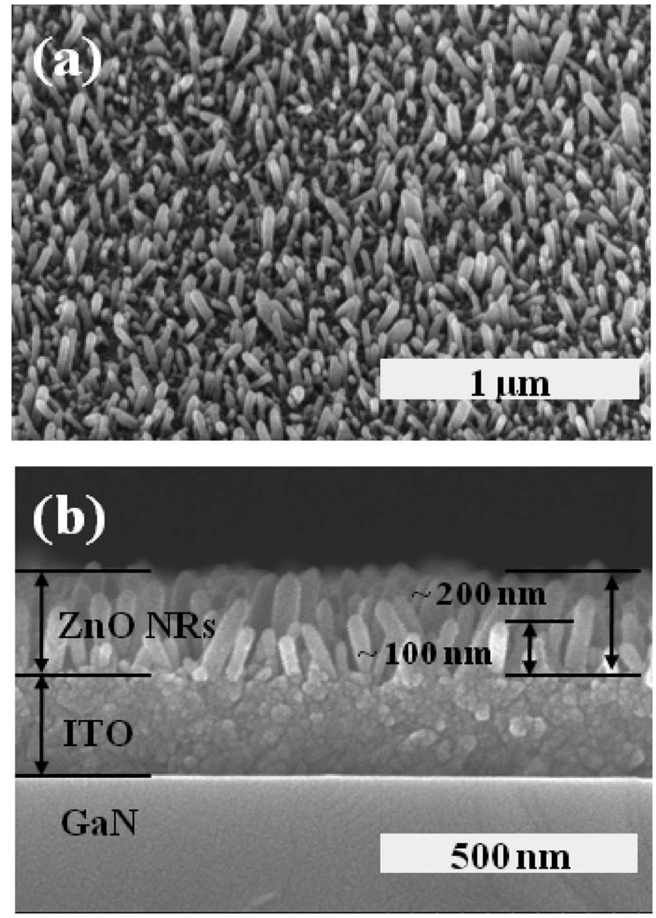

Figure 2. (a) Tilted and (b) cross-sectional SEM images of ZnO NRs grown on ITO films.

electron microscopy (SEM) image of the LEDs with ZnO NRs shows that the ZnO NRs were selectively grown on the open ITO area.

The SEM image in Fig. 2a shows that the ZnO NRs are grown on the transparent ITO electrode. Figure 2b shows a cross-sectional SEM image of ZnO NRs on an ITO electrode. ZnO NRs with different heights of 100 and 200 nm are formed on the ITO surface. The thickness of optimal single antireflection layer can be calculated from $\lambda_0/4n_{AR}$, where λ_0 is the wavelength of incident light in free space. The thickness of a single ZnO NR antireflection layer is estimated to be 94 nm for a green wavelength of 530 nm because n_{AR} between ITO and air is 1.4. Therefore, each layer of double ZnO NR layers can be considered as an antireflection layer on the green LEDs. The diameter of ZnO NRs with an average height of 100 nm is approximately 20 nm and that of ZnO NRs with an average height of 200 nm is in the range from 40 to 60 nm. The condition for the waveguide mode of light in the individual ZnO NR can be explained by the diameter of the 1D nanostructure.[15,16] It was reported that the critical diameter for single-mode waveguiding is in the range between 150 nm for $\lambda = 400$ and 350 nm for $\lambda = 800$ nm.[16] Therefore, the enhancement of extraction efficiency of ZnO NRs with a diameter of 100 nm is not explained by the waveguiding effect of green light ($\lambda = 530$ nm). This indicates that the enhancement of the extraction efficiency of LEDs in the present study is due to the antireflection effect of the ZnO NR layer.

As shown in Fig. 2b, the volume fraction of ZnO is different in each layer of the double layers of ZnO NRs. ZnO NRs with small (~ 20 nm) and large (40–60 nm) diameters are mixed in the first ZnO NR layer with a height of ~100 nm. ZnO NRs with a large diameter exist only in the second layer of ZnO NR. This indicates that the first ZnO NR layer has a larger volume fraction of ZnO than the second ZnO NR layer. The measured refractive index of ITO films grown by E-beam evaporation was 1.96 at a wavelength of 530 nm. Therefore, the effective refractive indexes of two ZnO NR layers are in the range of the refractive index of ITO ($n = 1.96$) and air ($n = 1$), and the refractive index of the first ZnO NR is larger than that of the second ZnO NR layer. These results imply that the Fresnel reflection at the interface between ITO film and air can be decreased by the double layers of ZnO NRs that serve as an antireflection layer to reduce the reflection at the interface between ITO and air to enhance the light extraction of LEDs.

To investigate the reduction of Fresnel reflection in ITO films with ZnO NRs, the transmittance of ITO films with and without ZnO NRs was measured. A 200 nm thick ITO was deposited on a glass substrate by E-beam evaporation, and ZnO NRs were deposited on the ITO layer using the two-step growth method. As shown in Fig. 3, the transmittance of the ITO film with ZnO NRs is increased in the visible-wavelength range (470–670 nm). This result shows that the reflection at the interface between the ITO film and air in the green wavelength region is decreased by the double layers of ZnO NRs.

Figure 4a shows the current–voltage (*I–V*) characteristics of green LEDs with and without ZnO NRs. The green LEDs with and without ZnO NRs showed very similar *I–V* characteristics with for-

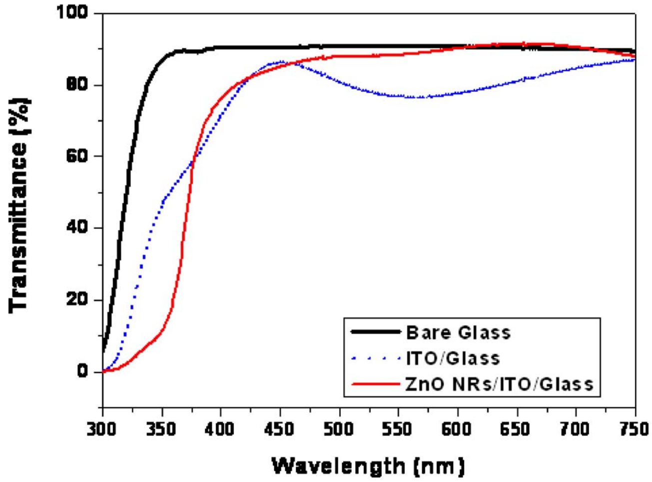

Figure 3. (Color online) Transmittance spectra of ITO with and without ZnO NRs.

ward voltages of 3.42 and 3.41 V at a current of 20 mA, respectively. This result indicates that the electrical properties of the ITO film and green MQWs are not degraded by the growth of double ZnO NR layers, owing to the low growth temperature of the ZnO

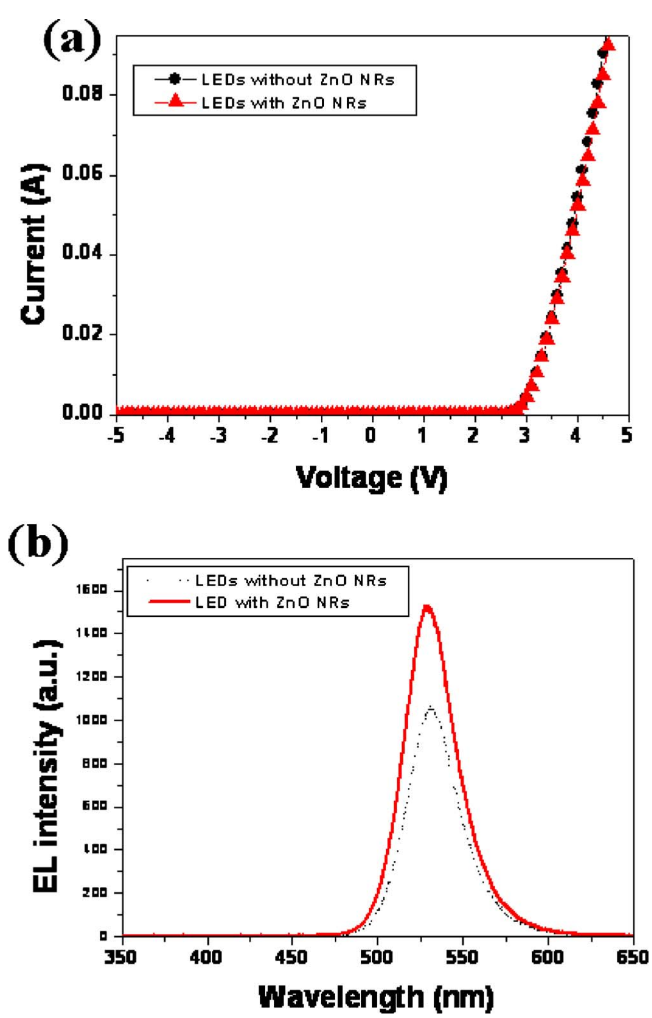

Figure 4. (Color online) (a) *I-V* curves of green LEDs with and without ZnO NRs. (b) EL spectra of green LEDs with and without ZnO NRs.

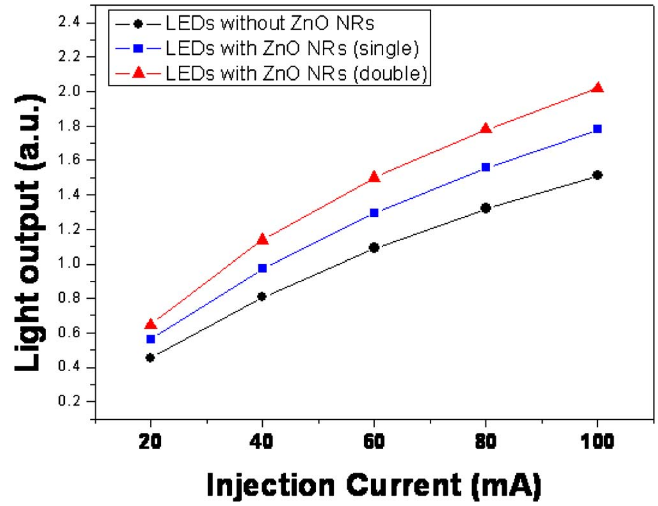

Figure 5. (Color online) Light output current characteristics of green LEDs with and without ZnO NRs.

NRs. It was reported that the *I–V* characteristics of LEDs with ZnO nanostructures grown at high growth temperature are degraded due to thermal damage to the p-electrode and MQWs.[17] The *I–V* characteristics clearly indicate that the ZnO NRs grown by the low-temperature solution method can be used as an antireflection layer without degradation of the structural property of green MQWs and the electrical properties of the current-spreading ITO layer. To further investigate the performance of green LEDs with ZnO NRs, room temperature electroluminescence (EL) intensity was measured from the top of the LEDs through the ZnO NRs as a function of current. Figure 4b shows the EL spectra of green LEDs with and without ZnO NRs at an injection current of 20 mA. As shown in the EL spectra, two green LEDs have a green emission at 530 nm.

Figure 5 shows the light output power of green LEDs with and without ZnO NRs as a function of injection current. To understand the antireflection effect of the ZnO NR double layer, LEDs with a ZnO NR single layer with an average height of 200 nm were fabricated. As shown in Fig. 5, the light output of LEDs with ZnO NR single and double layers are enhanced by 24 and 42.9% at an injection current of 20 mA, respectively, compared to that of LEDs without ZnO NRs. The increase in light output power of 24% by the first single layer and a further increase of 18.9% by the second layer indicate that the output powers of LEDs with ZnO NR layers are increased mostly by the reduction of Fresnel reflection because these values are slightly higher than the reported enhancement of light output of the LEDs with antireflection layers.[6,7] The slightly higher increase of light output power by 24 and 18.9% compared to the reported values of 15–17.8% (Refs. 6 and 7) suggests that the reduction of Fresnel reflection is a major cause of an increased light extraction efficiency and the surface roughening of ZnO NR layers is a minor cause of an increased light extraction efficiency of LEDs with ZnO NR layers. These results show that the ZnO NR antireflection layers grown on an ITO layer by low-temperature solution growth greatly enhance the light-extraction efficiency without showing thermal damage in green LEDs.

In summary, we fabricated GaN-based green LEDs with ZnO NRs on a transparent ITO electrode. The ZnO NR layer, which was grown by solution-based two-step growth, formed double ZnO NR layers with a step gradient of the refractive index. This was achieved via the control of the density and height of the ZnO NRs. The output power of green LEDs with ZnO NRs was enhanced by 42.9% compared to LEDs without ZnO NRs. The enhancement of the light extraction of the LEDs with ZnO NRs was attributed to an antireflection effect that resulted from a reduction of the Fresnel reflection.

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