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Research Article

Nanostructural Effect of ZnO on Light Extraction Efficiency of Near-Ultraviolet Light-Emitting Diodes

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The effect of ZnO nanostructures on the light output power of 375 nm near-ultraviolet light-emitting diodes (NUV-LEDs) was investigated by comparing one-dimensional (1D) nanorods (NR-ZnO) with two-dimensional (2D) nanosheets (NS-ZnO). ZnO nanostructures were grown on a planar indium tin oxide (ITO) by solution based method at low temperature of 90°C without degradation of the forward voltage. At an injection current of 100 mA, the light output efficiency of NUV-LED with NR-ZnO was enhanced by around 30% compared to the conventional NUV-LEDs without ZnO nanostructures. This improvement is due to the formation of a surface texturing, resulting in a larger escape cone and a multiple scattering for the photons in the NUV-LED, whereas the light output efficiency of NUV-LED with NS-ZnO was lower than that of the conventional NUV-LEDs due to the internal reflection and light absorption in the defective sites of NS-ZnO.

1. Introduction

An attempt to improve the performance of AlGaN based near-ultraviolet light-emitting diodes (NUV-LEDs) has attracted much attention due to their great potential for applications such as water purification, biochemical detection, and being a source for white Hg-free lamps [1–3]. However, UV-LEDs have suffered from low external quantum efficiency due to high electrical activation energy for Mg-doped *p*-GaN, low optical transmittance of transparent conductive layers, and low internal quantum efficiency. Several studies have reported improving the crystal quality of AlGaN by using AlN interlayer [4, 5] and AlN/AlGaN superlattices to enhance the optoelectrical performance of the NUV-LED, and using modified graphene [6, 7]. However, these researches only focused on the improvement of the crystal quality and have a large turn-on voltage with inefficient current spreading. An increase in the light extraction efficiency of NUV-LED without degradation of electrical properties is rarely discussed. One of the challenges which need to be overcome is the low light extraction efficiency, owing to the high internal reflection and narrow escape cone (~23.6°) due to the large difference of refractive indexes between nitride material ($\eta_{GaN} = 2.5$) and air ($\mu_{air} = 1$). In the past decade, several methods have been proposed for releasing the photons trapped inside the LEDs, including flip-chip LEDs [8], photonic crystals [9], and surface roughening [10, 11]. However, these methods involve complex, costly, long fabrication and dry etching process which may result in degradation of the electrical properties due to surface damage [12]. Alternatively, our previous study revealed that light extraction can be enhanced without degradation of electrical properties by using an aqueous solution method to grow ZnO nanostructures on top of LEDs. The use of ZnO nanostructures not only significantly increases the escape cones since the well-matched refractive indexes between ZnO and GaN materials but also allows emitted photons to escape through sidewall and rough surface due to surface scattering at the interface. Although aqueous solution is considered a facile, scalable, low

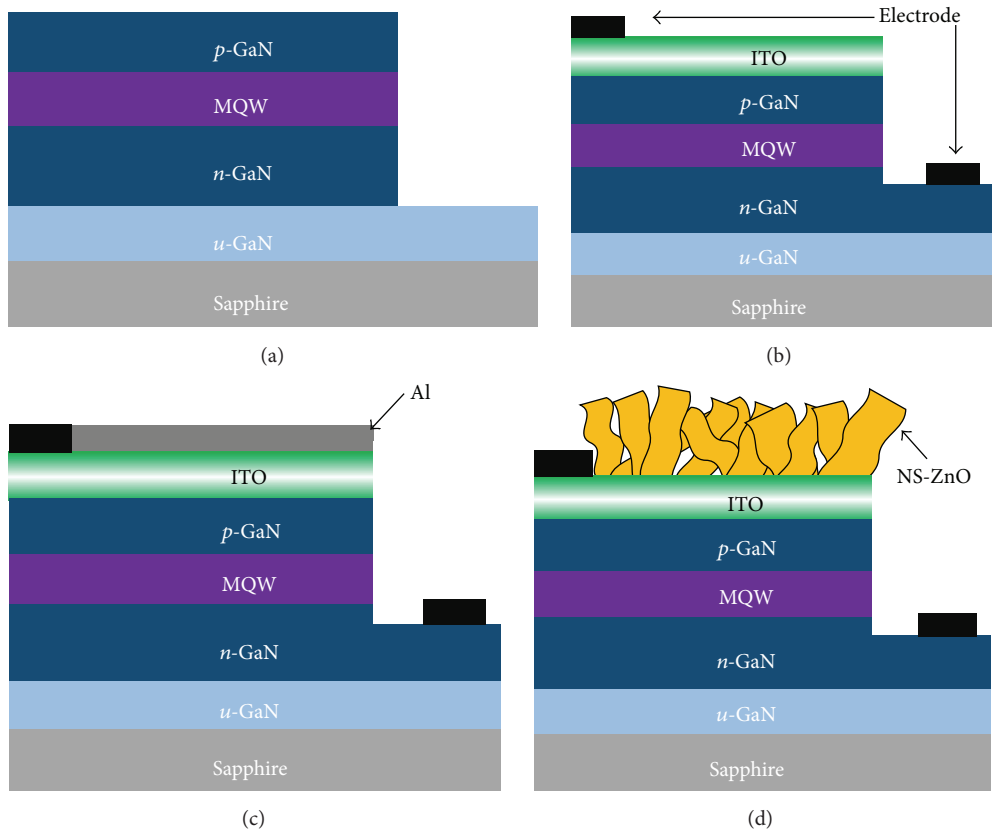

Figure 1: Schematic diagram of the process flow: (a) mesa etching after the UVLED structure growth on sapphire substrate, (b) deposition of bonding metal electrode after deposition of ITO layer onto *p*-GaN, (c) selective deposition of thin Al layer on the ITO area using a photolithography, and (d) ZnO nanostructure growth by a hydrothermal method.

temperature, and cost effective method, difficulties in controlling crystalline structure and morphology are the main obstacles to realizing this approach. It is believed that elucidating the effect of nanostructure morphology on light extraction efficiency of LED devices is very important for the development of NUV-LEDs with high luminance efficiency. In this work, two different nanostructures of ZnO, nanorods (NR) and nanosheets (NS), have been employed to investigate their effect on light extraction efficiency of NUV-LED devices.

2. Experimental

Figure 1 shows the schematic diagram of the processes for fabricating the UVLED with ZnO nanostructures. ZnO nanostructures were formed onto ITO films deposited on NUV-LED structures. The NUV-LED structure was grown on a 2 in. diameter *c*-plane sapphire substrate using metal organic chemical vapor deposition. Trimethylgallium (TMGa) and trimethylaluminum (TMAl) were used as Ga and Al metal organic precursors, and ammonia (NH_3) was used as a nitrogen source. Bis(cyclopentadienyl) magnesium (Cp_2Mg) and silane (SiH_4) were employed for *p*-type and *n*-type dopant sources, respectively. The device structure is *p*-GaN (0.15 μm)/AlGaN electron blocking layer/a 5-period InGaN/AlGaN multiple quantum wells (MQWs)/*n*-GaN (2 μm)/undoped GaN/sapphire. After mesa etching, a 100 nm ITO layer was deposited onto *p*-GaN by e-beam evaporation and was annealed at 500°C for 30 sec under $N_2 : O_2$ (8 : 2) mixed ambient. The bonding pad electrodes of Cr/Au (30/250 nm) were deposited onto the top surface of the ITO transparent electrode and *n*-type GaN by e-beam evaporation. We fabricated InGaN/AlGaN MQW NUV-LEDs with conventional planar ITO (C-LED), ZnO nanorod array/ITO (NR-LED), and ZnO nanosheet array/ITO (NS-LED). To realize ZnO nanomaterials on an ITO electrode, the ITO area of the p-electrode was made open by a photoresist lift-off process. NR- and NS-ZnO were formed by a hydrothermal growth method. This method creates the nanostructures by using an aqueous solution at 90°C on the transparent contact layer of ITO. The solution to grow the ZnO nanorods (NR-ZnO) and ZnO nanosheets (NS-ZnO) is described in detail elsewhere [13].

The morphologies and structures of the ZnO nanomaterials arrays were characterized via scanning electron microscopy (SEM, S-4700, Hitachi, Japan). The optical properties were investigated using photoluminescence spectra with a He-Cd excited source (325 nm), and light output power measured as a function of applied current (*L*-*I*) was carried out using an optical detector connected to a parameter analyzer. The current-voltage (*I*-*V*) characteristics were

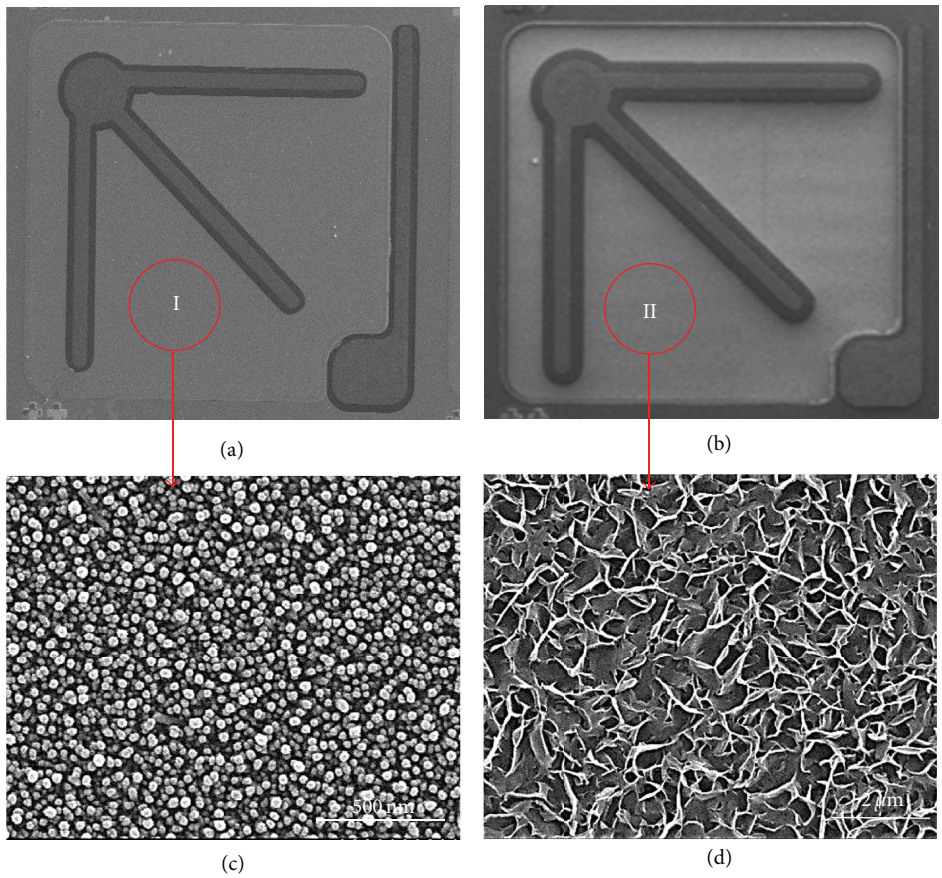

Figure 2: Top-view SEM images of ((a)-(b)) electrode pad configuration of NR-LED and NS-LED with two defined areas (c) and (d), respectively.

measured using a semiconductor characterization system (Keithley 4200-MSTech).

3. Results and Discussion

Figure 2 indicates that the ZnO nanostructures are well defined and grown on top of NUV-LED structures via hydrothermal growth method. In order to realize NR-ZnO on the ITO layer selectively, a conventional photolithography technique was performed to make the ITO layer open except the electrodes. A synthesized Ga-doped ZnO (GZO) solution [13] was spin-coated onto the substrate at 3000 rpm for 20 s to form a GZO buffer layer. The GZO buffer layer coated substrate was then annealed at 350°C in air for 60 min to form a seed layer for NR-ZnO. To grow NS-ZnO, a 10 nm thick Al was deposited onto ITO layer using e-beam evaporation. The NR-ZnO on GZO seeds and the NS-ZnO on Al thin film were grown by a dipping and holding process into a mixed solution containing DI water, 18 mM zinc nitrate hexahydrate, and 20 mM hexamethylenetetramine for 90 min at 90°C.

Figures 2(a) and 2(b) show a plan-view optical micrograph of the NR- and NS-LED, respectively. The ZnO nanostructures were selectively grown on ITO surface area as shown in regions I and II. In addition, clear pattern of Cr/Au electrode pad as well as ITO transparent conductive layer was also observed. The distinct surface morphologies of NR and NS are clearly exhibited in Figures 2(c) and 2(d). Figure 2(c) shows the typical SEM image of single crystalline NR-ZnO with orientation preferably vertical to the ITO surface. The length and the diameter of the nanorods are in the range of 40–50 and 200–250 nm, respectively. Figure 2(d) shows the NS-ZnO structure on ITO layer. The nanosheets have a length of about 500 nm. The two-dimensional growth of NS-ZnO is formed as a result of the Al element. The Al film deposited onto ITO layer had been incorporated into ZnO during hydrothermal reaction process and suppressed the growth along [001] direction. The primary reason is that the Al atom inhibited the growth rate of the polar surface by adsorbing; therefore, the growth rate of the nonpolar surface is faster than that of the polar surface [14].

Figure 3(a) shows UV-Vis spectra of the ITO, NS-ZnO, and NR-ZnO. The optical transmittance of LEDs devices in visible range does not degrade after fabricating ZnO nanostructures on top of the devices. The enhanced transmittance of NS- and NR-ZnO is mainly due to the formation of the nanotexturing surface. Rougher surface changed the light trajectory in a chaotic fashion, and the optical phase-space distribution turned into ergodic, resulting in improvement of the light transmittance. These results are in good agreement with previous study on textured ITO/ZnO surface [15]. It

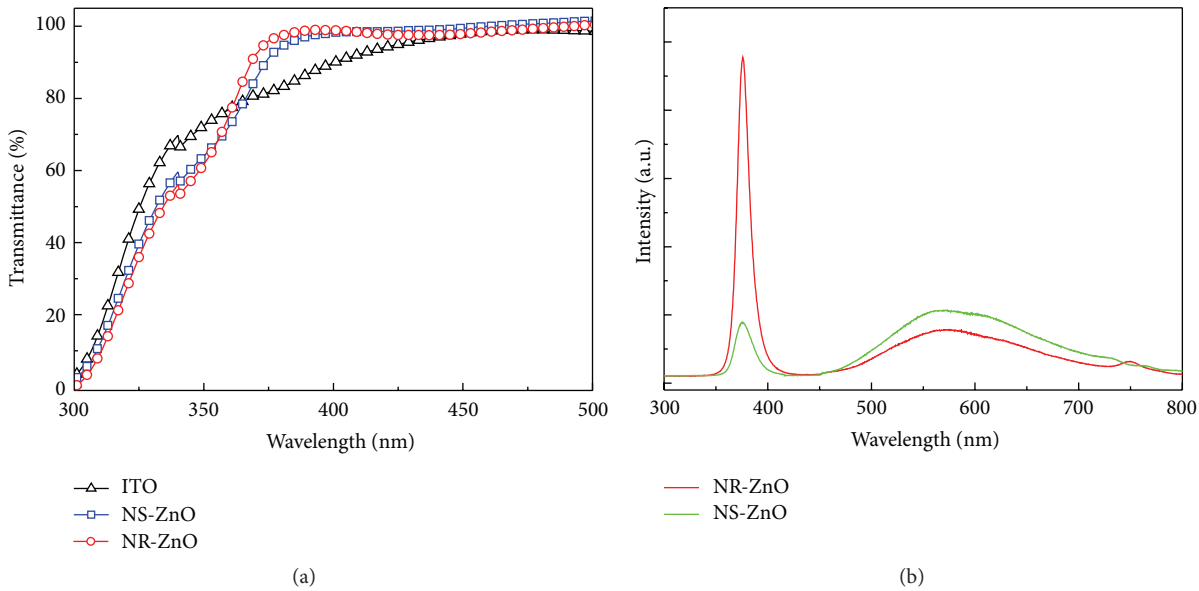

Figure 3: (a) UV-Vis and (b) PL spectra of NR-ZnO and NS-ZnO.

should be noted that the transmittance of NR-ZnO is slightly higher than that of NS-ZnO at NUV range (375 nm). On the other hand, the lower transmittance of NS-ZnO as compared to NR-ZnO has been attributed to the angular randomization of photons inside the nanosheets. Moreover, it is implicitly assumed that natural amorphous characteristic of nanosheets with large amount of defects can further limit the transmission.

Room temperature photoluminescence was measured with He-Cd laser excitation at a wavelength of 325 nm to evaluate the optical properties of NS-ZnO versus NR-ZnO, as shown in Figure 3(b). A main peak around 384 nm refers to the near band-edge emission. A broad low intensity peak in the visible region is associated with the defect-level emission, which is attributed to deep level defects, such as oxygen vacancies and Zn interstitial defects. It revealed that NR-ZnO shows better crystalline quality than NS-ZnO because of higher near band-edge emission and lower defect-level emission peak intensity. This result is an experimental support for our suggestion that the low crystalline quality of nanosheets is responsible for the low optical transmission of nanosheets as compared to nanorods in the UV-Vis spectra.

Electrical characteristics of the C-LED, NS-LED, and NR-LED were also studied from the current-voltage (I-V) curves. Figure 4(a) shows that the turn-on voltages of all samples were about 3.28 V at an injection current of 20 mA even though the ZnO nanostructures were grown on ITO layer. No significant difference in the I-V curves was observed at an injection current up to 100 mA. ZnO nanostructures based LED devices exhibited a slight change in leakage current after fabricating the NR-ZnO and NS-ZnO on top of the devices. The leakage currents were also all around 1.3 μA at −10 V. This small difference in leakage current at the reverse region may originate from the fabrication process of ZnO nanostructures. However, it would not lead to serious degradation of the electrical properties. Figure 4(b) shows light output power-current (L-I) characteristics of the C-LED, NS-LED, and NR-LED. Compared to C-LED, the optical output power of the NR-LED was dramatically increased with NR-ZnO (47%) at an injection current of 100 mA. The enhanced light output power of NR-LED is primarily due to the scattering effect by surface texturing of the NR-ZnO on ITO layer. NR-ZnO structure has a large number of sidewalls and can provide a larger escape cone for the photons in the NR-LED than that in the C-LED. Moreover, the sample with ZnO nanostructures on ITO layer had the more opportunity to scatter the light at the ZnO nanostructures, which resulted in an increase in light output power. On the other hand, the light output power of NS-LED was decreased by about 42%. A possible explanation for this observation is that the NR-ZnO possesses higher crystalline quality than that of NS-ZnO. It is observed that the visible emission of NS-ZnO is enhanced and the UV emission is greatly weakened compared to NR-ZnO, as shown in Figure 3(b). This result may be due to more defects originating from Al element doping. Consequently, photons generated from the MQWs of NUV-LEDs can be trapped in defected sites of NS-ZnO, resulting in a significant decrease of the light output power.

Figure 5 shows the micrograph images of the C-LED, NS-LED, and NR-LED device operating at an injection current of 20 and 100 mA, respectively. As shown in Figure 5, it is clearly observed that higher intensity of light emission is observed in the top emitting NR-LED due to the formation of a large number of textured surfaces having a larger escape cone. NR-ZnO can also enhance the escape probability. In other words, the photons have multiple opportunities to find the escape cone more easily. However, the light output intensity of NS-ZnO is decreased because the higher defective NS-ZnO can trap or absorb the photon emitted from the MQWs. We suggest that light extraction efficiency would be

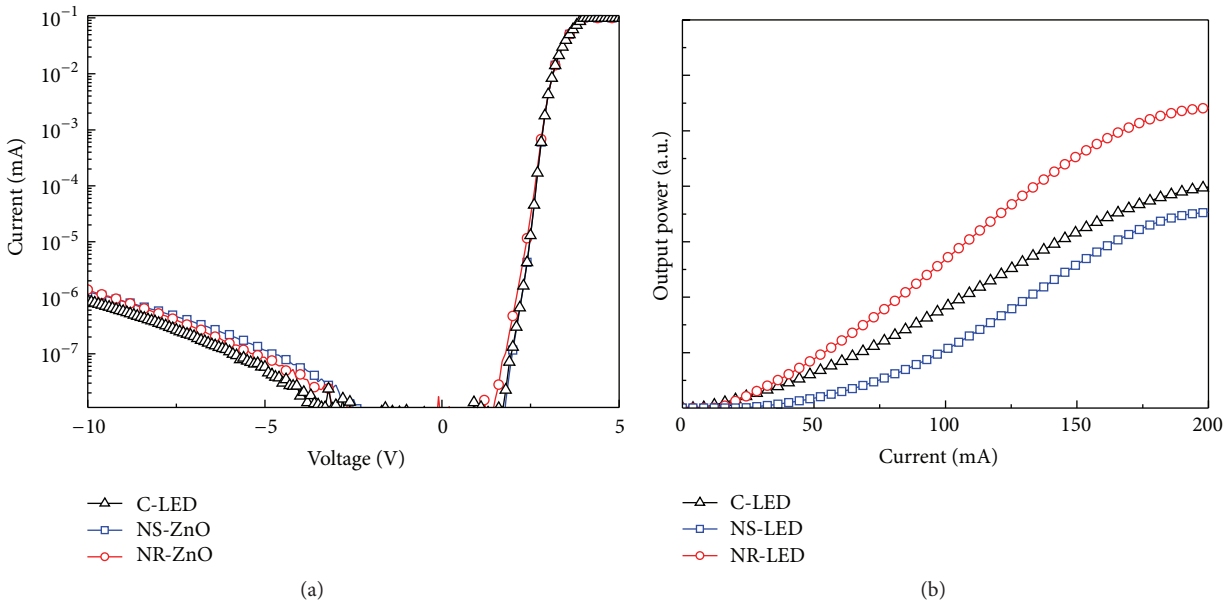

FIGURE 4: (a) I-V and (b) light output power as a function of applied current of fabricated NR-LED, NS-LED, and C-LED.

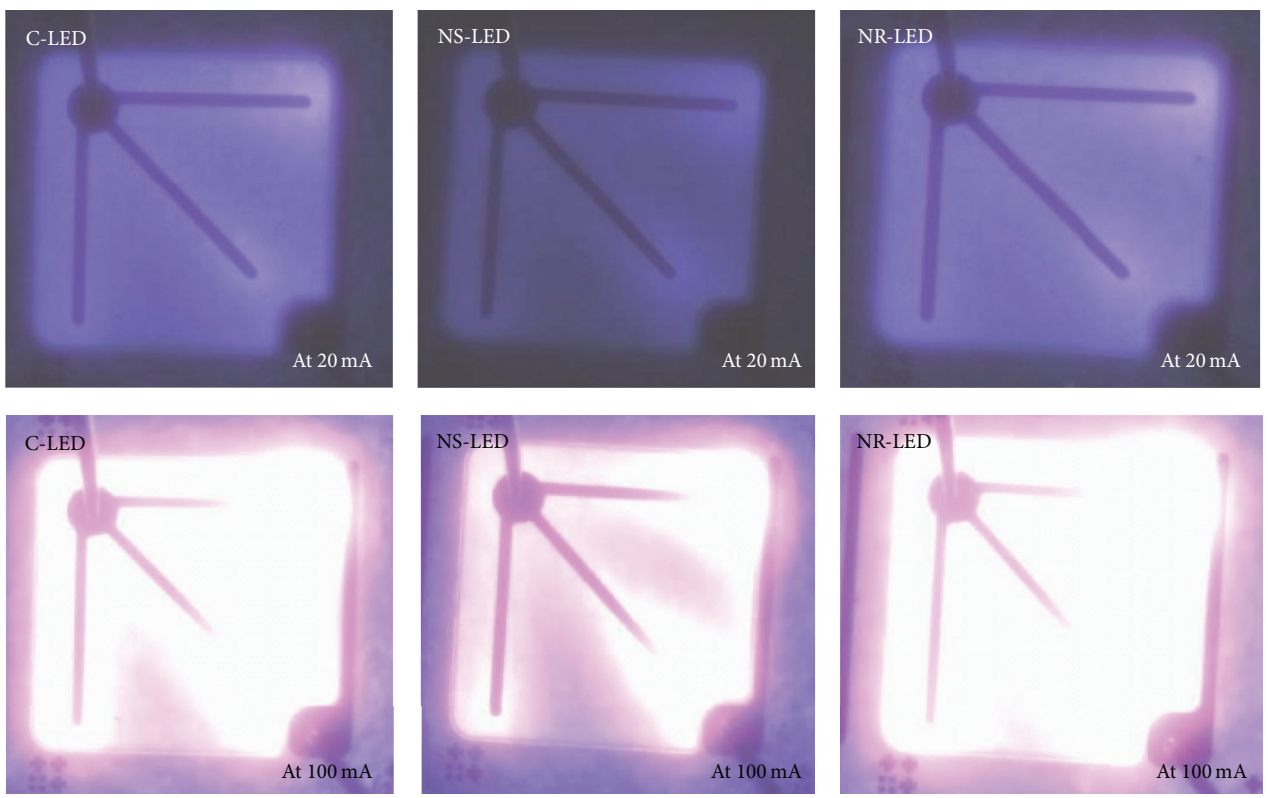

FIGURE 5: Optical micrographs of C-LED, NR-LED, and NS-LED at an operating current of 20 mA and 100 mA, respectively.

different depending on the forms of ZnO in the NUV-LEDs. In summary, NR-ZnO structure is more effective on the light extraction for the NUV-LED than NS-ZnO.

4. Conclusion

In conclusion, a facile method to enhance light extraction efficiency of 375 nm NUV-LEDs by ZnO nanostructures on a planar indium tin oxide (ITO) transparent electrode has been reported. NR-ZnO was compared with NS-ZnO to elucidate the effect of ZnO nanostructures on the light output power. At an injection current of 100 mA, the light output power of the NR-LED was enhanced by around 47% as compared to the C-LED. The increased light extraction by the NR-ZnO is due to the formation of a surface texturing, resulting in an enhancement of the escape probability and the multiple scattering for the photons in the NUV-LED. The light output efficiency of the NS-LED was decreased by 42% compared to the C-LED due to an increase of the internal reflection and light absorption in the defective NS-ZnO.

Competing Interests

The authors declare that there is no competing interests regarding the publication of this paper.

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