

Accepted Manuscript

Ultraviolet, blue, and green InGaN-based light-emitting diodes functionalized with ZnO nanorods

Hyun Jeong, Rafael Salas-Montiel, Gilles Lerondel, Mun Seok Jeong



PII: S0925-8388(17)30797-1

DOI: [10.1016/j.jallcom.2017.03.028](https://doi.org/10.1016/j.jallcom.2017.03.028)

Reference: JALCOM 41066

To appear in: *Journal of Alloys and Compounds*

Received Date: 7 September 2016

Revised Date: 20 February 2017

Accepted Date: 4 March 2017

Please cite this article as: H. Jeong, R. Salas-Montiel, G. Lerondel, M.S. Jeong, Ultraviolet, blue, and green InGaN-based light-emitting diodes functionalized with ZnO nanorods, *Journal of Alloys and Compounds* (2017), doi: 10.1016/j.jallcom.2017.03.028.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Ultraviolet, blue, and green InGaN-based light-emitting diodes functionalized with ZnO nanorods

Hyun Jeong^{a,c}, Rafael Salas-Montiel^a, Gilles Lerondel^{a,b}, and Mun Seok Jeong^{b,c,*}

^aLaboratoire de Nanotechnologie et d'InstrumentationOptique, Institut Charles Delaunay, CNRS-UMR 6281, Université de Technologie de Troyes, BP 2060, 10010 Troyes, France

^bDepartment of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea

^cCenter for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Sungkyunkwan University, Suwon 440-746, Republic of Korea.

KEYWORDS: Light extraction efficiency, Light-emitting diodes (LEDs), ZnO nanorods,

Effective refractive index, Finite-difference time-domain (FDTD)

*Corresponding author at: ^cCenter for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Sungkyunkwan University, Suwon 440-746, Republic of Korea. Tel.: +82 312996505.

E-mail address: mjeong@skku.edu (M.S. Jeong).

Abstract

We investigated the augmentation in the light-output power of InGaN light-emitting diodes (LEDs) functionalized with ZnO nanorods (NRs) according to the emission wavelength of the LEDs and the volume fraction of the ZnO NRs. The ZnO NRs were fabricated on top of the ultraviolet, blue, and green InGaN LEDs using the hydrothermal method. The optical properties of the LEDs and ZnO NRs were examined by electroluminescence, photoluminescence, and Raman scattering at room temperature. The measurements of light-output power versus current and current as a function of voltage showed that there were considerably different enhancements in the light-output power of InGaN LEDs functionalized with ZnO NRs at different emission wavelengths of the LEDs, while no changes were observed in the electrical properties. Three-dimensional finite-difference time-domain simulations were conducted to support the experimental results. Both experimental and theoretical results indicated that the light-extraction efficiency of InGaN LEDs functionalized with ZnO NRs was significantly affected by the differences between the refractive indices of the GaN layers, indium–tin oxide layer, and ZnO NRs, which could be changed by the emission wavelength of the LEDs and volume fraction of the ZnO NRs.

1. Introduction

Over the last two decades, III-nitride based light-emitting diodes (LEDs) have been comprehensively investigated for applications of general lighting because of their significantly lower energy consumption, higher light-emission efficiency, and longer lifetime than those of conventional light bulbs, fluorescent lamps, and incandescent electric lamps [1–7]. Moreover, light emission in nearly the entire visible spectral range (from ultraviolet (UV) to green colour) has been realized with reliable efficiency by modulating the indium content of the InGaN active layer in an LED [8–12]. Nevertheless, the low light-extraction efficiency (LEE) of InGaN LEDs is left as one of the unresolved critical issues hindering further improvement of their light-emission efficiency [13–15]. Several research studies have proposed diverse technologies such as surface texturing, oblique indium–tin oxide (ITO) and ZnO micro- or nanostructures on the LED surface to overcome the low LEE of InGaN LEDs [16–19]. Among the suggested technologies, hydrothermal growth of ZnO micro- and nanostructures on the LED surface is regarded as the most efficient way to improve the LEE because of its significant advantages such as the simple, rapid, large-scale compatible and low-cost process without changing the electrical properties of the LEDs [20–24]. By employing ZnO nanorods (NRs) on the LED surface, several research groups were able to augment the light-output power of LEDs [25–30]. However, there is still insufficient information on the optimal growth conditions of ZnO NRs for increasing the light-output power of InGaN LEDs even though the optimal length of the ZnO NRs for enhancing the light-output power of blue InGaN LEDs was recently reported [31]. According to previous works, an effective refractive index of the ZnO NRs, which is main parameter in the LEE improvement of LEDs, is strongly dependent on the LED emission wavelength and volume fraction of ZnO NRs. Therefore, investigations on the effects of these two factors on the light-output power of

InGaN LEDs functionalized with ZnO NRs are necessary to determine the optimal conditions of ZnO NRs for improving the LEE of InGaN LEDs.

In this study, we investigated the effects of the LED emission wavelength and volume fraction of ZnO NRs on enhancement of the light-output power of InGaN LEDs functionalized with hydrothermally grown ZnO NRs. UV, blue, and green LEDs were grown on the *c*-plane of sapphire substrates by modulating the indium content of InGaN quantum wells (QWs). The LED chips were fabricated by the conventional LED process. The ZnO NRs were simultaneously grown on the UV, blue, and green InGaN LEDs by the hydrothermal method to compare their enhancement of light-output power according to the emission wavelength. The morphology of ZnO NRs was examined by scanning electron microscopy (SEM). Using room-temperature electroluminescence (EL), photoluminescence (PL), and Raman scattering, the optical properties of the LEDs and ZnO NRs were determined. The device performance of the UV, blue, and green LEDs was estimated by the light-output power as a function of the injection current (*L*–*I*) and from the current–voltage (*I*–*V*) curves. Three-dimensional (3D) finite-difference time-domain (FDTD) simulations were conducted as a theoretical analysis to support the experimental results.

2. Experimental

The epitaxial structures for the UV, blue, and green InGaN LEDs were grown using metal–organic chemical vapour deposition on *c*-plane sapphire substrates. Trimethylgallium, trimethylindium, and ammonia were used as the precursors for Ga, In, and N, respectively, in the crystal growth process. For the growth of the MQWs, the flow rate of trimethylindium was controlled to modulate the bandgap of QWs, resulting in the emission of UV, blue, and green light. After epitaxial growth of the LED structure, an ITO was deposited as the transparent

conducting layer on the GaN-based epitaxial layers, and a Cr/Au layer was deposited as the electrodes.

A simple noncatalytic hydrothermal method was used for growing ZnO NRs on the fully fabricated UV, blue, and green InGaN LEDs. The experimental growth process proceeded as follows: The fabricated LEDs were cleaned using deionized water and isopropyl alcohol before hydrothermal growth. A precise amount of zinc acetate dehydrate [Zn(O₂CCH₃)₂(H₂O)₂] was first dissolved in deionized water to obtain a 0.05 M reaction solution. Next, NH₄OH was used to create an alkaline environment (pH ≈ 9). The concentration of NH₄OH solution is around 20% in water. The hydrothermal growth was performed at 150°C for 60 min in an autoclave at a pressure of 4 atm and the heating rate was 3 °C/s. The ZnO NRs were grown on the UV, blue, and green InGaN LEDs simultaneously in the same autoclave without stirring. After growing the ZnO NRs, LEDs chips were cleaned by deionized water. The volume of the autoclave is 200 ml and filling rate is around 80%.

Field-emission scanning electron microscopy (S-4700, Hitachi) was used to obtain the plane-and perspective-view images of ZnO NRs formed on the InGaN LEDs. Spectroscopic confirmation of the light generated from the UV, blue, and green InGaN LEDs were performed by a macro-EL spectrometer consisting of a static current supplier (SourceMeter 2400, Keithley), a 30-cm monochromator (SP2300, Princeton Instruments), and a thermoelectrically cooled charge-coupled device (PIXIS 100, Princeton Instruments). The optical characterizations of the ZnO NRs were performed by macro-PL spectroscopy with a He–Cd laser ($\lambda = 325$ nm) at room temperature. Micro-Raman scattering of the ZnO NRs was measured with a He–Ne laser ($\lambda = 633$ nm). The light-output power and electrical properties of the LEDs was measured with a

probe positioning system equipped with a power supply (SourceMeter 2400, Keithley) and a Si photodiode.

3. Results and discussion

Fig. 1(a) presents a 3D illustration of the final structure of an InGaN LED functionalized with ZnO NRs. The size of a single LED was approximately $300 \mu\text{m} \times 300 \mu\text{m}$. (Fig. S1 in Supplementary Material) The GaN-based epitaxial structures consisted of an undoped GaN layer, an n-type GaN layer, seven pairs of InGaN/GaN MQWs, and finally a p-type GaN layer. The side-view SEM image in Fig. 1(b) shows vertically aligned ZnO NRs with respect to the LED surface; the average length of the ZnO NRs was 400 nm, an average diameter and periodicity of ZnO NR is around 50 nm and approximately 60 nm, respectively. (Fig. S2 and S3 in Supplementary Material) Accordingly, the volume fraction of ZnO NRs in this study was determined to be around 0.7.

Fig. 2(a) shows the intensity-normalized EL spectra, obtained at room temperature, of the LEDs in this study. The main EL peaks of the UV, blue, and green LEDs were observed at 377, 457, and 526 nm, respectively. The insets show photographs of the LEDs operating at 5 mA. The full width at half maximum (FWHM) of the EL spectrum is increased as the peak shifted toward longer wavelengths, as shown in Fig. 2(a). The different FWHM of EL peak according to emission wavelength is typical for InGaN LEDs, and it is attributed to the increasing indium content of the InGaN QWs, which resulted in higher indium compositional fluctuation. The structural and optical properties of the ZnO NRs were confirmed by the macro-PL and micro Raman scattering spectra obtained at room temperature. Fig. 2(b) presents the PL spectrum of the ZnO NRs grown on a sapphire substrate with excitation by a He–Cd laser ($\lambda = 325 \text{ nm}$). The

strong and sharp peak at 382 nm is near-band-edge (NBE) emission of ZnO. Weak and broad yellow emission peaks also appear in the wavelength range of 500–700 nm; this yellow luminescence is associated with defects in the crystalline structure [32]. The strong NBE peak and weak yellow band indicate that the ZnO NRs had high optical and crystalline quality. The inset of Fig. 2(b) is the micro-Raman spectrum of ZnO NRs grown on a sapphire substrate. Raman spectrum was measured in a backscattering geometry with excitation by a He–Ne laser ($\lambda = 633$ nm). The black arrows in the figure indicate the Raman modes of the sapphire substrate. The peak marked by the red arrow at 439 cm^{-1} corresponds to the E_2^{high} optical phonon mode of the hexagonal wurtzite ZnO crystal. From the optical measurements of ZnO NRs, we found that the ZnO NRs exhibited a hexagonal wurtzite structure with high crystalline quality.

To demonstrate the device performance of the UV, blue, and green InGaN LEDs with ZnO NRs, their L – I and I – V curves were obtained by a probe positioning system equipped with a photodetector. Fig. 3(a), (b), and (c) show the L – I curves with an injection current from 0 to 100 mA for the UV, blue, and green InGaN LEDs, respectively. The hollow black squares represent the experimental L – I data points of the conventional LEDs without ZnO NRs, while the hollow red squares represent the L – I data points of the LEDs covered with ZnO NRs. Since the light-output power of the UV LEDs was considerably lower than that of other LEDs, resulting in a higher noise level, the data points were fitted with a conventional linear equation, as shown in Fig. 3(a); the fitted curves are represented by solid lines. On the contrary, the light-output power of the blue LEDs was higher than that of the green LEDs, which is typical for InGaN LEDs with QWs of different crystalline quality owing to their indium content [33]. The light-output power of the UV LEDs with ZnO NRs at an operating current of 20 mA was 27% lower than that of the conventional UV LEDs without ZnO NRs because of the energy transfer from the LEDs to the

ZnO NRs. Since the bandgap of ZnO ($E_g = \sim 3.20$ eV) is slightly lower than the energy of the light emitted by the LEDs ($E_{hv} = 3.29$ eV), the UV light could be absorbed by the ZnO NRs on top of the LEDs [34]. (Fig. S4 in Supplementary Material) On the other hand, the light-output power of the blue LEDs with ZnO NRs at 20 mA was approximately 20% higher than that of blue LEDs without ZnO NRs, as shown in Fig. 3(b). This is attributed to the enhanced LEE of the LEDs caused by the ZnO NRs acting as an optical waveguide layer [19]. The enhanced light-output power of the green LEDs with ZnO NRs at 20 mA was 47% higher than that of the green LEDs without ZnO NRs, as presented in Fig. 3(c). The difference between the enhancement of the light-output power of the blue and green LEDs with ZnO NRs can be explained by the unequal refractive indices of the GaN layers and ZnO NRs, which varied with the emission wavelength [27]. The electrical properties of the LEDs with and without ZnO NRs were examined by the I - V curves as shown in Fig. 3(d)–(f). The applied voltage for all the LEDs was in the range of 0–6 V. The I - V data points for the LEDs with ZnO NRs are represented by hollow red triangles, while the I - V data points for conventional LEDs without ZnO NRs are represented by hollow black squares. Fig. 3(d), (e), and (f) show the I - V curves of the UV, blue, and green LEDs, respectively. The I - V curves of all of the LEDs show negligible differences in terms of series resistance and threshold voltage of LEDs. This indicates that the ZnO NRs did not affect the electrical properties of the LEDs. Consequently, the L - I - V results confirm that the different enhancement in light-output power, which varied with the LED emission wavelength, was caused by changes in the LEE, which could be modulated by the refractive indices of the GaN layers, ITO layer, and ZnO NRs layer.

To confirm the optical origin of the light-output power enhancement, we simulated the optical response of the UV, blue, and green LEDs functionalized with ZnO NRs. We used the 3D FDTD

method to calculate the optical power radiated (P_{rad}) and the total power emitted ($P_{\text{tot}} = P_{\text{rad}} + P_{\text{loss}}$) by the LEDs. Perfectly matched layers (PML) were used as boundary conditions. We employed a non-uniform mesh with a grid size of 3 nm near the interfaces of the materials along the x -, y -, and z -axes and a grid size of 30 nm in the LED bulk region. A plane-top monitor was placed at (x, y_{top}, z) to calculate the power flux (i.e. the y -component of the Poynting vector) through the surface of the monitor. Four side monitors were placed above the LEDs to obtain the sum of the radiated optical power. Furthermore, we added four more side monitors to measure the optical power loss. Since the LED is an incoherent and randomly polarized light source, we independently simulated the optical power emitted by a single dipole source oriented in the three orthogonal directions, and then we calculated the sum of the results to account for the real device emission. It should be noted that we excluded the effect of energy transfer in the simulation to focus on the variation in optical power with the LED emission wavelength. The FDTD images obtained for the optical power flux of the conventional UV, blue, and green LEDs without ZnO NRs are presented in Fig. 4(a), (c), and (e), respectively. The colour bar indicates the power flux emitted from each LED. The optical power obtained from the UV, blue, and green LEDs varied considerably because of the particular refractive index of each LED layer, which depended on the emission wavelength. The blue and green LEDs exhibited the highest and the lowest optical power, respectively, which are in accordance with the experimental L - I values shown in Fig. 3(a)–(c). Fig. 4(b) displays the FDTD image of the UV LEDs with ZnO NRs, which shows that the monitored optical power was noticeably higher than that of the conventional UV LEDs without ZnO NRs. This result does not match the experimental data in the L - I curve because we excluded the effect of energy transfer from the LEDs to ZnO NRs. The FDTD image in Fig. 4(d) of the blue LEDs with ZnO NRs shows that the optical power was greatly increased as to

compare with conventional blue LEDs without ZnO NRs. The enhancement in optical power of the blue LEDs with ZnO NRs was higher than that of the UV LEDs with ZnO NRs, which agrees with the FDTD images. Fig. 4(f) presents the FDTD image of the green LEDs functionalized with the ZnO NRs. The optical power is much greater than that of the conventional green LEDs without ZnO NRs. Although the total optical power of the green LEDs with ZnO NRs was lower than that of the blue LEDs with ZnO NRs, the optical power of the green LEDs with ZnO NRs appeared to be more enhanced than that of the blue LEDs with ZnO NRs. Accordingly, it can be concluded that the theoretical results of the FDTD simulation are in agreement with the experimental results plotted in the L - I curves.

In order to analyse the variation in optical power enhancement with the emission wavelength, we fixed the refractive index of each layer of the UV, blue, and green LEDs. The refractive indices of the GaN layer were fixed at 2.61, 2.49, and 2.43 for UV, blue, and green emission, respectively [35]. It should be noted that the refractive index of the InGaN/GaN MQW layer was slightly higher than that of the GaN layer because of the InGaN QWs [36]. The refractive indices of the ITO layers were set at 2.07, 1.97, and 1.89 for the UV, blue, and green LEDs, respectively [37]. The effective refractive index of the ZnO NRs was calculated using the following equation:

$n_{\text{eff}} = [n_{\text{ZnO}}^2 f_{\text{ZnO}} + n_{\text{air}}^2 (1 - f_{\text{ZnO}})]^{1/2}$, where n_{ZnO} and n_{air} are the refractive indices of ZnO and air, respectively, and f_{ZnO} is the volume fraction of ZnO [38]. The volume fraction of ZnO NRs used in this study was 0.7. It was confirmed by the SEM images. The effective refractive index of the ZnO NRs was set at 1.92, 1.84, and 1.78 for UV, blue, and green emission, respectively. Using the refractive indices defined by the emission wavelength, the refractive indices along the vertical structure of the UV, blue, and green LEDs with ZnO NRs are shown in Fig. 4g. The purple, blue, and green solid lines represent the refractive indices of the UV, blue, green LEDs,

respectively, with ZnO NRs. Note that the refractive index could gradually change at the interface between the inhomogeneous media because of the uneven interfacial morphology. In fact, the enhancement of light-output power could be determined in the region of the ITO layer, ZnO NRs, and air because every sample contained identical interfaces below the ITO layer. Therefore, we calculated the gap between the refractive indices of ITO and ZnO NRs, obtaining values of 0.15, 0.13, and 0.11, for the UV, blue, and green LEDs with ZnO NRs, respectively. The smaller difference between the refractive indices of inhomogeneous media implies lower Fresnel reflection at the interfaces [19]. Therefore, more photons could escape from the ITO layer to the ZnO NRs layer in the green LEDs with ZnO NRs than in the UV and blue LEDs. Moreover, the smaller gap between the refractive indices of ZnO NRs layer and air, shown in the green LEDs with ZnO NRs, contributed to the higher enhancement of light-output power than that of the UV and blue LEDs.

Since the volume fraction of the ZnO NRs was a critical parameter for the effective refractive index of the ZnO NR layer, it appears essential to study on the light-output power of InGaN LED with ZnO NRs according to the volume fraction of ZnO NRs. The LEE of the InGaN LED is defined as the part of the optical power generated in LED active layer. This definition is equivalent to the ratio of the optical power radiated above the LED to the optical power generated from the active layer. The LEE is calculated with the following equation: $\text{LEE} = P_{\text{rad}}/(P_{\text{rad}} + P_{\text{loss}})$, where P_{rad} and P_{loss} are the radiated optical power above the LED and the optical power loss, respectively. Fig. 5 shows the LEE enhancement factor according to the emission wavelength for a range of volume fractions of ZnO NRs. The volume fraction of ZnO NRs in this part of the study ranged from 0.6 to 1 in increments of 0.1. The emission wavelength of the UV, blue, and green LEDs used for the experimental results are presented in Fig. 5 by

vertical thick lines in blurred purple, blue and green, respectively,. Considering a ZnO volume fraction of 0.7 which corresponds to the experiment, the data points represented by the filled red triangles were found to be in agreement with the experimental result of LEDs functionalized with the ZnO NRs, as shown in Fig. 5. The theoretical results of LEE enhancement agree with the experimental results of light-output power of the blue and green LEDs. (Fig. S5 in Supplementary Material) The different enhancement values between experimental light output power and FDTD result is attributed to slightly inhomogeneous length and volume fraction of synthesized ZnO NRs while the LEE enhancement factors calculated by FDTD are ideal case. According to the calculated LEE enhancement factor, an optimal volume fraction of 0.8 would have been necessary for the ZnO NRs to enhance the LEE of the UV, blue, and green InGaN LEDs. Note that every data curve shows somewhat periodic fringe patterns, which are attributed to the Fabry Perot interference observed in the transmission spectra. (Fig. S6 in Supplementary Material) This implies that the LEE enhancement of LEDs with ZnO is affected by the total thickness of the structure including the GaN layers, ITO layer, and ZnO NRs layer. The calculated LEE enhancement factors corresponding to different volume fractions show that the LEE of LEDs with ZnO NRs was noticeably influenced by the volume fraction of ZnO NRs and the Fabry Perot interference fringes. Consequently, the most efficient ZnO NRs layer for improving the light-output power of InGaN LEDs could be designed by controlling the volume fraction of the ZnO NRs, the LED emission wavelength and the thickness of the LED layers (including the ZnO NRs layer).

4. Conclusions

We have demonstrated the effects of the emission wavelength of LEDs and the volume fraction of ZnO NRs on the enhancement of the light-output power of InGaN LEDs functionalized with

ZnO NRs. The ZnO NRs were grown by a simple hydrothermal method on the surface of the UV, blue, and green InGaN LEDs. The emission properties of the UV, blue, and green InGaN LEDs were confirmed by macro-EL spectroscopy at room temperature. Using macro-PL spectroscopy, micro-Raman scattering, and SEM images, we verified that the ZnO NRs were hexagonal wurtzite structures with high crystallinity and were vertically aligned with respect to the substrate. Through conventional L - I and I - V measurements, we observed considerably different enhancement of the light-output power in the UV, blue, and green LEDs functionalized with ZnO NRs without incurring changes in the electrical properties. The origin of the different enhancement in light-output power was investigated by 3D FDTD simulation as a function of the emission wavelength. The theoretical results of optical power calculated for the UV, blue and green LEDs with ZnO NRs were remarkably compatible with the experimental measurements of light-output power. This has been explained by a better refractive index matching between the GaN layers, ITO layer, and ZnO NRs layer. Moreover, the LEE enhancement factors of the InGaN LEDs functionalized with ZnO NRs were calculated for different emission wavelengths and volume fractions of ZnO NRs. As a result, we found that a volume fraction of 0.8 is the optimal value for improving the LEE of InGaN LEDs, and the LEE enhancement factor is significantly influenced by the thickness of each layer. We believe that our quantitative description of the light-output powers of InGaN LEDs functionalized with ZnO NRs as a function of the emission wavelength of the LEDs and the volume fraction of ZnO NRs will eventually lead to high-efficiency lightings and full-colour devices.

Acknowledgments

We acknowledge support by IBS-R011-D1 of Korea and the FUI MULTISS project (F1305008 M) of France.

REFERENCES

- [1] H. Morkoç, S.N. Mohammad, High-Luminosity Blue and Blue-Green Gallium Nitride Light-Emitting Diodes, *Science* 267 (1995) 51-55.
- [2] P. Waltereit, O. Brandt, A. Trampert, H.T. Grahn, J. Menniger, M. Ramsteiner, M. Reiche, K.H. Ploog, Nitride semiconductors free of electrostatic fields for efficient white light-emitting diodes, *Nature* 406 (2000) 865-868.
- [3] J.J. Wierer, M.R. Krames, J.E. Epler, N.F. Gardner, M.G. Craford, J.R. Wendt, J.A. Simmons, M.M. Sigalas, InGaN/GaN quantum-well heterostructure light-emitting diodes employing photonic crystal structures, *Appl. Phys. Lett.* 84 (2004) 3885-3887.
- [4] J.J. Wierer, A. David, M.M. Megens, III-nitride photonic-crystal light-emitting diodes with high extraction efficiency, *Nat. Photon.* 3 (2009) 163-169.
- [5] J.H. Choi, A. Zoukarneev, S.I. Kim, C.W. Baik, M.H. Yang, S.S. Park, H. Suh, U.J. Kim, H. Bin Son, J.S. Lee, M. Kim, J.M. Kim, K. Kim, Nearly single-crystalline GaN light-emitting diodes on amorphous glass substrates, *Nat. Photon.* 5 (2011) 763-769.
- [6] S.P. DenBaars, D. Feezell, K. Kelchner, S. Pimplakar, C.-C. Pan, C.-C. Yen, S. Tanaka, Y. Zhao, N. Pfaff, R. Farrell, M. Iza, S. Keller, U. Mishra, J.S. Speck, S. Nakamura, Development of gallium-nitride-based light-emitting diodes (LEDs) and laser diodes for energy-efficient lighting and displays, *Acta Mater.* 61 (2013) 945-951.
- [7] E. De Ranieri, Nobel Prize in Physics: Nitrides in the spotlight, *Nat Nano*, 9 (2014) 880-880.
- [8] A. Khan, K. Balakrishnan, T. Katona, Ultraviolet light-emitting diodes based on group three nitrides, *Nat. Photon.* 2 (2008) 77-84.
- [9] Y. Jiang, Y. Li, Y. Li, Z. Deng, T. Lu, Z. Ma, P. Zuo, L. Dai, L. Wang, H. Jia, W. Wang, J. Zhou, W. Liu, H. Chen, Realization of high-luminous-efficiency InGaN light-emitting diodes in the “green gap” range, *Sci. Rep.* 5 (2015) 10883.
- [10] Z. Deng, Y. Jiang, Z. Ma, W. Wang, H. Jia, J. Zhou, H. Chen, A novel wavelength-adjusting method in InGaN-based light-emitting diodes, *Sci. Rep.* 3 (2013) 3389.
- [11] S. Shinji, H. Rei, H. Jongil, N. Shinya, InGaN Light-Emitting Diodes on c -Face Sapphire Substrates in Green Gap Spectral Range, *Appl. Phys. Express* 6 (2013) 111004.

- [12] H. Jeong, H.J. Jeong, H.M. Oh, C.-H. Hong, E.-K. Suh, G. Lerondel, M.S. Jeong, Carrier localization in In-rich InGaN/GaN multiple quantum wells for green light-emitting diodes, *Sci. Rep.* 5 (2015) 9373.
- [13] P. Pust, P.J. Schmidt, W. Schnick, A revolution in lighting, *Nat. Mater.* 14 (2015) 454-458.
- [14] K.-J. Byeon, J.-Y. Cho, H.-B. Jo, H. Lee, Fabrication of high-brightness GaN-based light-emitting diodes via thermal nanoimprinting of ZnO-nanoparticle-dispersed resin, *Appl. Surf. Sci.* 346 (2015) 354-360.
- [15] S. Jiang, Y. Feng, Z. Chen, L. Zhang, X. Jiang, Q. Jiao, J. Li, Y. Chen, D. Li, L. Liu, T. Yu, B. Shen, G. Zhang, Study on Light Extraction from GaN-based Green Light-Emitting Diodes Using Anodic Aluminum Oxide Pattern and Nanoimprint Lithography, *Sci. Rep.* 6 (2016) 21573.
- [16] T.-X. Lee, K.-F. Gao, W.-T. Chien, C.-C. Sun, Light extraction analysis of GaN-based light-emitting diodes with surface texture and/or patterned substrate, *Opt. Express* 15 (2007) 6670-6676.
- [17] J.K. Kim, S. Chhajed, M.F. Schubert, E.F. Schubert, A.J. Fischer, M.H. Crawford, J. Cho, H. Kim, C. Sone, Light-Extraction Enhancement of GaInN Light-Emitting Diodes by Graded-Refractive-Index Indium Tin Oxide Anti-Reflection Contact, *Adv. Mater.* 20 (2008) 801-804.
- [18] H. Jeong, Y.H. Kim, T.H. Seo, H.S. Lee, J.S. Kim, E.-K. Suh, M.S. Jeong, Enhancement of light output power in GaN-based light-emitting diodes using hydrothermally grown ZnO micro-walls, *Opt. Express*. 20 (2012) 10597-10604.
- [19] H. Jeong, D.J. Park, H.S. Lee, Y.H. Ko, J.S. Yu, S.-B. Choi, D.-S. Lee, E.-K. Suh, M.S. Jeong, Light-extraction enhancement of a GaN-based LED covered with ZnO nanorod arrays, *Nanoscale* 6 (2014) 4371-4378.
- [20] S. Baruah, J. Dutta, Hydrothermal growth of ZnO nanostructures, *Sci. Technol. Adv. Mater.* 10 (2009) 013001.
- [21] M.N.R. Ashfold, R.P. Doherty, N.G. Ndifor-Angwafor, D.J. Riley, Y. Sun, The kinetics of the hydrothermal growth of ZnO nanostructures, *Thin Solid Films* 515 (2007) 8679-8683.
- [22] K.S. Kim, S.-M. Kim, H. Jeong, M.S. Jeong, G.Y. Jung, Enhancement of Light Extraction Through the Wave-Guiding Effect of ZnO Sub-microrods in InGaN Blue Light-Emitting Diodes, *Adv. Funct. Mater.* 20 (2010) 1076-1082.

- [23] S.J. An, J.H. Chae, G.-C. Yi, G.H. Park, Enhanced light output of GaN-based light-emitting diodes with ZnO nanorod arrays, *Appl. Phys. Lett.* 92 (2008) 121108.
- [24] G. Haiyong, Y. Fawang, L. Jinmin, Z. Yiping, W. Junxi, Synthesis and characterization of ZnO nanorods and nanoflowers grown on GaN-based LED epiwafer using a solution deposition method, *J. Phys. D-Appl. Phys.* 40 (2007) 3654.
- [25] Z. Yin, X. Liu, Y. Wu, X. Hao, X. Xu, Enhancement of light extraction in GaN-based light-emitting diodes using rough beveled ZnO nanocone arrays, *Opt. Express* 20 (2012) 1013-1021.
- [26] Y.-H. Hsiao, C.-Y. Chen, L.-C. Huang, G.-J. Lin, D.-H. Lien, J.-J. Huang, J.-H. He, Light extraction enhancement with radiation pattern shaping of LEDs by waveguiding nanorods with impedance-matching tips, *Nanoscale* 6 (2014) 2624-2628.
- [27] H. Jeong, M.S. Jeong, Confocal electroluminescence investigations of highly efficient green InGaN LED via ZnO nanorods, *J. Alloy. Compd.* 660 (2016) 480-485.
- [28] K.-K. Kim, S.-d. Lee, H. Kim, J.-C. Park, S.-N. Lee, Y. Park, S.-J. Park, S.-W. Kim, Enhanced light extraction efficiency of GaN-based light-emitting diodes with ZnO nanorod arrays grown using aqueous solution, *Appl. Phys. Lett.* 94 (2009) 071118.
- [29] C.B. Soh, C.B. Tay, S.J. Chua, H.Q. Le, N.S.S. Ang, J.H. Teng, Optimization of hydrothermal growth ZnO Nanorods for enhancement of light extraction from GaN blue LEDs, *J. Cryst. Growth* 312 (2010) 1848-1854.
- [30] P. Hyoungwon, B. Kyeong-Jae, Y. Ki-Yeon, C. Joong-Yeon, L. Heon, The fabrication of a patterned ZnO nanorod array for high brightness LEDs, *Nanotechnology* 21 (2010) 355304.
- [31] H. Jeong, R. Salas-Montiel, M.S. Jeong, Optimal length of ZnO nanorods for improving the light-extraction efficiency of blue InGaN light-emitting diodes, *Opt. Express* 23 (2015) 23195-23207.
- [32] Y.Y. Gong, T. Andelman, G.F. Neumark, S. O'Brien, I.L. Kuskovsky, Origin of defect-related green emission from ZnO nanoparticles: effect of surface modification, *Nanoscale Res. Lett.* 2 (2007) 297-302.
- [33] S. Pleasants, LEDs: Overcoming the 'green gap', *Nat. Photon.* 7 (2013) 585-585.
- [34] D.P. Norton, Y.W. Heo, M.P. Ivill, K. Ip, S.J. Pearson, M.F. Chisholm, T. Steiner, ZnO: growth, doping & processing, *Mater. Today* 7 (2004) 34-40.

- [35] A.S. Barker, M. Ilegems, Infrared Lattice Vibrations and Free-Electron Dispersion in GaN, Phys. Rev. B 7 (1973) 743-750.
- [36] M.M.Y. Leung, A.B. Djurišić, E.H. Li, Refractive index of InGaN/GaN quantum well, J. Appl. Phys. 84 (1998) 6312-6317.
- [37] T.A.F. König, P.A. Ledin, J. Kerszulis, M.A. Mahmoud, M.A. El-Sayed, J.R. Reynolds, V.V. Tsukruk, Electrically Tunable Plasmonic Behavior of Nanocube–Polymer Nanomaterials Induced by a Redox-Active Electrochromic Polymer, ACS Nano 8 (2014) 6182-6192.
- [38] Y. Ono, Y. Kimura, Y. Ohta, N. Nishida, Antireflection effect in ultrahigh spatial-frequency holographic relief gratings, Appl. Opt. 26 (1987) 1142-1146.

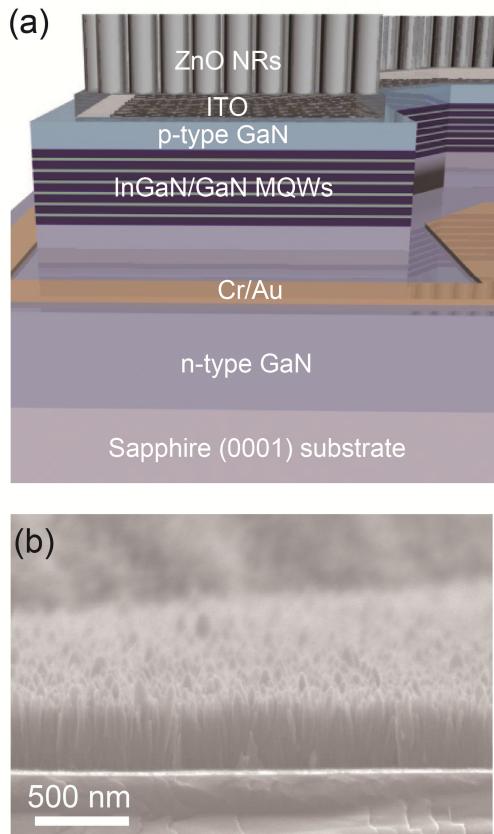


Fig. 1. (a) Magnified 3D schematic of InGaN LED structure with ZnO NRs. (b) Side-view SEM images of ZnO NRs grown on the surface of InGaN LEDs.

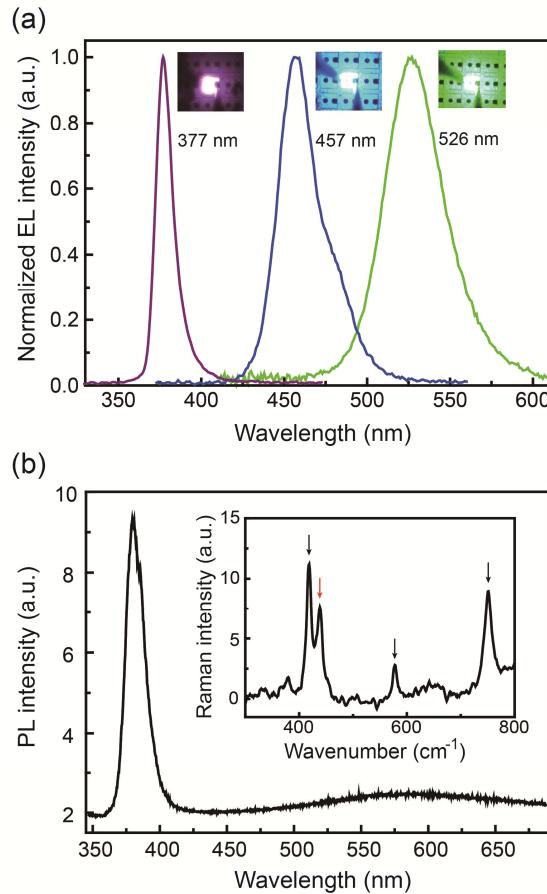


Fig. 2. (a) Intensity-normalized EL spectra of the UV, blue, and green InGaN LEDs; the insets show photographs of emission from the LEDs at an operating current of 5 mA. (b) Room-temperature PL spectrum of ZnO grown on a sapphire substrate. The inset presents the micro-Raman spectrum of ZnO NRs.

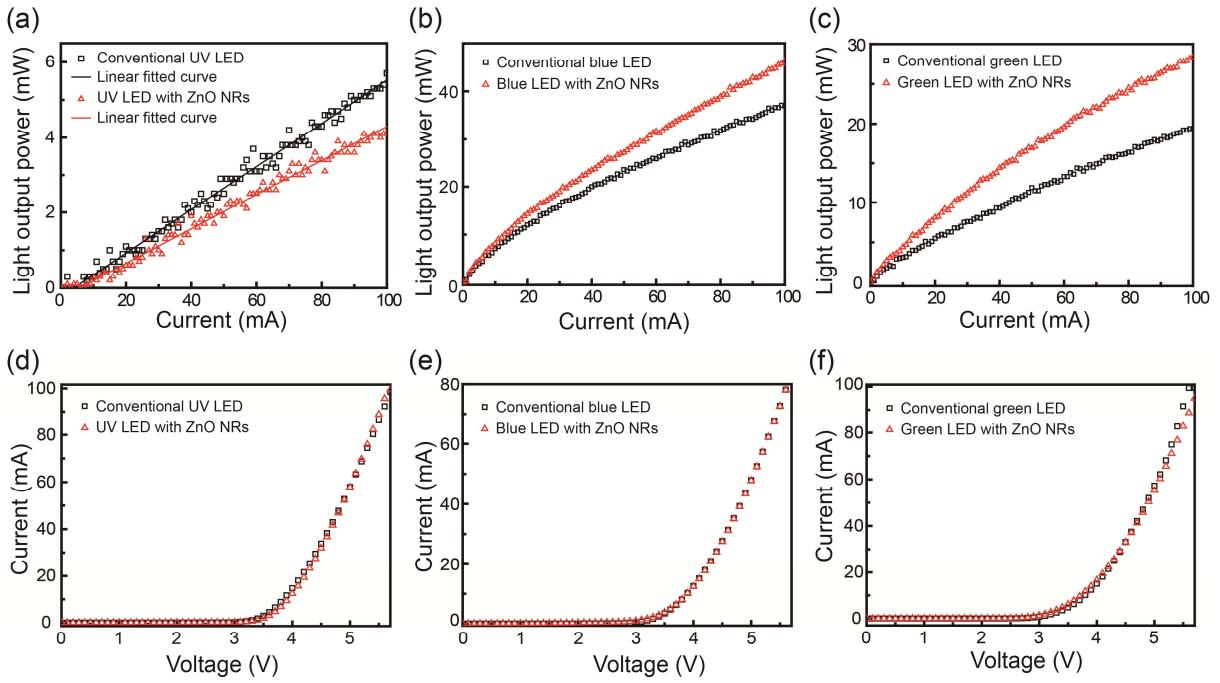


Fig. 3. L - I curves of (a) UV, (b) blue, (c) green LEDs with and without ZnO NRs. I - V curves of (d) UV, (e) blue, and (f) green InGaN LEDs with and without ZnO NRs. The hollow triangles represent the L - I and I - V data points of InGaN LEDs with ZnO NRs.

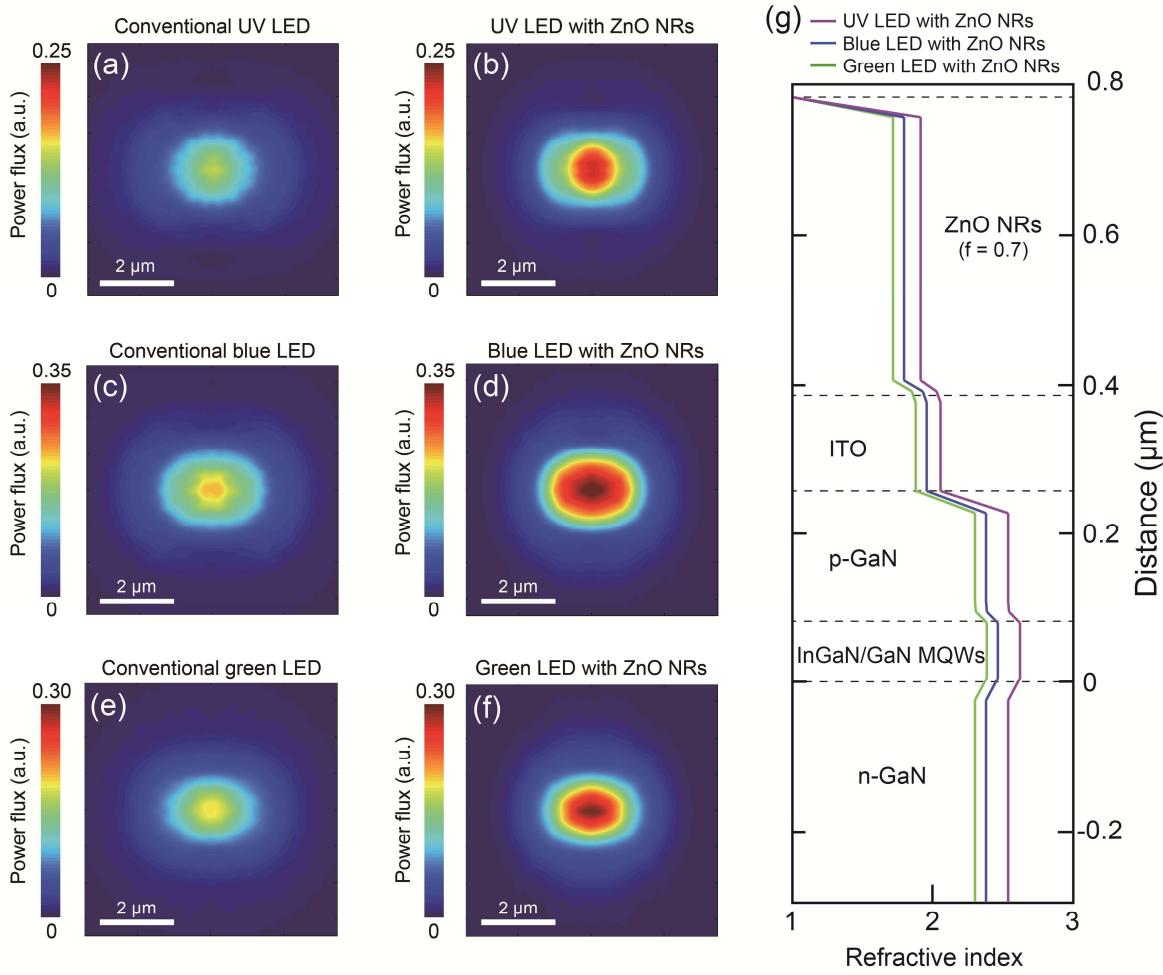


Fig. 4. The FDTD images of optical power flux for a (a) conventional UV LED, (b) UV LED with ZnO NRs, (c) conventional blue LED, (d) blue LED with ZnO NRs, (e) conventional green LED, and (f) green LED with ZnO NRs. (g) Refractive index profile along the vertical direction for the UV, blue, and green LED structure.

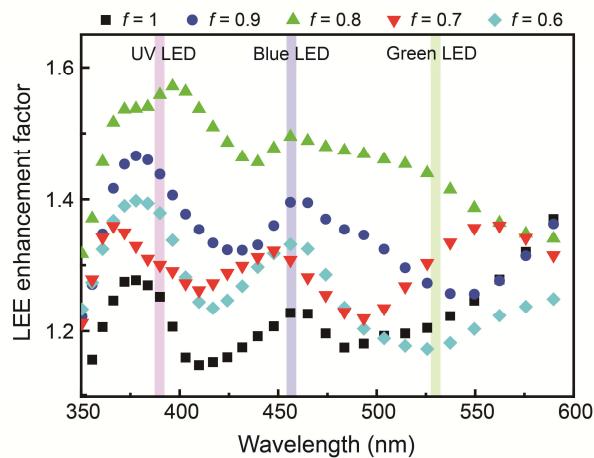


Fig. 5. LEE enhancement factors of InGaN LEDs with ZnO NRs as a function of the emission wavelength of LEDs for volume fractions of ZnO NRs.

Highlights

- ZnO nanorods are functionalized on surface of UV, blue, and green LEDs.
- Light output power of LED is augmented by ZnO nanorods due to light waveguide.
- Light extraction efficiency is notably influenced by emission wavelength of LED.
- Volume fraction of ZnO nanorods is significant for light extraction efficiency.