Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Three-dimensional GaN dodecagonal ring structure for highly efficient phosphor-free warm white light-emitting diodes

*Young Chul Sim, Seung-Hyuk Lim, Yang-Seok Yoo, Min-Ho Jang, Sunghan Choi, Hwan-Seop Yeo, Kie Young Woo, Sangwon Lee, Hyun Gyu Song and Yong-Hoon Cho**

Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea. Tel: (82) 42-350-2549, Email: yhc@kaist.ac.kr

S1. PL excitation (PLE) experiment

A PLE experiment was performed at 10 K to confirm that the PL emission at 580 nm in the DRS originated from the InGaN QWs, not from the yellow defect emission. The excitation source was a quasi-monochromatic light dispersed by a monochromator from the white emission of a xenon lamp. The PLE curves were measured for blue and yellow emissions (420 nm and 580 nm). The PLE spectra showed a broad absorption edge (375 nm and 450 nm) with a large Stokes'-like shift. The broad and Stokes'-like shifts were related to the strong localization effect of the excitons and the large potential fluctuation. These spectra were clearly different, with a PLE result for the yellow defect band.[1] Even though there was an intesity drop in the GaN bandgap near 355 nm, an intensity drop at 355 nm means a carrier transition from the GaN core structure to the InGaN MQWs layer.

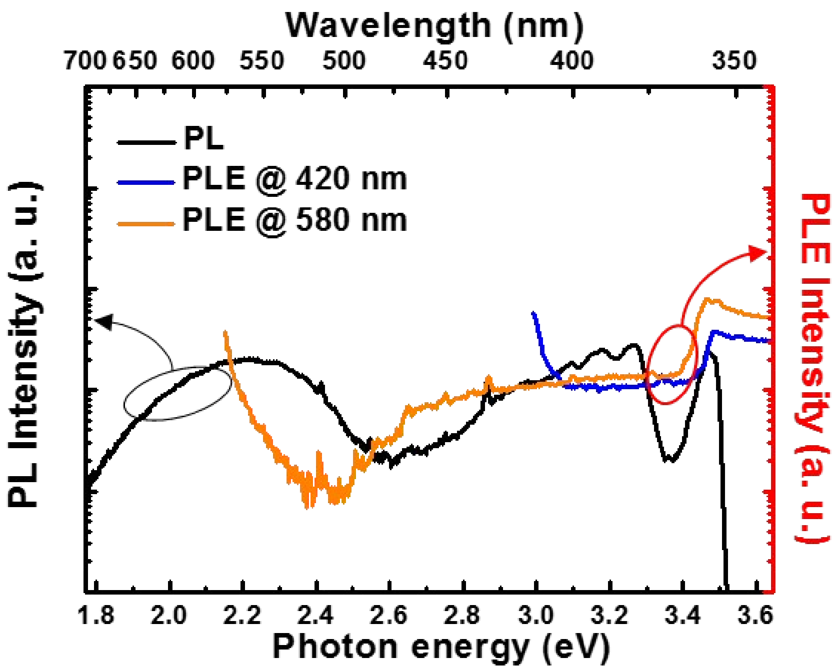

Figure S1. PL and PLE spectra for the InGaN/GaN core-shell DRS. The PL spectrum of the InGaN/GaN core-shell DRS (black solid line) and the PLE spectra measured at 420 nm (blue solid line) and 580 nm (orange solid line), respectively.

S2. Indium composition in InGaN QWs

The HAADF-STEM images of the MQWs were taken at the $\{10\bar{1}2\}$ and (0001) facets. The profile of the intensity of the MQWs of the $\{10\bar{1}2\}$ and (0001) facets was extracted along the blue and green arrows direction, respectively. The indium composition inside the InGaN QWs of each facet was estimated using the following Equation.[2]

$$I_{InGaN}/I_{GaN} = \frac{xZ_{In}^{\epsilon} + (1-x)Z_{Ga}^{\epsilon} + Z_{N}^{\epsilon}}{Z_{Ga}^{\epsilon} + Z_{N}^{\epsilon}}$$

where x is the indium concentration, Z is the atomic number, and ϵ is a factor as a function of the collection angle of the HAADF-STEM detector, which typically lies between 1.4 and 2. The average values of the indium composition x inside the QWs was 0.091 $\pm$ 0.014 for the $\{10\bar{1}2\}$ facet and 0.181 $\pm$ 0.030 for the (0001) facet.

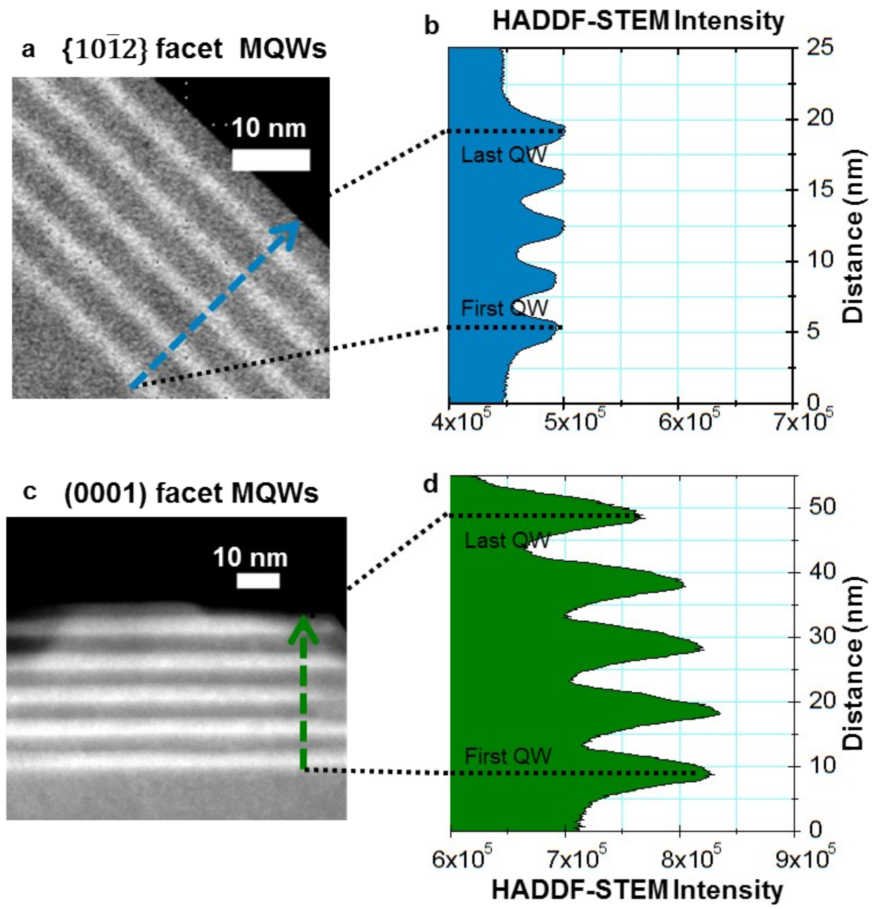

Figure S2. Indium composition analysis. High magnification HAADF-STEM images of the MQWs on (a) the $\{10\bar{1}2\}$ facet and (c) the (0001) facet. Blue and green arrows indicate the scan direction and the profile for the HAADF-STEM intensity of the MQWs on (b) the $\{10\bar{1}2\}$ facet and (d) the (0001) facet.

S3. Raman spectroscopy experiment

Raman spectroscopy was employed to measure the built-in strain in the 3D structure. Raman measurements were carried out at four different points, on the mask, outside, top and inside of the 3D structure, corresponding to P1, P2, P3, and P4, respectively. [Figure 3 b, c] We investigated the position of the E_2(high) Raman mode since it was the only observable photon affected entirely by strain. Figure 3 (a) shows the Raman shift of the E_2(high) mode for each excitation point. Each value is the mean peak position and the given error bars refer to the standard deviations, giving a measure for each point. The measured peak positions of the E_2(high) mode for the patterned GaN template and on the mask layer were 570.0 cm^{-1} which are the higher wavenumbers and indicate compressive stress, compared with the reference values of the unstrained bulk GaN reported by Harima [E_2(high): 567.6 cm^{-1}].[3] The strain relaxed 3D structure was obtained using the SAG technique. Moreover, the wet etching method using the KOH solution relaxed the built-in strain of the grown 3D structure close to the unstrained GaN structure.

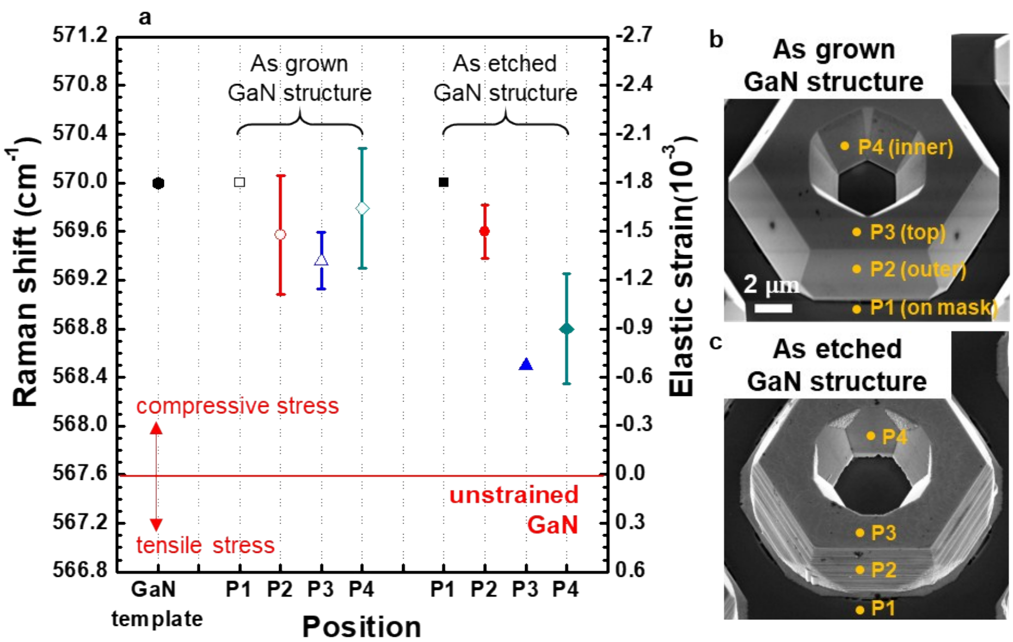

Figure S3. Raman spectroscopic characterization for strain analysis of 3D structures. (a) The mean E_2 (high) peak positions of the GaN template and each measuring point on the 3D structure. The yellow dots indicate excitation points from the Raman measurements for (b) the 'as-grown GaN structure' and (c) the 'as-etched GaN structure'.

S4. Device performances of DRS LEDs

The DRS LED devices were fabricated to characterize the electrical and optical properties with current injection. The procedure of fabricating the DRS LEDs and devices were illustrated in Fig. S4 a. We conducted masa-etching to expose the underlying *n*-GaN layer using the DRS LEDs. After mesa-etching, the indium tin oxide layer of 200 nm thick was deposited on the p-GaN for the current spreading. Finally, the metal layers of Cr/Au (50 nm / 200 nm) were locally deposited on the mesa-etched component and the ITO for the *n*- and *p*-type electrodes, respectively. Figure S4 b shows the light power-current-voltage (L-I-V) characteristics. There are typical rectifying behaviour with a turn on voltage of about 3.5 V and a leakage current of 6.34×10^{-3} A at -4.5 V. A large leakage current means that device fabrication process for three-dimensional based LEDs should be optimized.

Since the DRS LED devices is still in a wafer-level research, the directly measuring the optical output power, which is the radiant flux (W), is difficult using an integrating sphere. Therefore, in order to obtain the luminous efficiency, the light out-coupling model of DRS LEDs was considered to estimate the total optical power. The far-field radiation pattern from DRS LEDs has an emitting angle of about $\pi/3$ rad which was measured by the angle-resolved PL experiment with an objective lens of N.A. 0.9 as shown in figure S5. A solid angle of about π sr was obtained from the calculation. Considering the total output power versus the solid angle of the emitting light, a factor of π was multiplied to the intensity of light, which is the radiant intensity (mW/sr), collected by the detector.[4, 5] The estimated optical powers of devices are displayed at the right axis in figure S4 b. The optical power is 7.8 mW at an applied current of 100 mA and a voltage of 6.4 V, corresponding to a wall-plug efficiency (W/W) of 1.2% in radiometry unit. The luminous efficiency (lm/W) in photometry unit is 3.9 lm/W in consideration of eye sensitivity function (CIE 1978).

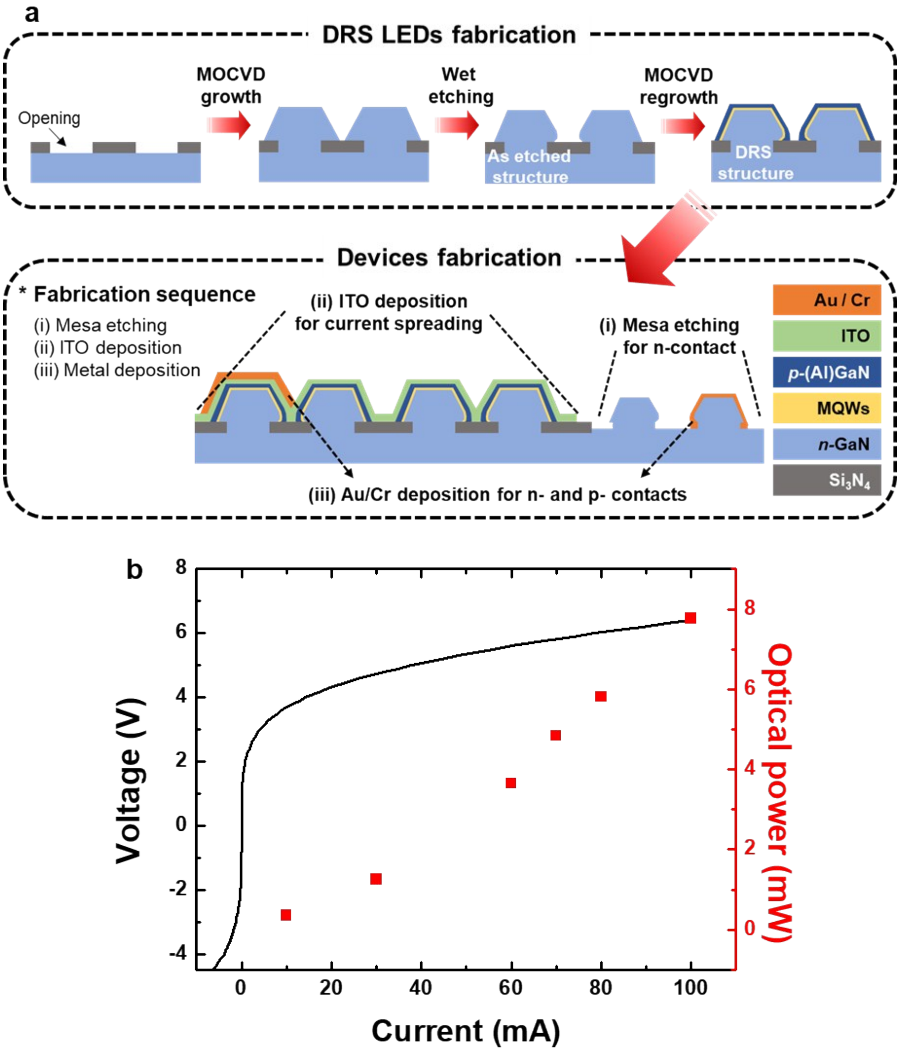

Figure S4. (a) Schematic representation of fabrication sequence for DRS LED devices. (b) The light power-current-voltage (L-I-V) characteristics of DRS LED devices. A black solid line is I-V curve and the red squares indicate optical output power at each applied current, respectively.

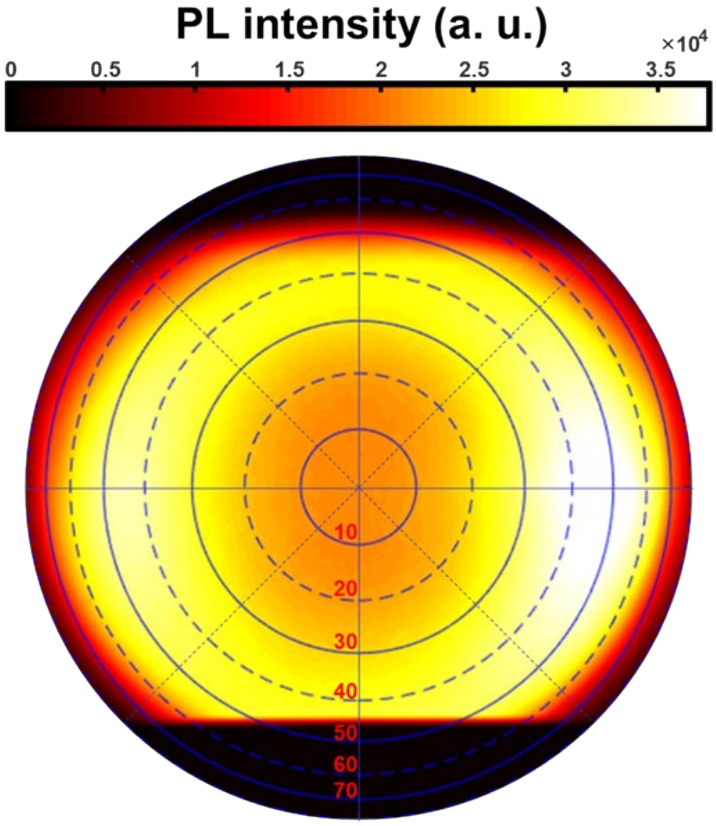

Figure S5. The far-field radiation pattern from DRS LEDs measured by the angle-resolved PL experiment with an objective lens of N.A. 0.9

References

1. I. Shalish, L. Kronik, G. Segal, Y. Rosenwaks, Y. Shapira, U. Tisch and J. Salzman, *Physical Review B*, 1999, **59**, 9748-9751.
2. H. Amari, I. M. Ross, T. Wang and T. Walther, *Phys. Status Solidi C*, 2012, **9**, 546-549.
3. C. Röder, F. Lipski, F. Habel, G. Leibiger, M. Abendroth, C. Himcinschi and J. Kortus, *Journal of Physics D: Applied Physics*, 2013, **46**, 285302.
4. J. H. Choi, A. Zoulkarneev, 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 and K. Kim, *Nat. Photonics*, 2011, **5**, 763-769.
5. Y. Tchoe, J. Jo, M. Kim, J. Heo, G. Yoo, C. Sone and G. C. Yi, *Advanced materials*, 2014, **26**, 3019-3023.