Size-controlled InGaN/GaN nanorod array fabrication and optical characterization

Si-Young Bae, Duk-Jo Kong, Jun-Yeob Lee, Dong-Ju Seo, and Dong-Seon Lee*

School of Information and Communications, Gwangju Institute of Science and Technology, 261 Cheonnan-si, Gwangju 500-712, South Korea
dslee66@gist.ac.kr

Abstract: We demonstrate a cost-effective top-down approach for fabricating InGaN/GaN nanorod arrays using a wet treatment process in a KOH solution. The average diameter of the as-etched nanorods was effectively reduced from 420 nm to 180 nm. The spatial strain distribution was then investigated by measuring the high-resolution cathodoluminescence directly on top of the nanorods. The smaller nanorods showed a higher internal quantum efficiency and lower potential fluctuation, which can subsequently be exploited for high-efficiency photonic devices.

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References and links
1. Introduction

Due to their significant improvement in efficiency, III-nitride-based solid-state light emitters have achieved some potential in replacing traditional lights [1]. However, these InGaN/GaN materials still have inherent difficulties to overcome before efficient light-emitting diodes (LEDs) can ultimately be fabricated. One factor is the strong piezoelectric polarization that exists along the c-axis due to the large lattice mismatch between InN and GaN [2]. This unintentionally induced polarization leads to a quantum confined Stark effect (QCSE), thereby decreasing the radiative recombination efficiency of LEDs [3]. Another factor is the high dislocation density (10^9–10^11 cm^{-2}) of the epitaxial layer grown on the heterosubstrate, leading to a debasing influence on the device performance [4]. Several techniques have been explored in attempts to overcome these detrimental properties. For example, to suppress charge separation in a c-plane InGaN/GaN quantum well (QW), a staggered InGaN QW design or ternary InGaN substrates have been employed, thereby enhancing the electron-hole wavefunction overlap [5–7]. The use of nonpolar/semipolar InGaN QWs can be more beneficial for ultimately reducing the QCSE, even though it still requires the growth of low-defect-density nonpolar or semipolar GaN templates compared to using commercial c-plane GaN [8–10]. Reducing the dislocation density of grown GaN is also an important issue in order to achieve high efficiency GaN-based devices, regardless of the GaN polarity. For this task, nano-patterned substrates, lateral epitaxial overgrowth, homosubstrates, and nanoscale structures can be effectively utilized [11–16]. In particular, recent advances in fabricating nanoscale InGaN/GaN structures using bottom-up approaches have enabled spectral tunability—from blue to even red in the visible spectrum range—by controlling the size of nanorods (NRs) or the current density [17–19]. In addition, the GaN nanostructures selectively grown have multiple facets, which have different strain distribution and quantum dot/wire/well characteristics, enabling a broadband color emission [20, 21]. Indeed, a bottom-up approach for growing InGaN/GaN NRs has been deemed the most promising technique to reduce piezoelectric polarization by exposing the nonpolar planes (m- or a-planes) [18, 19, 22]. The increased effective emission area obtained by stretching the length of GaN nanorods can also potentially enhance the light output power [23]. For a more enlarged emission area, highly ordered nanostructure arrays are of importance for mask templates in wafer scales. These arrays can be achieved by using recently advanced self-assembled patterning methods such as nanospheres, diblock copolymer lithography, and rapid convective deposition [24–27].
However, it is extremely difficult to form GaN NRs using bottom-up approaches due to the elaborate parameter controls required during growth, thereby limiting the uniformity of the whole wafer area and subsequently constraining the wafer scale-up [16]. To date, top-down approaches using metal dewetting, nanospheres, laser holographic lithography, and nanoimprinting have been regarded as easier and more cost-effective methods for fabricating uniform GaN NRs [28–31]. These top-down approaches have additional advantages such as strain-relief, dislocation ruptures, and light extraction enhancement [32–35].

One notable issue in top-down approaches, however, is how to control the small diameter of GaN NRs, since the nanosize effect can be prominent when reducing the diameter of GaN NRs [17]. Generally, the size or shape of the nanoscale mask pattern is crucial in determining the diameter of GaN NRs. When the mask materials are adequate for a dry etching process, the size of the etched GaN NRs is normally compatible to the size obtained using nanoscale masks. To form smaller GaN NRs, metal dewetting techniques can also be applied, though the pattern may have an irregular shape and size [28, 32, 33]. In addition, the anisotropic etching rate between Ga-face and N-face GaN in a KOH solution has provided an adequate method to further reduce the size of GaN NRs, with the N-face GaN displaying a higher etching rate than Ga-face GaN due to the relatively higher surface energy obtained by exposing N atoms [36]. Previously, wet treatments with KOH solution have been primarily used to reduce the leaky characteristics of LEDs [37]; however, the size control of GaN NRs becomes possible by using a consecutive KOH wet treatment technique after a dry etching process.

Based on these considerations, in this paper, we introduce size-controlled InGaN/GaN NRs by combining a top-down approach with a wet treatment, and then present the results of our investigation into the spatial strain distribution of InGaN/GaN NRs obtained via a high-resolution optical characterization.

2. Experimental procedures

To fabricate InGaN/GaN NRs, we prepared an LED epitaxial structure that was grown on a c-plane sapphire by metal organic chemical vapor deposition (MOCVD). The LED structure mainly consists of a 150-nm p-GaN layer, five pairs of InGaN/GaN (2 nm/15 nm) MQWs, and a 2-μm n-GaN layer. Figure 1(a-i)–1(a-iv) show the schematic for fabricating the InGaN/GaN NRs. In brief, a 200-nm SiO₂ mask layer was first deposited on the LED film by plasma-enhanced chemical vapor deposition (PECVD). Then, a 400-nm thick photoresist (PR) was spin-coated on this layer, and laser holographic lithography was performed twice in order to create a rectangular array of nanoscale circles. Next, the exposed SiO₂ area was removed using reactive ion etching (RIE) to form a nano-etch mask; using an inductively coupled plasma (ICP) etching process, the as-etched InGaN/GaN NR structure was subsequently obtained, as shown in the scanning electron microscope (SEM) image in Fig. 1(b).

Next, in order to reduce the diameter of InGaN/GaN NRs we prepared a boiling KOH solution (150 °C). To investigate the rate of diameter reduction of InGaN/GaN NRs, as-etched samples were dipped into the KOH solution for 1 min, 3 min, and 5 min. In this way, we obtained clearly reduced InGaN/GaN NRs after 5 min [Fig. 1(c)]. Furthermore, the interconnected bridge region between the as-etched rods was effectively removed, subsequently enhancing the overall uniformity.
3. Results and discussions

Figure 2(a)–2(d) show cross-sectional SEM images of the InGaN/GaN NR structures. The as-etched NRs have a height of ~450 nm and a trapezoidal profile [Fig. 2(a)]. By dipping the samples into the KOH solution, the NR diameters were effectively reduced and the trapezoidal shape of the as-etched samples considerably changed into a vertical shape. The diameters of the as-etched NRs were ~420 nm, and the average diameter of the NRs was reduced to 340 nm, 265 nm, and 180 nm by wet treatments for 1 min, 3 min, and 5 min, respectively. Note that the etch rate for the first 1 min was approximately twice as fast as that for the further etched samples.

To understand how vertical shapes were obtained at an initially fast etch rate, we first need to consider the surface state of the as-etched NRs. Due to ion bombardment during the ICP etching process, a relatively N-rich face is exposed on the trapezoidal sidewall compared to the c-plane Ga-face. Then, the higher etch rate on this N-rich face in the KOH solution effectively removes the trapezoidal shape [36]. Finally, once the Ga and N atoms reach a chemical equilibrium by exposing nonpolar planes, the etch rate in the KOH solution becomes almost constant, indicating the controllability of fabricating InGaN/GaN NRs.
Figure 3 shows the room-temperature micro-photoluminescence (μ-PL) obtained using a 325 nm He-Cd laser. As in literature [28, 32, 33], we also observed that as-etched NRs exhibited a significant blueshift and weak intensity compared to the parent planar LED structure (short dashed line). Previous studies have suggested that the blueshift behavior from the parent planar epitaxial structures is attributed to strain relaxation due to plasma-induced damage [32]. By using the KOH wet treatment, however, the PL peak was redshifted to almost that of the parent planar LED and the PL intensity was significantly increased, indicating a recovered strain; then, as the diameter of the NR was reduced, the peak wavelength became slightly longer. In addition, whereas the as-etched NRs have the lowest PL intensity, the highest PL intensity was observed for the 1-min treated NRs, and the intensity was reduced with additional wet treatment. Normally, critical factors affecting the PL intensity in LEDs include the internal quantum efficiency (IQE), light-extraction efficiency (LEE), and volume-to-surface ratio (or, emitting area) [32, 33].

Even though the LEE of LEDs can be considerably affected by nanostructures and/or microstructures [38–40], all structures fabricated in this study are limited to nanoscale textures. In this case, the LEE is mainly affected by the geometry of the nanostructure, such as the shape, period, and height [41, 42]. Here, the period and height of the NRs are same, whereas the truncated pyramid-like shape of the as-etched sample is different from the vertical NR shape of the wet-treated samples. Generally, a higher LEE is expected for the truncated pyramid structures than the vertical NRs due to effective refractive index variation or more reduced total internal reflection [41, 42]. However, in this study, the truncated pyramid-like as-etched sample showed the weakest PL intensity, indicating that the IQE or light-emitting area are more critical factors than the shape. To then consider the light-emitting area of NRs, the fill factor was simply calculated using NR area per unit area: 25.9%, 17%, 10.3%, and 4.8%, for the as-etched, 1 min, 3 min, and 5 min samples, respectively. Even though the NR density appears to be relatively low, it can be improved by reducing the period of the mask pattern or employing advanced lithography techniques [24–27]. Then, to estimate the IQEs, the temperature-dependent PL was measured and the Arrhenius plot of the normalized integrated PL intensity was obtained, as shown in Fig. 4; we then approximated the IQEs using the PL efficiency, defined as \( \eta_{PL} = 100 \times \frac{I_{300K}}{I_{10K}} \) [43]. The estimated IQEs of the as-etched, 1 min, 3 min, and 5 min samples were 8.5%, 23.3%,
24.8%, and 24.8%, respectively. Hence, the lowest PL intensity of as-etched sample—in spite of having the largest emitting area—was seen to be due mostly to its low IQE. Furthermore, the reduced PL intensity of NRs by the wet treatment was attributed to the reduction of the light-emitting area since all wet-treated samples have a similar IQE.

![Figure 3. Room-temperature μ-PL of InGaN/GaN NRs. The short dash line indicates the peak of the parent planar LED structure.](image)

![Figure 4. Arrhenius plot of normalized integrated PL intensity.](image)

To investigate the spatial emission properties of NRs, we measured the low-temperature (80 K) cathodoluminescence (CL) using spot mode using a beam size of ~25 nm × 25 nm on the top of NRs, as shown in Fig. 5; the inset of Fig. 5 shows the schematic of the NR top. Here, the measured spot positions on the sample were specified as the relative spot position P = R / R₀, where R is the measured spot position and R₀ is the NR radius. The measurements on the top of NRs were performed at near center (P = ~0), middle (P = ~0.5), and edge (P = ~1), respectively. From these measurements, the CL peak of the as-etched NRs was seen to
be slightly redshifted from the center to the edge on the NRs, whereas the CL peaks of the wet-treated samples were blueshifted. It is noteworthy that there have been two main mechanisms identified for the peak shift of InGaN/GaN NRs formed by top-down methods. One is by the aforementioned plasma-induced damage and the other is by the weak lateral confinement of MQWs around the edges; both mechanisms affect the strain relaxation of NRs, thereby resulting in a blueshift behavior [28, 32, 33].

In this study, the as-etched samples were seen to be significantly affected by plasma-induced damage on the sidewall, being relatively blueshifted compared to the parent planar MQW, as shown in Fig. 3. The damage depth during the plasma etching has normally been considered to be ~50 nm, with only a slight depth deviation [44]. As for the second mechanism, the lateral confinement of MQWs reported to exist around the edge boundary [33] was not observed in the as-etched sample. As we consider the removal rate of InGaN/GaN NR by the KOH treatment, it was observed that the removal depths from the edge boundaries were ~40 nm, ~73 nm, and ~115 nm for the 1 min, 3 min, and 5 min wet-treated samples, respectively. In this case, we suggest that the plasma-induced damage was almost or completely removed and that the lateral confinement of the MQW became more dominant. As a result, we observed monotonic spatial strain distribution from the center to the edge; the more severe peak shift from the 1 min and 3 min samples was possibly due to the partially residual damaged region. By further reducing the NR size, the peak deviation also decreased, indicating the mostly similar strain distribution of small NRs. We believe that further reducing the strain distribution and surface recombination can be achieved by employing additional passivation and/or annealing process [45–47].

Figure 6 shows the PL peak wavelengths of NRs as a function of temperature. For the entire temperature range, the as-etched NRs displayed the lowest wavelengths, as was similarly observed in the μ-PL in Fig. 3. Interestingly, the as-etched NRs and 1 min wet-treated NRs displayed very clear S-shaped curves, whereas the 3 min and 5 min NRs had a relatively reduced S-shape. These S-shaped curves are known to originate from the potential fluctuation of InGaN MQWs [48], and the partial relaxation of NR edges likely plays a major role in non-homogeneous indium distribution similar to that in the enhanced S-shaped curves obtained from pyramidal semipolar MQWs [49]. Hence, the obvious S-shapes of the as-etched and 1 min wet-treated NRs were attributed to spatial strain distribution from the center
to the edge regions of the NRs. Therefore, in addition to the reduced diameter, which accordingly reduced the spatial strain, the more homogeneous indium distribution obtained by removing the damaged region through wet treatment improved the effectiveness of small-sized NRs for use in light-emitting devices.

![Graph showing PL peak wavelength as a function of temperature.](image)

Fig. 6. PL peak wavelength of NRs as a function of temperature.

4. Conclusions

In summary, we demonstrated the size-controlled fabrication of InGaN/GaN NR arrays by combining a top-down method with a wet treatment process, and then characterized the spatial strain distribution of NRs. The size of the NRs could be reduced accurately by dipping as-etched NRs into a boiling KOH solution. Whereas the PL intensity of the as-etched NRs was the lowest due to plasma-induced damage, the wet-treated NRs displayed a much improved PL intensity. Then, through a spot-mode CL analysis both the spatial strain deviation and potential fluctuation were observed to decrease due to the reduced NR size. Thus, it is expected that this approach for fabricating InGaN/GaN NRs can be applied to future photonic devices requiring a large area.

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