InGaN–GaN Nanorod Light Emitting Arrays Fabricated by Silica Nanomasks

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***Abstract*—We present a practical process to fabricate InGaN–GaN multiple quantum well nanorod structures. By using silica nanoparticles as the etch mask and followed by dry etching, nanorods with diameter 100 nm can be uniformly fabricated over the entire 2-in wafer. The photoluminescence spectra of the InGaN–GaN p-i-n nanorod structure are extracted at room and low temperatures. Also, discrete density of states can be observed at the temperature below 60 K. We further fabricate nanorod light emitting devices using a planarization approach to deposit p-type electrode on the tips of nanorods. Current–voltage curves and electroluminescent results of nanorod light emitting diode arrays are demonstrated.**

***Index Terms*—Light-emitting diode (LED), nanorod, silica nanomask.**

I. Introduction

WIDE-BANDGAP GaN-based semiconductor nanostructures have been extensively studied in recent years due to the interest in fundamental physical science and the potential applications to visible and ultraviolet optoelectronic devices. The intrinsic nature of quantum confinement in more than one dimension in quantum wires or quantum dots results in a low-threshold current as well as a narrower spectral linewidth of a low-dimensional laser [1]. As for nanostructure light-emitting diodes (LEDs), due to the increase of surface area provided by the sidewalls of nanowires or nanorods, the extraction efficiency can be enhanced. So far, there have been considerable efforts in the growth of GaN based nanorods, -wires, -pillars, or -columns. The common approach is to use metal nanoparticles, such as Fe, Au, and Ni, as catalysts during vapor–liquid–solid (VLS) growth to control the critical nucleation and subsequent elongation steps of nanowires [2]–[5]. Furthermore, high density GaN nanorods have been reported by molecular-beam-epitaxy (MBE) or metal–organic vapor phase epitaxy (MOVPE) [6]–[8]. In addition, vertically aligned and faceted GaN nanorods were fabricated on a GaN layer with a patterned SiO_2 template [9].

Despite various growth methods proposed and demonstrated, most approaches for fabricating nanostructures have difficulties controlling the exact diameter over the entire sample or achieving excellent spatial alignment of nanostructures. Other than complicated growth procedures, the realization of nanorods that contain heterostructures or active layers for light emission is also challenging. Previous studies have shown that the n- and p-type materials required in active devices can be realized in crossed and axial structures [10], by growing p-i-n GaN based material structures on patterned SiO_2 templates [11], or by growing n- (or p-) type nanowires on top of the planar p- (or n-) type structures [12].

Contrary to the bottomup synthesis, top-down etching process is another way to achieve nanorod structures. Nan-scale high-resolution etch masks can be fabricated by e-beam lithography, with excellent uniformity and precise control of patterns but with the disadvantages of low-throughput and cost issues. Another top-down approach for higher fabrication throughputs proposed in the literature is the technology of self-assembled metal nanomasks [13] or self-organized nanometer holes [14], which usually results in nonuniform distribution of nanorods.

In this paper, a practical process to fabricate InGaN–GaN p-i(MQW)-n nanorod structures is demonstrated. By using silica nanoparticles as the etch mask and inductively coupled plasma reactive ion etching (ICP-RIE) to define the pattern, nanorods with diameter 100 nm can be fabricated over the entire 2 inch wafer. The photoluminescence (PL) spectra of the InGaN–GaN multiple quantum well (MQW) nanorod structures are investigated at room and low temperatures. Furthermore, we also fabricate nanorod LEDs using a polymer planarization approach to deposit p-type electrodes on the tips of nanorods. Current–voltage curves and electroluminescent (EL) results are demonstrated.

II. Fabrication and Characterization of Nanorod Structures

A. Implementation of Nanorod Structures by a Silica Nanomask

The LED samples were grown on c-plane sapphire substrates by MOVPE. The material structure is composed of a 25-nm GaN buffer layer, a 1.8-μm Si-doped n-type GaN layer, a ten-period $In_xGa_{1-x}N$–GaN MQW structure, and a 200-nm p-type GaN layer. The average composition x of indium is around 0.2 with the quantum well thickness 3 nm. The MQW structure is designed to achieve a optical emission at 470 nm for planar LEDs. The nanorod structure was fabricated by spin coating a monolayer of silica nanoparticles as the etch mask. Fig. 1 shows the scanning electron microscopic (SEM) images of nanoparticles. The nanoparticles are self-aligned to each other with a diameter 100±5 nm and can firmly stick to the GaN surface due to the electrostatic force. The sample was then subjected to ICP-RIE etching. The dry etching process was performed using $SiCl_4$–Cl_2–Ar (1/20/15 sccm) as etching gases

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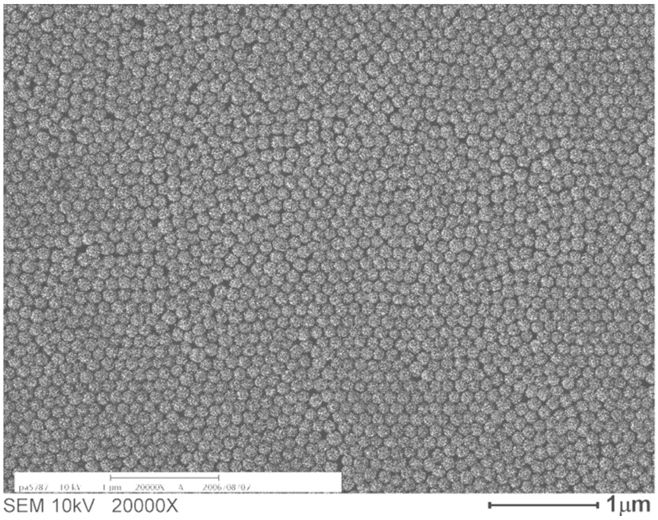

Fig. 1. SEM image of the monolayer silica nanoparticle mask.

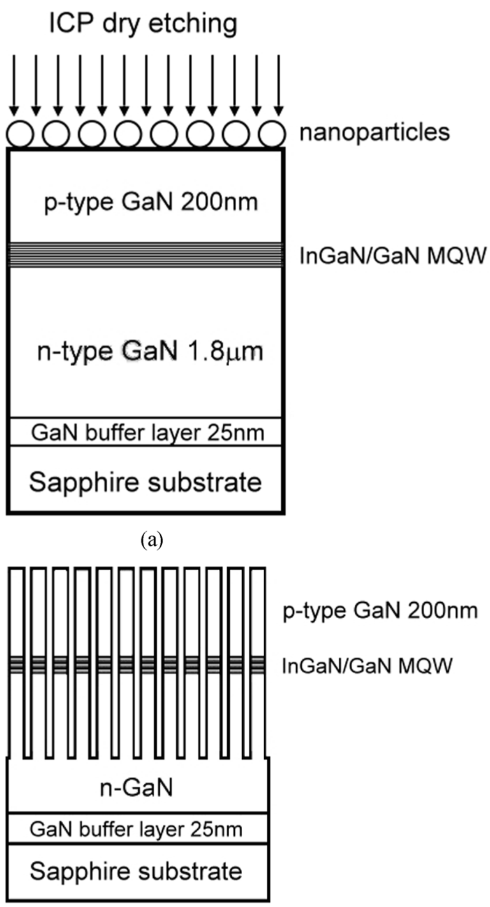

Fig. 2. Schematic diagram of the formation process of InGaN–GaN MQW nanorods. The nanoparticle mask (a) is first coated on top of the GaN LED sample and (b) then ICP RIE etching is performed to define nanorods.

with source power 200 W and bias power 100 W at 13.56 MHz. The etching rate is about 400 nm/min. The whole nanorod formation is straight forward and only involves process steps of nanoparticle coating and etching as illustrated in Fig. 2. Since

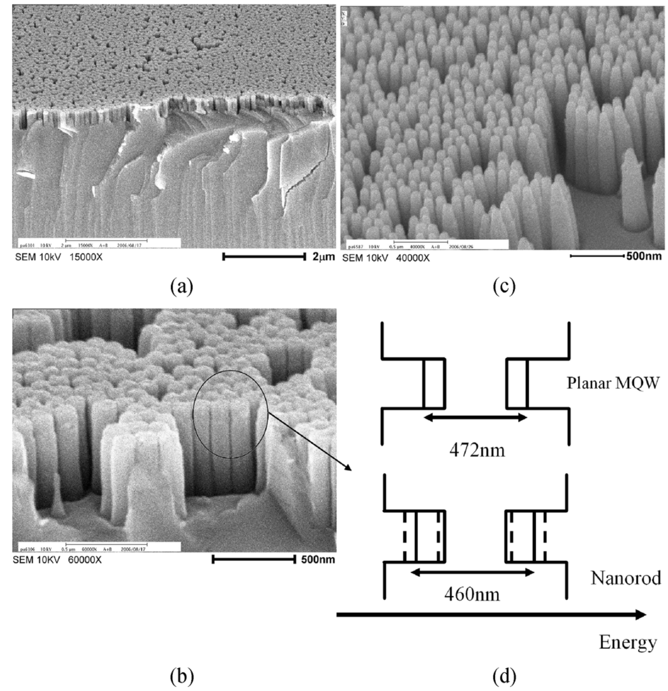

Fig. 3. (a) SEM image of GaN-based nanorod LED sample with etching depth around 600 nm. (b) Close-up view of the sample. (c) Pyramidal shape appears as the nanorod sample is further etched. The rod length is approximately 850 nm. (d) Band diagrams describing light emission from the planar LED structure and the nanorod. The light emission is blue shifted from planar to nanorod structure due to carrier confinement. The energy level shifts higher at lower temperature (dashed lines) according to the Varshni law.

the silica particles were spin-coated on the sample, nanorods can be uniformly fabricated over a large size of substrates.

The cross-sectional view of SEM images of GaN nanorods is demonstrated in Fig. 3(a). The etching depth is approximately 600 nm. All of the vertically aligned cylindrical GaN nanorods exhibit good uniformity in terms of cylindrical diameter, height, and density over the entire substrate. The diameter of GaN nanorods is 100 nm and the density is approximately 8.2×10^7 cm^{-2}. The formation of nanorod structures with various cylindrical size and depth can be simply controlled by choosing the size of silica nanoparticles and the duration of ICP dry etching. The close-up view of 600-nm-height nanorods in Fig. 3(b) shows that those rods are in cylindrical shape. As we etch the sample further to 850 nm (see Fig. 3(c)), the rods are slightly in pyramidal shape, indicating that the ICP dry etching is not anisotropic in our etching conditions. The lateral etching rate is influenced by gas flow rates and RF bias power.

B. Optical Properties of Nanorods

We next characterize optical properties of GaN nanorod light emitting structures. PL measurements were performed using a continuous wave He–Cd laser ($\lambda = 325$ nm) as the excitation light source. As shown in Fig. 4, the spectra of the nanorod sample are compared with those of the as-grown planar LED epistructure, that is, the LED sample prior to the ICP etching process. The fringes in the PL spectra are attributed to microcavity effects between p-GaN–air and sapphire–n-GaN interface [15]. Therefore, the form of the PL spectra is due to the combined effects of carrier recombination in the MQWs as

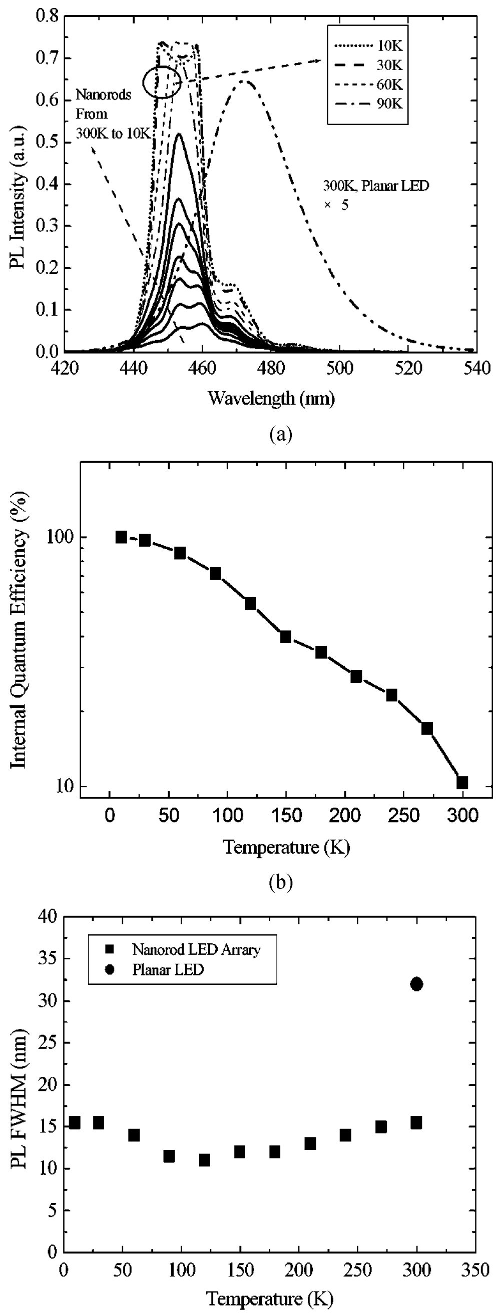

Fig. 4. (a) PL spectra of a GaN-based nanorod sample and a planar GaN-LED. The temperature is decreased from 300 K (the lowest curve) to 30 K at a step of 30 K along with an additional PL spectrum at 10 K. (b) Normalized IQEs of a nanorod sample at various temperatures. IQE is assumed to be 100% for the sample at 10 K. (c) PL FWHMs of nanorods at various temperatures and that of a planar LED at room temperature.

well as Fabry–Pérot resonance. As shown in Fig. 4(a), that peak wavelength of nanorods occurs at 460 nm at room temperature while the wavelength maximum of a planar LED is at 472 nm. Such a blue shift was also observed in other reports with different fabrication methods of nanorods and is attributed to the quantum confinement effect in the low-dimensional nanostructures [16], [17]. Band diagrams describing light emission from the planar LED structure and the nanorod are illustrated in Fig. 3(d). As the carriers in the intrinsic MQW region are further confined in a lower dimension structure, the recombination energy is shifted higher.

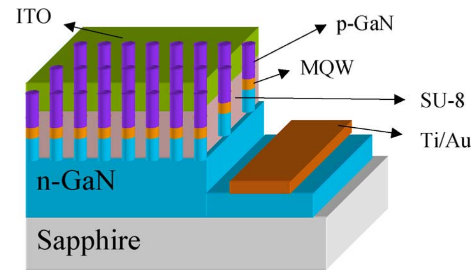

Fig. 5. Schematic process procedure of fabricating an InGaN–GaN MQW nanorod light emitting device.

To investigate carrier confinement in such a nanorod structure, low-temperature PL spectra were extracted from 300 (the lowest curve) to 30 K at a step of 30 K along with an additional 10-K spectrum. The results are also shown in Fig. 4(a). When the temperature is decreased, the internal carrier recombination spectra experience a blue shift according to the Varshni law [18]. As a result, the wavelength maximum shifts from 460 nm at 300 K to another fabry perot resonance peak at 453 nm at temperatures between 240 and 90 K. Also, the increase of PL intensity suggests that the internal quantum efficiency (IQE) of the MQW light emitting layers is enhanced at low temperature. By assuming 100% IQE at 10 K, the IQEs at different temperatures are plotted in Fig. 4(b). The decrease of IQE with the increase of temperature is due to nonradiative recombination in the sidewall of nanorods as well as in the interface of epilayers. When the temperature is below 60 K, two discrete states have become apparent especially for PL spectra at 30 and 10 K. The discrete density of states indicates that the nanostructure has confined carriers not only in the vertical direction due to original MQW design but also in the lateral direction due to nanorod structures.

In Fig. 4(c), we plot full-width at half-maximum (FWHM) of PL spectra of the nanorod sample at various temperatures. The FWHM of PL spectrum of the planar LED is also marked for comparison. From this plot, room temperature spectral linewidth of the nanorod sample is 15.5 nm while that of the planar LED is 32 nm. As we reduce the temperature, the linewidth of PL spectra decreases correspondingly until two discrete states appear at temperatures below 60 K.

III. Nanorod LEDs

A. Process Procedure of Nanorod LEDs

We next fabricate nanorod light emititng arrays. First, well-aligned InGaN–GaN MQW nanorod arrays were fabricated by a silica nanomask and followed by ICP-RIE. The average length and diameter of the nanorods are 400 and 100 nm, respectively. A schematic diagram of a nanorod LED array device is shown in Fig. 5. The gaps between the nanorods were filled with SU-8 polymer. High temperature reflow at 190 °C for 10 min was carried out to provide a smooth space layer. The current spreading layer, indium tin oxide (ITO), was sputtered on top of nanorods, resulting in a continuous contact layer over the InGaN–GaN MQW nanorod light emitting array. Finally, the n-GaN contact metal (Ti–Al) was evaporated and alloyed to complete the device fabrication.

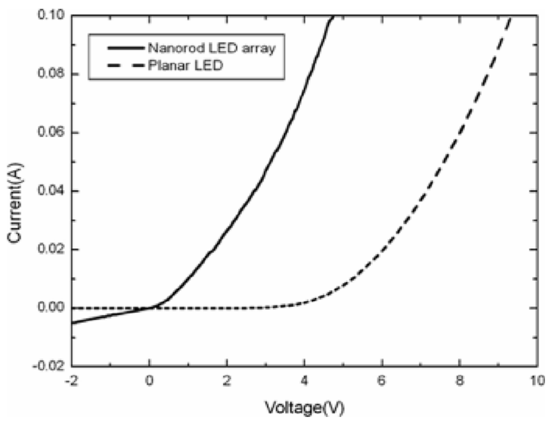

Fig. 6. I–V curves of the nanorod LED array and the planar LED.

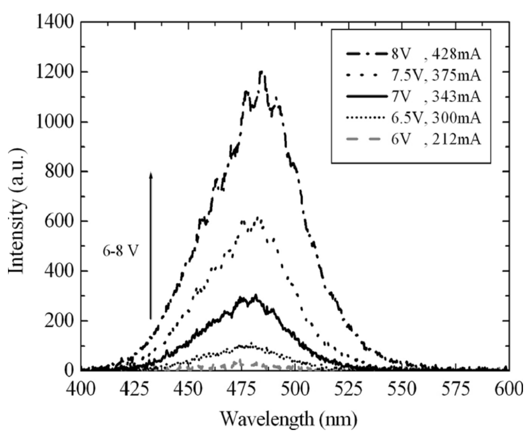

Fig. 7. EL spectra of the nanorod LED array.

B. Device Properties of Nanorod LEDs

Fig. 6 shows the current–voltage diode curve of a nanorod LED array and that of a planar LED is also plotted for comparison. Even though a resistor-like leaky path is in parallel to the p-i-n nanorod structure, rectifying behavior can still be observed from the I–V curve. The leaky path is believed to be related to poor contact resistance between ITO and GaN semiconductor interface and surface defects along the nanorods. We further measure room temperature EL spectra of the nanorod LED device at different injection currents. As shown in Fig. 7, the EL wavelength peaks are red shifted from 474 to 484 nm as the injection current is increased from 212 to 428 mA. The dependence of EL spectra on the operating currents is related to quantum-confined stark (QCSE) effect, which results from the strong piezo-electric coefficient due to the lattice mismatch between the InGaN and GaN layers [19], [20]. Such a field causes significant red shift of the QW emission wavelength.

IV. CONCLUSION

In summary, we present a practical process to fabricate dislocation free InGaN–GaN p-i(MQW)-n nanorod structures. Well-aligned GaN nanorods over the entire 2 inch wafer were demonstrated. The PL spectra show a blue shift of the peak wavelength from 472 nm planar structures to 460 nm for nanorods. The linewidth of nanorod samples shrinks almost half as compared with that of planar LED structures, suggesting carrier confinement in the low-dimensional structures. Also, discrete density of states can be observed at the temperature below 60 K. We further fabricate nanorod light emitting devices using an SU-8 as the spacer layer so that p-type electrode can be deposited on the tips of nanorods.. Rectifying behavior can be shown from I–V curves and blue light emission in the range of 474 to 483 nm from a nanorod LED array is demonstrated.

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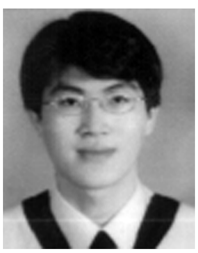

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