

Optical characterizations of GaN nanorods fabricated by natural lithography

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Abstract—We fabricated GaN/Sapphire nanorods by nanosphere lithography (NSL) using SiO₂ nanospheres. Arrays of SiO₂ nanospheres were packed on GaN, followed by dry-etching via inductively coupled plasma (ICP) etching. SiO₂ nanospheres served as the etching mask under our etching conditions. Finally, a sapphire substrate under GaN was exposed by dry-etching. A significant blue shift was observed in the room temperature photoluminescence (PL) spectrum from GaN/Sapphire nanorods when the underlying Al₂O₃ was exposed. GaN nanorods were fabricated by simple and reproducible methods, where SiO₂ nanospheres were successfully used as the etching mask. In addition, a blue-shift in PL by the band-filling effect was observed due to the GaN nanostructures.

Key words: Natural Lithography, Quantum Effects, Nanorods, Band Filling

INTRODUCTION

GaN-based semiconductors are very attractive because of their potential applications in photonic devices such as blue, UV light emitting diodes (LEDs) and blue laser diodes because GaN is a direct band gap material [1,2]. In addition, nanostructures in GaN-based LEDs have been shown to be effective in enhancing the light extraction efficiency [3]. Nanostructures, such as nanorods, nanopost and nanoporous structures, have been employed to enhance the light extraction efficiency [4-6]. Chen et al. showed the strain relaxation and quantum confinement in InGaN/GaN nanoposts [5], where InGaN/GaN nanoposts enhanced the photon energy and a blue shift phenomenon in the PL spectra was observed. Also, the enhanced photon energy was dependent on both the size of the nanoposts and temperature. Thus, these nanoposts, nanorods and nanostructures can be used for GaN nanophotonics. Nanorods can be fabricated by either the bottom-up (growth) or the top-down (etching) method. Nanorods have been successfully synthesized by bottom-up methods such as the vapor-liquid-solid (VLS) growth method [7]. Furthermore, GaN nanorods have been fabricated by other bottom-up methods such as molecular-beam epitaxy (MBE), hybrid vapor-phase epitaxy and metal-organic vapor phase epitaxy (MOVPE) [8-11]. However, it is difficult to control the length, diameter and carrier concentrations of nanorods when bottom-up methods are used. The top-down methods, such as inductively coupled plasma-reactive ion etching (ICP-RIE) without mask and electron-beam lithography methods, can be used for fabricating GaN nanorods [12]. However, electron-beam lithography requires very complex and expensive processes. In this study, we fabricated GaN nanorods by a nanosphere lithography (NSL) technique using SiO₂ nanospheres. We believe that our technique is very easy to implement for the fabrica-

tion of GaN nanorods with uniform qualities. Also, the quantum-confinement effect was observed from our GaN nanorods.

EXPERIMENTAL

SiO₂ nanospheres were synthesized by the Stöber method by the hydrolysis of tetraethylorthosilicate (TEOS) in ethanol medium with water and ammonia [13]. Ammonia formed the sphere shape of the SiO₂ particles, which were used as the catalyst. The diameter of SiO₂ nanospheres was adjusted by controlling the mole fraction of TEOS, water and ammonia. In our experiments, we used SiO₂ nanospheres that had a diameter of 300 nm and 400 nm. The diameter of the SiO₂ nanospheres was measured by scanning electron microscopy (SEM).

A schematic diagram of the fabrication process is shown in Fig. 1.

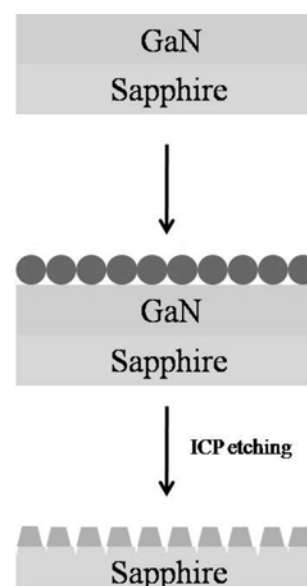


Fig. 1. A schematic of the process used to fabricate GaN/Sapphire nanorods.

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^{*}This paper is dedicated to Professor Jae Chun Hyun for celebrating his retirement from Department of Chemical and Biological Engineering of Korea University.

Commercial GaN with hexagonal structure grown on Al_2O_3 substrate was used as the starting material, where the thickness of GaN was about 1 μm . First, the GaN/Sapphire substrate was cleaned by acetone and isopropyl alcohol and SiO_2 nanospheres were spin-casted on GaN. Then, the GaN/Sapphire sample was dry-etched by inductively coupled plasma (ICP) etching using multiplex ICP (STS) instrument, where the etching gas was Cl_2 (30 sccm) and BCl_3 (5 sccm). The ICP power was 800 W, and the chuck power was 100 W. The etching pressure was 5 mTorr, and the DC bias was 228 V. Under these conditions, the etch rate of GaN and SiO_2 nanospheres was 9 nm/s and 1.5 nm/s, respectively [14]. The etching time was 2 minutes and 4 minutes 30 seconds for 300 nm SiO_2 nanospheres, and 5 minutes for 400 nm SiO_2 nanospheres. The size of the GaN/Sapphire nanorods after ICP dry-etching was confirmed by scanning electron microscopy (SEM). The room temperature photoluminescence spectra were collected by 325 nm line of UV lamp with/without GaN/Sapphire nanorods. In the PL instrument, the UV lamp was exposed to the face of the sapphire, and the detector collected the PL spectra on the GaN side.

RESULTS AND DISCUSSION

Fig. 2 is an SEM image of closed-packed arrays of SiO_2 nanospheres on GaN, where these SiO_2 nanospheres served as the etching mask and the underlying GaN was protected from ICP dry-etching. Fig. 3 is a tilted-view of the SEM images of GaN/Sapphire nanorods fabricated using 300 nm SiO_2 nanospheres after (a) 2 minutes 30 seconds and (b) 4 minutes of etching. The etching rates of GaN and SiO_2 nanospheres were approximately 9 nm/s and 1.5 nm/s, respectively. Fig. 4 is a tilted-view of the SEM images of GaN/Sapphire nanorods fabricated by using 400 nm SiO_2 nanospheres after 5 minutes of ICP dry-etching. The SEM images shown in Fig. 3 confirm the successful formation of GaN/Sapphire nanorods, which were uniform in diameter and length. However, the etching rate was dramatically enhanced by increasing the etching time, so the length of the nanorods in Fig. 3(a) and (b) was not proportional to the etching time. The nanorods in Fig. 3(a) consisted of only GaN material. In contrast, the GaN in Fig. 3(a) consisted of both GaN and

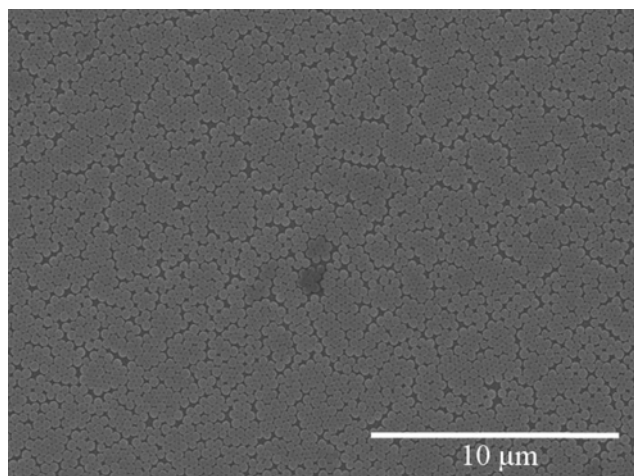
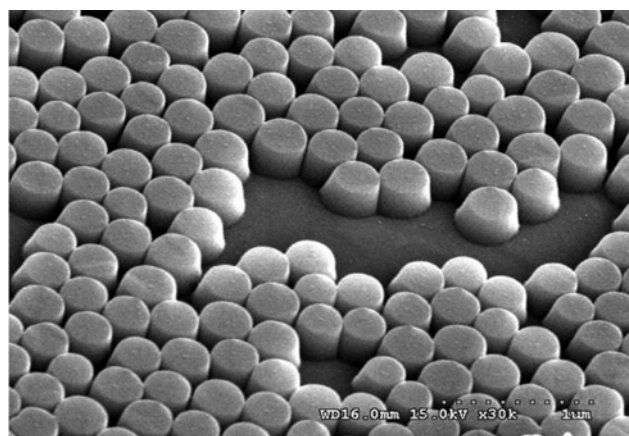
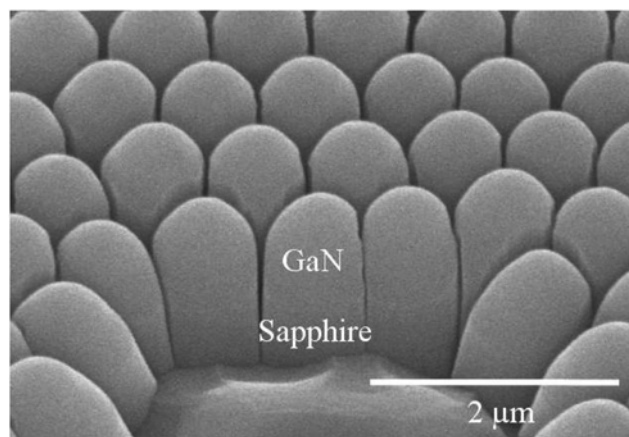


Fig. 2. Top-view of an SEM image of closed-packed arrays of SiO_2 nanospheres on GaN/Sapphire.



(a)



(b)

Fig. 3. Tilt-view of SEM images of GaN/Sapphire nanorods fabricated using inductively coupled plasma etching of SiO_2 nanospheres with a diameter of 300 nm for (a) 2 minutes and (b) 4 minutes 30 seconds.

Sapphire. The length of the GaN nanorods in Fig. 3(a) was approximately 200 nm, and that of the GaN and sapphire layers in the nanorods in Fig. 3(b) was 350 nm and 350 nm, respectively. At this condition, about a half of the GaN was already etched after SiO_2 nanospheres were removed. The length of the GaN/Sapphire nanorods in Fig. 4 was approximately 800 nm, and that of the GaN and sapphire layer in the nanorods was approximately 500 nm and 300 nm, respectively. The etching rate of sapphire was much slower than that of GaN, so the sapphire layer was used as the etch stop layer in our previous study [14]. However, GaN/sapphire substrates were dry-etched to produce the GaN/Sapphire nanorods by extended etching. In case the etching time was very long, SiO_2 nanospheres were completely removed by just ICP etching. Therefore, GaN under SiO_2 nanospheres was also dry-etched, such as those shown in Fig. 3(b) and Fig. 4.

Fig. 5 shows the room temperature PL spectra of the samples after 2 minutes of etching and 4 minutes 30 seconds of etching for 300 nm SiO_2 nanospheres and 5 minutes of etching for 400 nm SiO_2 nanospheres. First, we compared the effect of etching time (i.e., 2 minutes vs 4 minutes 30 seconds) when 300 nm SiO_2 nanospheres were used. The PL intensity of the sample that was dry-etched for

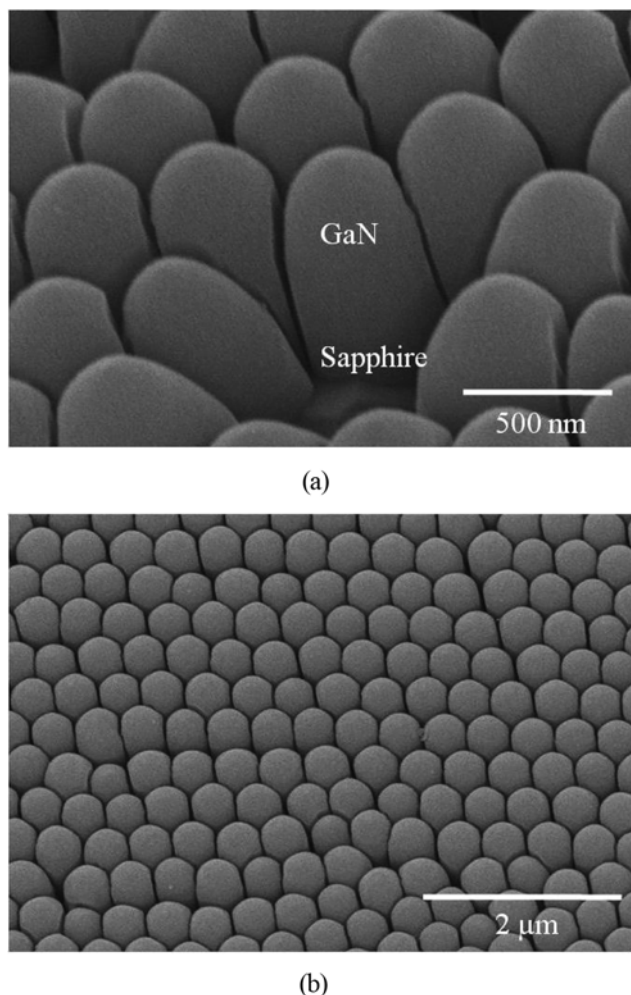


Fig. 4. Tilt-view of (a) high magnification and (b) low magnification SEM images of GaN/Sapphire nanorods fabricated using inductively coupled plasma etching of SiO₂ nanospheres with a diameter of 400 nm for 5 minutes.

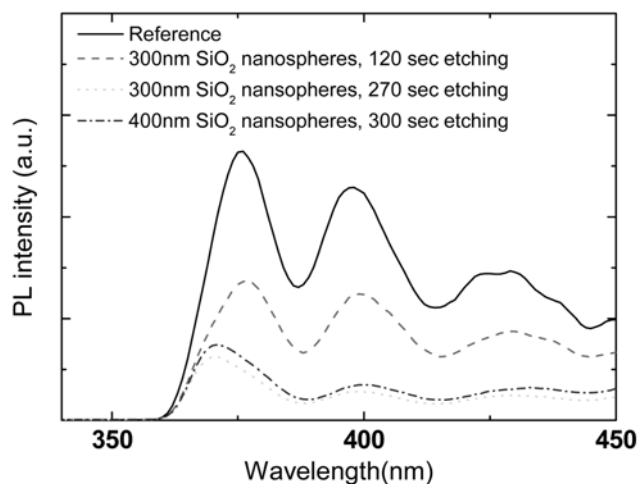


Fig. 5. PL spectra of GaN/Sapphire nanorods fabricated using 300 nm SiO₂ nanospheres with an etching time of 2 minutes and 4 minutes 30 seconds and 400 nm SiO₂ nanospheres with an etching time of 5 minutes.

2 minutes was lower than the reference sample, and the PL intensity of the sample that was dry-etched for 4 minutes 30 seconds was even lower by the increased etching time. The reduction in PL intensity can be attributed to the decreased volume in the GaN layer, since the volume of the GaN layer became smaller under extended dry-etching time. Also, the plasma damage can decrease PL intensity [15]. A significant blue shift (6 nm) was also observed from the sample that was etched for 4 minutes 30 seconds. This shift can be explained by the band filling effect and the strain relaxation. In polar-plane GaN, a local electric field was produced by polarization, which makes the holes and electrons in the c-plane GaN separate to the opposite edge of the energy band. Therefore, the efficiency of the recombination of the holes and electrons decreased. In addition, a red-shift could be observed, which is called the quantum-confinement Stark effect (QCSE). In our experiment, band-filling by excessive carriers under UV exposure led to the blue shift in PL spectra, and the quantum-confinement effect was confirmed by this phenomenon. Recently, non-polar GaN layers with an a-plane or m-plane structure have been extensively investigated to enhance the efficiency of GaN-based LEDs to minimize the local electric-field of the polar-plane GaN structure. The recombination of the holes and electrons cannot be limited by the local electric fields in the non-polar GaN LED structure. A decrease in PL intensity and blue shift (6 nm of PL peak wavelength) was observed in samples that were etched for 5 minutes using 400 nm SiO₂ nanospheres. The change in intensity and peak shift in the PL spectra was similar to the changes observed when the samples were etched for 4 minutes 30 seconds using 300 nm SiO₂ nanospheres, where we also confirmed the presence of the band filling effect. The amount of the blue shift was almost the same as the sample fabricated using 400 nm SiO₂ nanospheres, because the difference in the size of the SiO₂ nanospheres was nominal. Consequently, we were able to observe the quantum confinement effect by GaN nanorods fabricated by the SiO₂ NSL technique. We are currently conducting experiments to improve the light extraction efficiency of various LEDs such as UV LEDs, blue LEDs and non-polar LEDs by employing NSL-based nanofabrications.

CONCLUSION

We successfully fabricated GaN/Sapphire nanorods by nanosphere lithography and dry-etching via an inductively coupled plasma etcher. The diameter and length of the nanorods were easily adjusted by varying the diameter of SiO₂ nanospheres and the etching time. A blue shift in the PL spectra from GaN/Sapphire nanorods by the screening of the band-tail of the bandgap was observed.

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