Improvement of Epitaxy GaN Quality Using Liquid-Phase Deposited Nano-Patterned Sapphire Substrates

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***Abstract*— A relatively simple and easy and inexpensive liquid-phase deposition (LPD) method is employed to introduce nanoscale silica hemispheres on sapphire substrates for fabricating a nano-patterned sapphire substrate (NPSS). Compared with GaN grown on sapphire without any pattern, the NPSS-GaN film is of much better quality as observed by scanning electron microscopy, transmission electron-microscopy, X-ray diffraction, cathodoluminescence, and photoluminescence. This is because GaN is initiated from the c-plane instead of the LPD-silica surface. In addition, many dislocations within the NPSS-GaN bend toward the patterns, or end at the GaN/void interfaces.**

***Index Terms*— Light-emitting diode (LED), nano pattern, sapphire.**

I. Introduction

LIGHT-EMITTING diodes (LEDs) have been widely used in a variety of applications including traffic signals, backlighting in liquid-crystal displays, and projectors. For the next-generation application of solid-state lighting, GaN-based LEDs with high brightness are in great demand. The micron-sized patterned sapphire substrate (MPSS) has attracted intense attention for the reason that it can improve GaN crystal quality and enhance light extraction efficiency (LEE) [1]–[3]. Furthermore, the defect density of GaN can be further reduced if a nano-patterned sapphire substrate (NPSS) is used [4]–[8]. Unfortunately, methods for fabricating NPSS usually involve complex processes and require expensive equipment. On the other hand, the solution-cast seed layer formation process has been employed to grow GaN epitaxial layers [9], [10].

In this letter, a relatively simple, easy and inexpensive liquid-phase deposition (LPD) method was employed to introduce nanoscale SiO_2 hemispheres on sapphire substrates for fabricating NPSS [11], [12]. With NPSS, the crystal quality and optical performance of GaN were improved.

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II. Experiments

Two kinds of sapphire substrates were employed to grow GaN. Samples designated as “FLAT” are c-plane sapphire substrates without any pattern, while samples designated as “NPSS” are nano-patterned sapphire substrates.

To fabricate a NPSS, a two-inch c-plane sapphire substrate was immersed in a mixed solution of H_2SiF_6 saturated with silica gel and H_3BO_3 (0.01 mol/l) for 60 min. LPD-SiO_2 can be formed after the dehydration of OH-bonded siloxane oligomer $[SiF_m(OH)_{4-m}]$ by catalytic reaction and the growth mechanism had been previously reported [13]–[15]. The main reaction equations are listed as follows [16]:

$$H_3BO_3 + 4\text{HF} \leftrightarrow BF_4^- + H_3O^+ + 2H_2O. \quad (1)$$

$$H_2SiF_6 + 2H_2O \leftrightarrow 6HF + SiO_2. \quad (2)$$

Sample was then annealed at 900 °C in N_2 ambient for 30 minutes to improve LPD-SiO_2 quality. Nano-patterned LPD-SiO_2 was used as the wet-etching hard mask. Samples were then etched in a $3H_2SO_4$:$1H_3PO_4$ mixed solution at 270 °C for 60 seconds.

Samples were cleaned in a clean room using acetone, isopropyl alcohol and H_2SO_4 base solution at 80 °C. After the cleaning process, LED structures were grown by metal-organic chemical vapor deposition (MOCVD). The structures consisted of AlN as the buffer layer on the sapphire substrate, a 2.5-μm undoped GaN layer film, a 1.5-μm n-GaN layer, a 70-nm Si-doped AlGaN cladding layer, five pairs of InGaN-GaN multiple quantum wells (MQWs), a 400-nm Mg-doped AlGaN cladding layer and a p-GaN layer. The quantum well structure comprised a 2-nm InGaN well and a 10-nm GaN barrier. The features of LPD-SiO_2 and the crystal quality of GaN were characterized by scanning electron microscopy (SEM), transmission electron-microscopy (TEM), X-ray diffraction (XRD), cathodoluminescence (CL) and photoluminescence (PL).

III. Results and Discussion

The SEM images of as-deposited LPD-SiO_2 and NPSS are shown in Fig. 1. The LPD-SiO_2 deposited on the sapphire surface was in the shape of hemispheres having a diameter of 200–300 nm and a height of 100–150 nm. As shown in Fig. 1(a), the LPD-SiO_2 was uniformly distributed on the sapphire surface and the pattern coverage was about 45%.

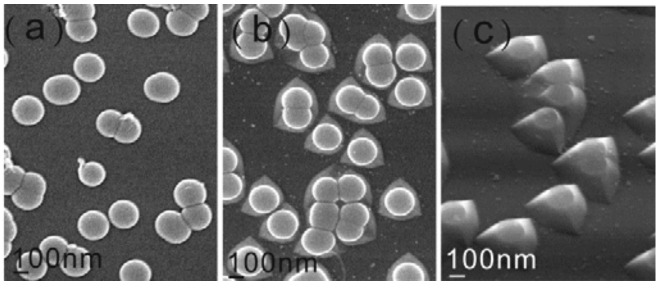

Fig. 1. Plane-view SEM images of (a) as-deposited LPD-SiO_2, (b) nano patterns formed by wet etching process, and (c) side-view SEM image of nano patterns.

After the wet etching process, pyramid-shapednano patterns having a diameter of 250–300 nm and a height of 200–300 nm were formed, as shown in Fig. 1(b) and (c). The appearance of these pyramid-shaped nano patterns is similar to that of micron patterns in Ref. [2].

The GaN crystal quality was first analyzed by XRD rocking curves (XRCs), which show that the full-width at half-maximum (FWHM) of NPSS-GaN was less than that of FLAT-GaN. Compared with FLAT-GaN, NPSS-GaN had FWHM of (002) GaN decreased from 427.9 to 367.1 arcsec, and FWHM of (102) GaN reduced from 586.9 to 362.7 arcsec. These results indicate that the GaN crystallinity of NPSS-GaN was superior to that of FLAT-GaN.

In addition to XRCs, the CL method was also employed to evaluate the GaN crystal quality. Figure 2(a) is the cross-sectional SEM image of NPSS-GaN. It clearly shows voids around nano patterns and a fully coalesced GaN. The CL spectra were collected from the area near nano patterns (spot 1) and the middle of the GaN film (spot 2) in both samples. The spectra integral intensity of NPSS-GaN at spot 1 was 9.3×10^4, which was 3.2 times higher than that of FLAT-GaN. As for spot 2, the integral intensity of NPSS-GaN was 2.2×10^6, which was even 7.3 times higher than that of FLAT-GaN (3×10^5).

The improvement in structural quality of the middle region (spot 2) was verified by measuring the etching pit density (EPD). Samples were grinded till undoped GaN was revealed ($\sim$2.5 μm from the GaN/sapphire interface), followed by etching samples in 270 °C H_3PO_4 for 3 minutes. The EPD of NPSS-GaN was 2.7×10^6 cm^{-2}, which was much lower than that of FLAT-GaN, 3.3×10^7 cm^{-2}. These results indicate that the GaN crystallinity of NPSS-GaN was superior to that of FLAT-GaN in the middle region.

TEM was also employed to investigate the crystal quality of NPSS-GaN. As shown in Fig. 3, voids were found at the corner of nano patterns. Dislocations originated from the GaN/sapphire interface due to the large lattice misfit. Lots of dislocations then extended to the upper region. However, around the nano-patterned regime, with increase in growth time, GaN epilayers on the c-plane sapphire covered these nano patterns with lateral growth, thus causing the threading dislocation to bend towards the patterns, or end at the GaN/void interfaces [17]–[19]. Therefore, not many dislocations were found on the top of the nano patterns.

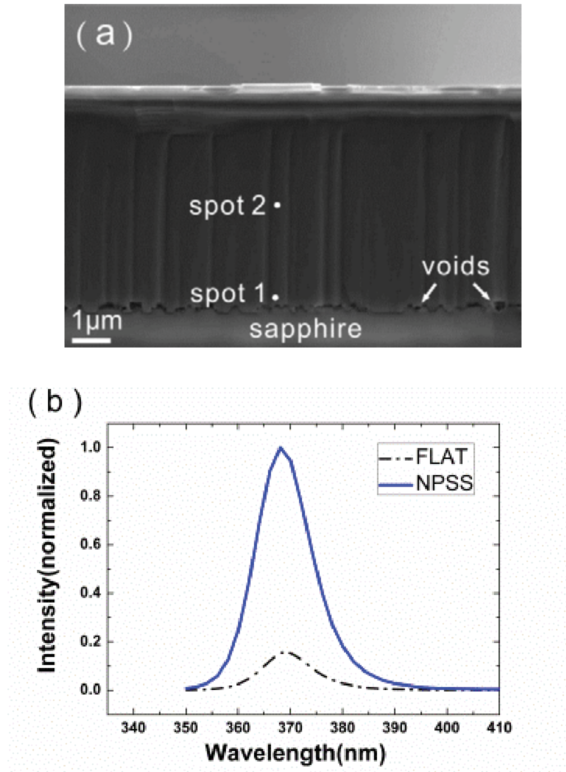

Fig. 2. (a) Cross-sectional SEM image of NPSS-GaN. (b) CL spectra of NPSS-GaN and FLAT-GaN from spot 2.

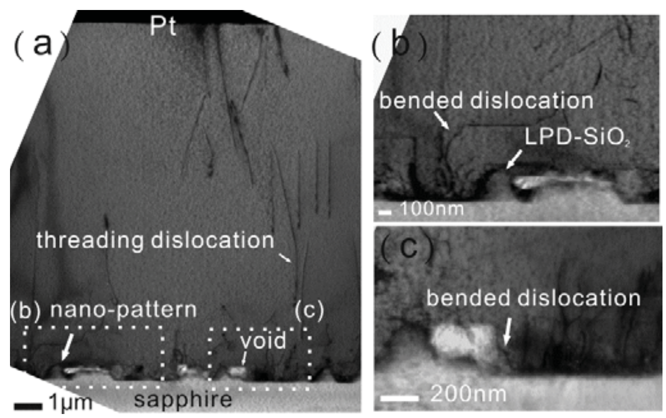

Fig. 3. (a) Cross-sectional bright-field TEM image of GaN grown on NPSS. (b) and (c) High-magnification images of Fig. 3(a).

These TEM images clearly explain the CL observations. As shown in Fig. 3, most of the growth of GaN was initiated from the c-plane instead of the LPD-SiO_2 surface Compared with FLAT-GaN, NPSS has less area to initiate GaN, thus reducing the total GaN defect density at spot 1. These results are similar to the conclusions drawn by Ref. [12] in their GaN growth studies. The total defect density (EPD) was reduced from 4.31×10^7 to 0.52×10^7cm^{-2} when the c-plane-area ratio decreased from 59.6% to 9.6%. Therefore, NPSS-GaN had higher CL intensity than FLAT-GaN at spot 1.

As for spot 2, since the dislocations bend towards the patterns, or end at the GaN/void interfaces, NPSS-GaN has much higher CL intensity than FLAT-GaN.

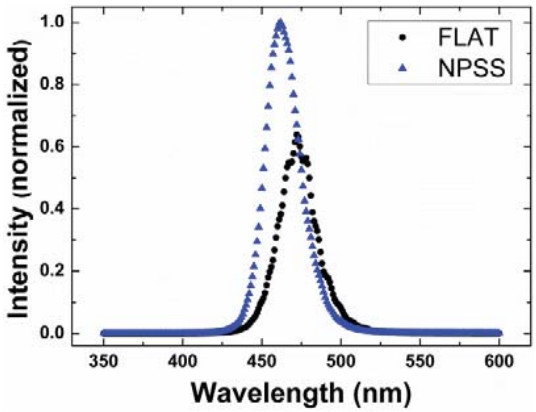

Fig. 4. Photoluminescence of multiple quantum wells grown on NPSS and FLAT sapphire.

PL was employed to investigate the quality of multiple quantum wells (MQWs) shown in Fig. 4. The excitation source was a 325-nm, 30-mW He-Cd continuous wave laser. The slight shift in PL peaks might be due to the same growth conditions of both samples. The conditions should be different since these two substrates have different surface morphologies. However, in order to reduce the experimental variables, same growth conditions were used in this letter. The PL peak intensity of MQWs grown on NPSS is 1.5 times higher than that grown on FLAT. This observation suggested that with threading dislocations bending toward the nano patterns at lower regions, NPSS can efficiently enhance the quality of MQWs by improving the crystal quality at the upper region.

IV. Conclusion

In this letter, a maskless and relatively simple LPD method was employed to deposit nanoscale SiO_2 hemispheres on sapphire substrates. Then, LPD-deposited sapphire was etched in a $3H_2SO_4$:$1H_3PO_4$ mixed solution to fabricate NPSS. The GaN films were fully coalesced and voids can be found on the corners of nano patterns. The XRCs, EPD and monochromated CL maps show that NPSS-GaN has better quality than FLAT-GaN. TEM analysis reveals that GaN was initiated from the c-plane instead of the LPD-SiO_2 surface. Moreover, lots of dislocation on NPSS-GaN bend toward the patterns, or end at the GaN/void interfaces. As a result, the defect density in the middle region of NPSS-GaN was further reduced. The MQWs grown on NPSS show PL peak intensity of 1.5 times higher than that on FLAT.

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