Using BCl_3-Based Plasma to Modify Wet-Etching Pattern Sapphire Substrate for Improving the Growth of GaN-Based LEDs

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***Abstract*— Wet-etching pattern sapphire substrates (PSS) have been used to grow GaN-based light-emitting diodes (LEDs). However, after wet etching, several sidewall facets are exposed on the patterns of PSS. These sidewall facets would grow zincblende GaN and form irregular voids. In this letter, BCl_3-based plasma is used to solve this problem and improve the performance of GaN-based LEDs.**

***Index Terms*— BCl_3, light-emitting diode (LED), pattern, sapphire.**

I. Introduction

LIGHT-EMITTING diodes (LEDs) are expected to play an important role in next-generation light source due to their advantages of high efficiency, long life, small size, environmental protection, various colors and wide applications. In particular, high-brightness GaN-based LEDs (HB-LEDs) have attracted considerable attention for white light solid-state lighting. Patterned sapphire substrate (PSS) has been used to improve both internal quantum efficiency (IQE) and light extraction efficiency (LEE) of HB-LEDs[1]-[4].

PSS could be fabricated either by dry-etching or wet-etching method Generally, wet-etching is preferred to dry-etching because its process is cheaper, throughput is higher, and surface damage is lower. However, after wet etching, several etched (sidewall) facets were exposed [5]-[6]. It has been found that beside normal wurtzite GaN, zincblende GaN has been found on these facets [6]. Besides, during the GaN coalescence process, irregular voids are formed in the GaN films [8]. These structures may degrade the performance of LED.

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The growth of GaN on these facets can be suppressed by using CF_4 plasma [9]. This is because CF_4 can roughen these incline facets. Unfortunately, CF_4 plasma also damaged the bottom c-plane. In this study, CF_4 plasma was replaced with BCl_3-based plasma because BCl_3-based plasma is generally used to fabricate dry-etching PSS. Effect of BCl_3-based plasma on the crystalline and the performance of LEDs were investigated.

II. Experiments

Two kinds of PSSs were employed to grow GaN-based LEDs. Samples designated as (1) "WPSS" is wet-etching PSS, and (2) "DWPSS" is WPSS modified by dry etching. The WPSS was prepared by standard photolithography (2-μm circle diameter and 1-μm spacing). A 220-nm-thick SiO_2 film served as the wet-etching hard mask and was deposited on the sapphire surface using the plasma-enhanced chemical vapor deposition (PECVD). The photoresist pattern was used as the mask, and the buffer-oxide etching (BOE) solution was utilized to etch SiO_2 to get SiO_2 mask. Samples were then etched in hot H_3PO_4–based solutions [10]-[11]. As for the DWPSS, WPSS was etched using BCl_3-based plasma for 5 and 10 min, respectively (denoted as DWPSS-1, and -2).

Fig. 1 shows the surface morphology of PSS. The structure of PSS comprised of a hexagonal pyramid covered with several etched facets [5]. The height and bottom width of patterns was about 1.2 and 2.6μm, respectively.

After the clean process, the LED structures were grown by metalorganic chemical vapor deposition (MOCVD). The structures comprised a buffer layer on the PSS, a undoped-GaN layer film, a n-GaN layer, a Si-doped AlGaN cladding layer, an InGaN-GaN multiple quantum well (MQW) with emission wavelength in the blue region, a Mg-doped AlGaN cladding layer and a p-GaN layer.

The device mesa with a chip size of 1145 × 1145 μm^2 was then defined by ICP to remove Mg-doped GaN layer and MQW until the Si-doped GaN layer was exposed. The indium tin oxide (ITO) layer was then deposited to form a p-side contact layer and a current spreading layer. The Cr/Au layer was deposited onto the ITO layer to form the p-side and n-side electrodes.

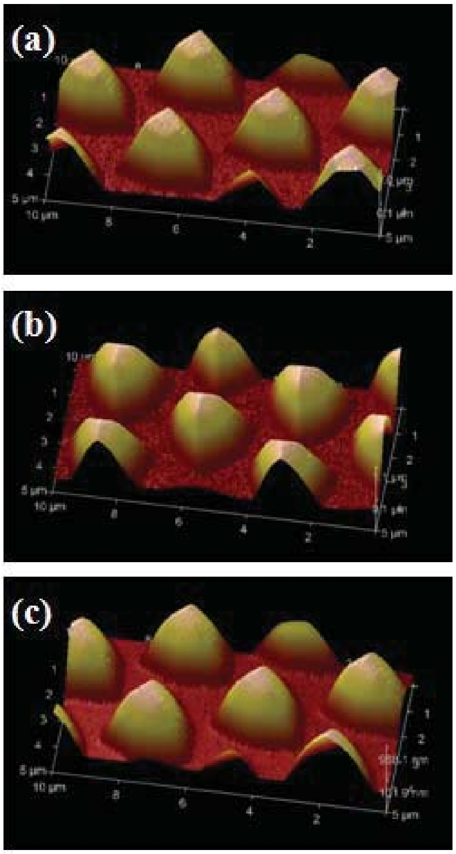

Fig. 1. AFM images of (a) WPSS, (b) DWPSS-1, and (c) DWPSS-2.

III. Results and Discussion

Fig. 2 displays the light output power and the external quantum efficiency (EQE) of LEDs. The performance of LED-DWPSS-2 was better than that of LED-DWPSS-1 and LED-WPSS. The measured device performances are summarized in Table I. LED-DWPSS-2 achieved an output power of 453.8 mW at 350 mA, which was 6.7% higher than LED-WPSS, and 3.7% higher than LED-DWPSS-1. The EQE of LED-DWPSS-2 was 46.1%, which was 5.3% higher than LED-WPSS, and 2.0% higher than LED-DWPSS-1. As for LEE, we believe the LEE of LED-DWPSS should be similar to that of LED-WPSS since they have similar morphology. These results indicate that IQE and GaN crystal quality of LED-DWPSS-2 was better than that of LED-DWPSS-1 and LED-WPSS.

The nature of GaN crystal quality was analyzed by (1) X-ray diffraction (XRD), (2) photo luminescence (PL) and (3) screw dislocation density, which can be characterized by etching pit density (EPD). The results of XRD rocking curves are listed in Table I. The full width at half maximum (FWHM) of (002) GaN of LED-DWPSS-2 was 308.6 arcsec, which was less than that of LED-DWPSS-1(335.9) and LED-WPSS (340.9). Besides, the FWHM of (102) GaN of LED-DWPSS-2 was 338.6 arcsec, which was also less than that of LED-DWPSS-1(384.1) and LED-WPSS (408.1). This indicates that the GaN structural quality of LED-DWPSS-2 was superior to that of LED-DWPSS-1 and LED-WPSS.

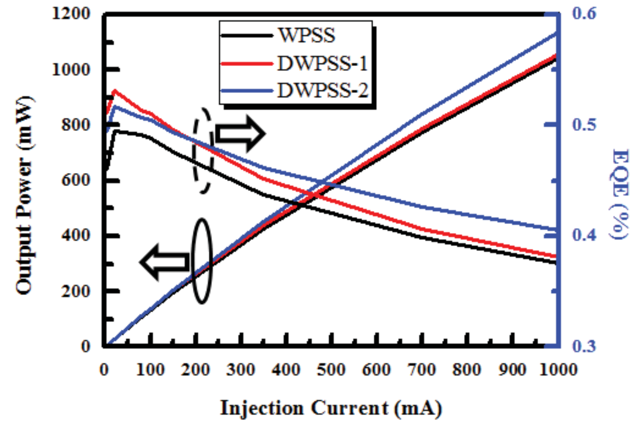

Fig. 2. Effects of injection current on the light output powers and external quantum efficiencies of the LEDs.

TABLE I
PARAMETERS AND PERFORMANCES OF LEDs

	XRD FWHM		EPD	PL	LED		
	(002)GaN	(102)GaN		FWHM	Voltage	Power	EQE
	arsec	arsec	$cm^{-2}(\times 10^7)$	nm	V	mW	%
WPSS	340.9	408.1	1.74	21.10	3.7	425.3	43.8
DWPSS-1	335.9	384.1	0.96	19.9	3.7	437.6	45.2
DWPSS-2	308.6	338.6	0.66	19.2	3.7	453.8	46.1

The quality of the GaN films were also analyzed by photo luminescence (PL). LED-DWPSS-2 has a smaller FWHM value (24.1nm) than LED-DWPSS-1 (27.3nm) and LED-WPSS (27.3nm) as shown in Table I. Besides, the measured EPD of LED-DWPSS-2 was 0.66×10^7 cm^{-2}, which was less than that of LED-DWPSS-1 (0.96×10^7) and LED-WPSS (1.74×10^7). These results also indicate that the crystallinity of LED-DWPSS-2 was better than that of LED-DWPSS-1 and LED-WPSS.

Fig. 3 shows transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) cross-section images of GaN around pyramid patterns. These images were taken from (1210) plane of sapphire. As shown in Figs. 3(a), 3(c) and 3(e), the left edge of the pattern image were the intersection (ridge) of two sidewall facets, while the right edge is the projection of the sidewall facets.

STEM analysis revealed that GaN grains were found on the sidewall surfaces (right edges) as shown in Figs. 3(b), 3(d) and 3(f). The size of these GaN grains decreased as the BCl_3-based plasma etching time increased.

We believe this decrease of grain size is because the sidewall facets suffered from BCl_3-based plasma etching, in which the etching of sapphire was controlled by the BCl radicals through the reaction of Al_2O_3 [12]. As the time increased, the reaction between sidewall facets and BCl radicals increased. As a result, the sidewall facets of patterns were not favorable to grow GaN. Besides, BCl radicals do not effect the growth of GaN on bottom c-plane since BCl_3-based plasma is usually used to fabricate dry-etching PSS.

The etching of CF_4-based plasma is quite different from BCl_3-based plasma [8]. In CF_4-based plasma, etching of PSS has been largely attributed to a process of physical sputtering

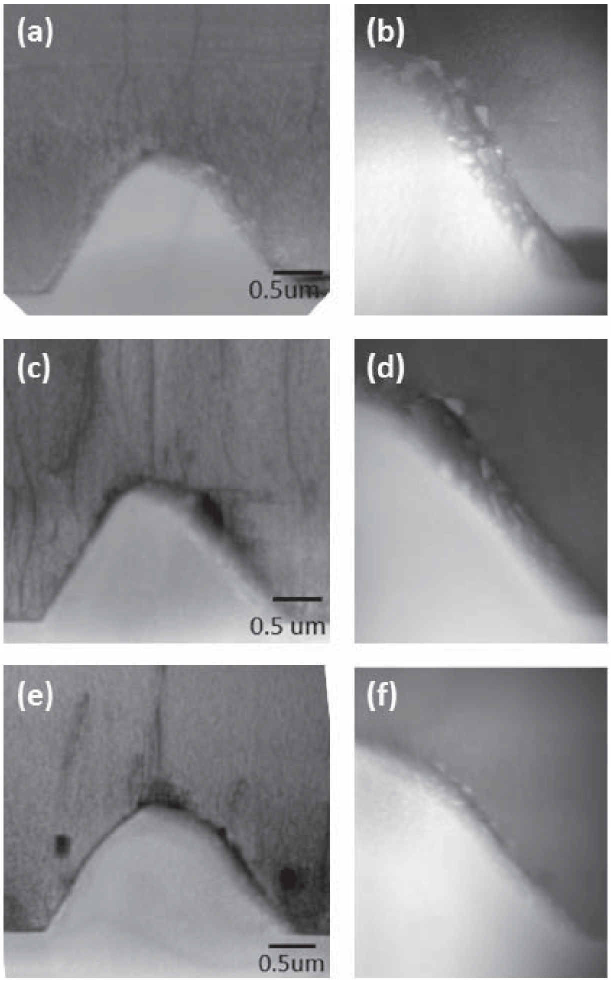

Fig. 3. TEM cross-section images of (a) LED-WPSS, (c) LED-DWPSS-1, and (e) LED-DWPSS-2. STEM cross-section images of sidewall facets of (b) LED-WPSS, (d) LED-DWPSS-1, and (f) LED-DWPSS-2.

[13]. As a result, both sidewall facets and bottom c-plane were damaged (roughened) by CF_4-based plasma [9].

IV. Conclusion

BCl_3-based plasma was used to modify wet-etching PSS (WPSS) for 5 min (DWPSS-1) and 10 min (DWPSS-2), respectively. It was found that the performance of LED-DWPSS-2 was better than that of LED-DWPSS-1 and LED-WPSS. LED-DWPSS-2 achieved an output power of 453.8 mW at 350 mA, which was 6.7% higher than LED-WPSS, and 3.7% higher than LED-DWPSS-1.

The crystallinity of LED-DWPSS-2 was better than that of LED-DWPSS-1 and LED-WPSS. The EQE of LED-DWPSS-2 was 46.1%, which was 5.3% higher than LED-WPSS, and 2.0% higher than LED-DWPSS-1. Besides, the results of XRD rocking curves, the PL and EPD measurements all show crystallinity of LED-DWPSS-2 was better than that of LED-DWPSS-1 and LED-WPSS.

This improvement is because the sidewall facets suffer from BCl_3-based plasma etching. As the time increased, the reaction between sidewall facets and BCl radicals increased. At the same time, since BCl_3-based plasma is usually used to fabricate dry-etching PSS, BCl radicals do not effect the growth of GaN on bottom c-plane.

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