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Fabrication of GaN hexagonal cones by inductively coupled plasma reactive ion etching

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There is a growing demand for the patterning of gallium nitride for light extraction/absorption to improve the performance of photoelectric devices. In this paper, hexagonal cones were fabricated on Ga-polar GaN substrates using the inductively coupled plasma reactive ion etching method. It was found that the etch rate of different crystal faces could be altered by changing the ratio of BCl_3 to Cl_2 in the reactive gas mixture, which enabled hexagonal cone structures to be fabricated on the wurtzite GaN crystal. The mechanism of the GaN hexagonal cone formation was analyzed based on physical sputtering and chemical reaction, wherein the physical sputtering by heavy radicals assisted the bond breaking and the chemical erosion by Cl radicals that preferentially etched specific crystal planes. The hexagonal cones can be used on light-emitting diodes, photovoltaic devices, and for site control of quantum dots. © 2016 American Vacuum Society.

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I. INTRODUCTION

Gallium nitride (GaN) plays an important role in the field of photoelectronic devices such as light-emitting diodes (LEDs), laser diodes, and ultraviolet photodetectors, as well as electronic devices such as field effect transistors. This usefulness of GaN is owing to its large, direct bandgap, excellent light absorbing and emitting properties, and high thermal conductivity.¹ GaN-based LEDs are one of the most promising solid-state lighting devices, exhibiting the advantages of stable long term light emitting performance, energy saving, and long lifetime. However, to achieve high quantum efficiency in the LEDs, planar surfaces need to be avoided to reduce the total internal reflection. Therefore, nanostructures such as semispheres,^{2,3} photonic crystals,^{4,5} and cones^{6,7} on the surface of LEDs have been widely used to improve the light extraction efficiency (LEE). These structures can be obtained by either wet etching or dry etching methods.

Wet etching can be used to fabricate conelike structures on (000 $\bar{1}$) GaN because of the occurrence of selective etching on specific crystal planes.^{8–10} These cones are hexagonally shaped with sixfold-symmetry, and the taper angle has a fixed value of 58.4°. The cone density is comparable to the dislocation density of GaN, and the arrangement of the cones is random and irregular. In contrast, dry etching mainly using inductively coupled plasma reactive ion etching (ICP-RIE) is typically insensitive to the crystalline structure and can provide more varieties of patterns such as hole and pillar structures with upright edges^{11–13} or cones with oblique sidewalls.^{6,7} Further, the arrangement of these structures can be designed, and the tilt level of the sidewalls can be changed.

Until now, circular cones have been fabricated by ICP-RIE (Refs. 6 and 7) while hexagonal cones have only been fabricated by the wet etching process, and have been randomly arranged on N-polar (000 $\bar{1}$) GaN (Ref. 8) or with selective area growth on nucleation layers.^{14,15} Pyramidlike structures on LEDs have been theoretically proven to greatly increase the LEE using numerical simulations.^{16,17} Furthermore, in addition to improving the LEE on LEDs, hexagonal cones can also be used for photovoltaic devices¹⁸ or site control of quantum dots.¹⁵

In this paper, we demonstrate that hexagonal cones can be fabricated by dry etching with ICP-RIE on Ga-polar (0001) GaN. By changing the ratio of BCl_3 to Cl_2 in the mixed reactive gas, the side wall of the cones can be modified from upright to oblique, indicating that the etching effect can be either isotropic or anisotropic. The study shows that, in the etching process, both physical sputtering and chemical etching effects are involved, and the weight of these effects can be controlled by the gas ratio. This provides an easy way to fabricate circular and hexagonal structures on wurtzite GaN.

II. EXPERIMENTAL DETAILS

A schematic of the fabrication process of the GaN hexagonal cones is shown in Fig. 1, wherein a Ga-polar GaN layer about 4 μm thick was grown on a sapphire substrate by metal-organic chemical vapor deposition. After being cleaned with acetone, alcohol, and deionized water, the samples were spin-coated with poly(methyl methacrylate) (PMMA) resist. Subsequently, a hexagonal array of circular holes was formed in the PMMA by electron beam lithography and development [Fig. 1(a)]. Chromium was then evaporated onto the samples [Fig. 1(b)], followed by acetone

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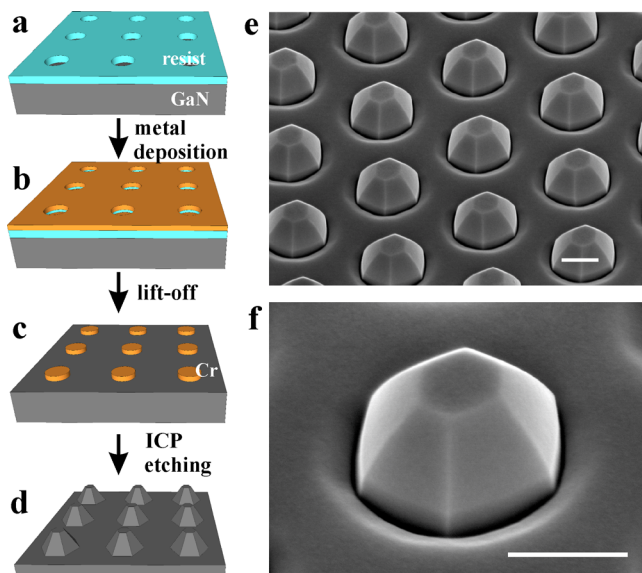


FIG. 1. (Color online) (a)–(d) Schematic of fabrication process of GaN cones by the ICP-RIE method. (e) and (f) SEM images of the GaN hexagonal cones. The scale bars are 500 nm.

lift-off, to form an array of circular Cr dots for the mask on the GaN [Fig. 1(c)]. Then, a dry etching process was performed in the ICP-RIE system (Oxford Plasmalab System 100 ICP 180) with a mixed reactive gas of BCl_3 and Cl_2 to create GaN cone structures [Fig. 1(d)], and a silicon load wafer was used as the sample holder. In the etching process, the ratio of $\text{BCl}_3:\text{Cl}_2$ was altered to obtain hexagonal GaN cones, as shown in the scanning electron microscope (SEM) images (Helios 600i, FEI) in Figs. 1(e) and 1(f). The pattern was over-etched during the etching process, wherein the operating pressure was 7 mTorr, the radio-frequency (RF) power was 75 W, the ICP power was 300 W, and the temperature was kept at 30 °C.

III. RESULTS AND DISCUSSION

A. Reactive gas ratio-related etch rate

During the GaN etching process with BCl_3 and Cl_2 by ICP-RIE, the active ions in the chamber are mainly Cl^+ , Cl_2^+ , and BCl_2^+ dissociated from Cl_2 and BCl_3 , as well as SiCl^+ and SiCl_3^+ that derive from the reaction between Cl_2 and the Si load wafer.¹⁹ Two effects are involved in the process, comprising a chemical etching effect and a physical sputtering effect. The chemical etching effect mainly arises from the interaction between the Ga in the GaN and Cl from the Cl_2 gas. The physical sputtering effect, on the other hand, is caused by the bombardment of the heavy BCl_2^+ , SiCl^+ , and SiCl_3^+ ions. The etch rate of both processes is related to the energy and density of the ions, which are both highly correlated to the direct current (DC) bias that is generated by the electrons gathered on the electrodes as a result of the RF power.

The etch rate and the DC bias are given in Fig. 2(a) as a function of the $\text{BCl}_3:\text{Cl}_2$ ratio. By increasing the proportion of Cl_2 from 1/6 to 5/6, the GaN etch rate increases from 68

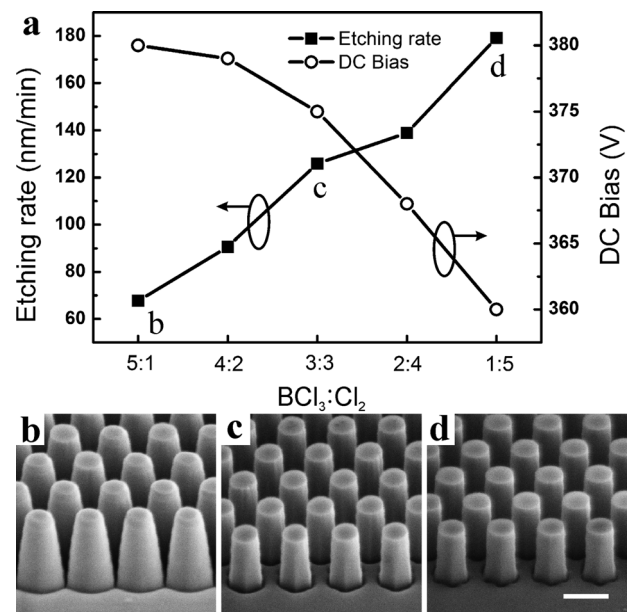


FIG. 2. (a) Etch rate and DC bias as a function of the $\text{BCl}_3:\text{Cl}_2$ ratio. The SEM images show the GaN cones/pillars etched by different $\text{BCl}_3:\text{Cl}_2$ ratios of (b) 5:1, (c) 3:3, and (d) 1:5. The scale bar is 500 nm.

to 178 nm/min while the DC bias decreases slightly. The dominating effect is the chemical etching of the Ga in the GaN by the Cl from the Cl_2 and BCl_3 gases.^{12,13} When the proportion of Cl_2 is 5/6, Cl^+ and Cl_2^+ ions are dominant in the chamber¹⁹ and chemical etching plays the leading role. At this ratio, the DC bias is slightly smaller with fewer¹³ and lower energy ions, while the etch rate remains high because of the existence of Cl^+ ions. As the proportion of BCl_3 goes up, the DC bias increases (increasing the energy of the ions) as the density of BCl_2^+ increases.^{12,19,20} However, the density of the Cl^+ decreases,^{12,19,20} thus lowering the chemical etching effect and the etch rate of GaN.

The SEM images in Figs. 2(b)–2(d) reveal that the shape of the cones changes with the gas ratio, though the etching times were varied to ensure the same etching depth. The images show that when BCl_3 is predominant, cones with oblique sidewalls are fabricated [Fig. 2(b)]. By increasing the Cl_2 proportion to 50%, the sidewalls become less oblique and edges appear at the bottom of the cones while the top of cones remain round [Fig. 2(c)]. By further increasing the Cl_2 proportion to 5/6, the sidewalls become vertical with more obvious six-fold-symmetry edges [Fig. 2(d)].

B. Formation of hexagonal cones

To observe the sixfold symmetry of the GaN cones more clearly, thinner masks and longer etching times were used to obtain over-etched structures. Figure 3 shows the over-etched results producing GaN cones with an intercone period of 1.5 μm etched with different ratios of $\text{BCl}_3:\text{Cl}_2$. When $\text{BCl}_3:\text{Cl}_2 = 5:1$, circular truncated cones were formed in accordance with the circular Cr masks. As the proportion of Cl_2 was increased, six edges gradually appeared and the faces between the two edges changed gradually from a curved surface to a flat surface. Finally, when the Cl_2

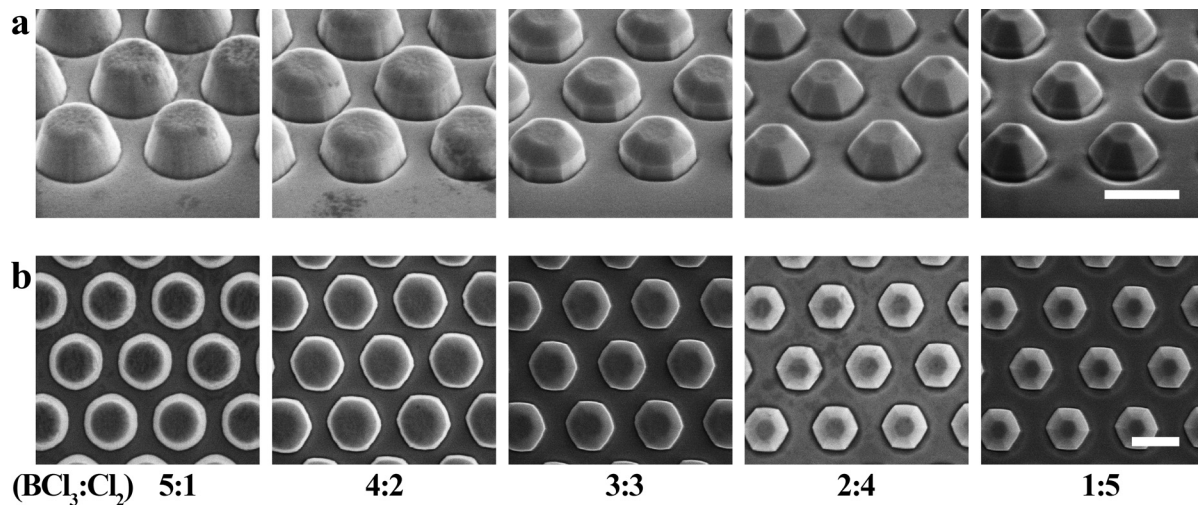


FIG. 3. SEM images of the (a) side view and (b) top view of the GaN cones with a period of $1.5 \mu\text{m}$ created with a varying reactive gas ratio. The scale bar is $1 \mu\text{m}$.

proportion reached 5/6, hexagonal cones were formed with well-defined sixfold sidewalls. It is obvious that after the masks were depleted, specific planes were selectively etched and hexagonal truncated cones were thus achieved.

It should be noticed that the mask on the GaN is a hexagonal array and has the same symmetry as the hexagonal cones. To examine the possibility that adjacent structures may affect the shape of the cones, including charging effects or the gas flow pattern on the target surface, rectangularly arranged structures were also fabricated and are shown in Fig. 4. The Cr masks were arranged rectangularly to avoid sixfold symmetry, but the resulting cones also seem to possess sixfold symmetry, and from the top view in Figs. 4(c) and 4(d), it is obvious that the cones have a hexagonal shape. This proves that the formation of hexagonal cones has nothing to do with the packing pattern of the mask.

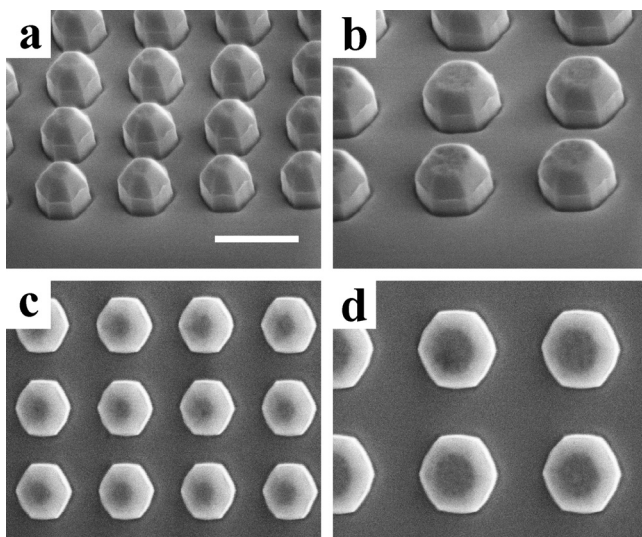


FIG. 4. SEM images showing the [(a) and (b)] side view and [(c) and (d)] top view of GaN hexagonal cones with period of [(a) and (c)] $1 \mu\text{m}$ and [(b) and (d)] $1.5 \mu\text{m}$. The scale bar is $1 \mu\text{m}$.

C. Mechanism of hexagonal cone formation

Because the GaN is a wurtzite crystal with sixfold symmetry [shown in Fig. 5(a)], the hexagonal cone shape should therefore be related to the hexagonal close-packed lattice structure by the anisotropy of etching. In GaN, the $(10\bar{1}1)$ plane has the lowest surface energy⁸ and was therefore etched preferentially in the chemical etching process compared to the (0001) plane, and was exposed outmost after etching. This explains how the hexagonal GaN cones are formed by wet etching in a KOH solution. However, in a dry etching process, the situation is quite different. In the plasma

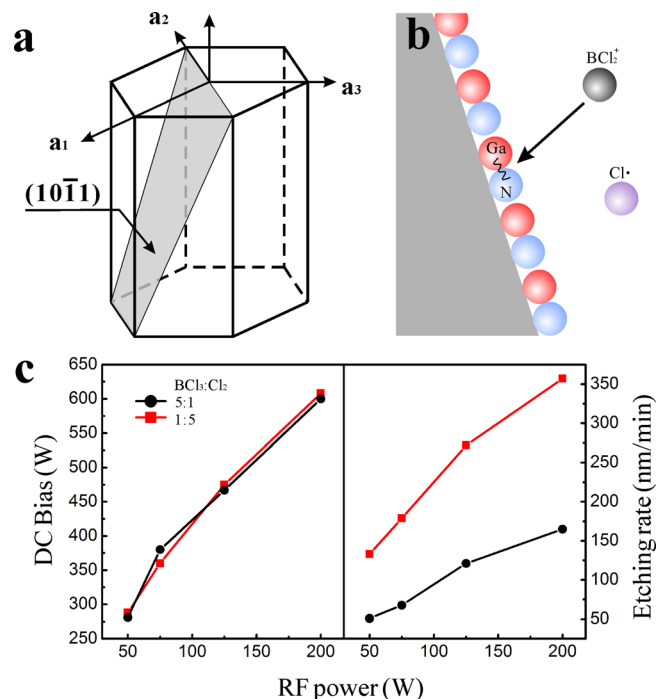


FIG. 5. (Color online) (a) Crystal structure of the wurtzite GaN and the $(10\bar{1}1)$ plane. (b) Schematic of heavy radical-assisted bond breaking of GaN. (c) DC bias and etch rate as a function of RF power.

of the dry etching process, the GaN material is simultaneously exposed to a chemical reaction by the Cl radical and to bombardment by heavy radicals. The proportion between these two effects changes with the gas ratio, which determines the final profile of the GaN structures.

The bombardment by heavy radicals contributes to GaN etching in two ways. First, the physical sputtering effect¹² is isotropic to the crystal and is only related to the ion incident angle, ion energy, and the species of incident/target atoms.²¹ Second, the bombardment helps to break the bond between Ga and N, as shown in Fig. 5(b), which speeds up the chemical etching process.

When the BCl₃ proportion is 5/6, the primary ions in the plasma are BCl₂⁺ and SiCl₂⁺.¹⁹ The predominance of these heavy radicals in the chamber leads to isotropic etching of GaN and forms circular cones with oblique sidewalls. As the proportion of Cl₂ increases, the amount of BCl₂⁺ in the plasma decreases and that of Cl⁺ and Cl₂⁺ increases; thus, the physical sputtering effect is weakened while the assisted bond-breaking effect is still present. This sputtering assists the chemical etching process, which selectively etches the (10 $\bar{1}$ 1) plane. When the Cl₂ proportion is 5/6, very few BCl₂⁺ radicals^{12,19} exist in the chamber, so the dominant effect is chemical etching and heavy radical-assisted bond breaking in the chamber. Therefore, the (10 $\bar{1}$ 1) plane gradually appears at the outmost edge and leads to the hexagonal cone structures.

To verify this point of view, we examined the DC bias and etch rate of GaN as a function of RF power in the conditions of the two gas ratios 5:1 and 1:5, as shown in Fig. 5(c). For a certain RF power, the DC bias is essentially the same for the different gas ratios, which indicates the same ion energy. The etch rates increase rapidly with RF power for both gas ratios. When BCl₃:Cl₂ = 5:1, the increase in the etch rate with the RF power is reasonable owing to the nature of the physical sputtering. However, when BCl₃:Cl₂ = 1:5, the increase in the etch rate with the RF power exhibits characteristics not typical of chemical etching. In a pure chemical etching process, the etch rate should be almost independent of the DC bias.²² Here, however, the RF power-dependent etch rate indicates that the ion energy plays an important role in the etching process. Because there are very few heavy radicals BCl₂⁺ and SiCl₂⁺ in the chamber, the physical sputtering effect is much smaller compared to that of gas ratio = 5:1, and the heavy radical-assisted bond-breaking is dominant.

It should be noted that when the reactive gas is pure Cl₂, the etch rate of GaN is 150 nm/min (data not shown), which is smaller than the 178 nm/min rate found with 5/6 Cl₂. This difference is because no BCl₂⁺ radicals are in the chamber with pure Cl₂, and only a few SiCl⁺ and SiCl₃⁺ ions exist from the interaction between Cl₂ and Si wafer.¹⁹ This lack of heavy radicals weakens the assisted bond-breaking effect and finally reduces the etch rate of GaN.

IV. CONCLUSION

We presented a new ICP-RIE process for the fabrication of well-organized GaN hexagonal cones. By changing the BCl₃:Cl₂ ratio of the active gas, the chemical etching and physical sputtering effect could be controlled to make the sidewall of GaN cones either vertical or oblique. Hexagonal cones were formed because of the anisotropic etching on different planes of the GaN crystal, whereupon the (10 $\bar{1}$ 1) plane was left on the surface of the structure. This technique showed good controllability for the sidewall oblique angle and surface profile and was homogeneous in a large area, which has great potential for light emitting enhancement of LEDs, light absorption for photovoltaic devices, and site control of quantum dots.

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