

## A Study of Sapphire Etching Characteristics Using BCl<sub>3</sub>-based Inductively Coupled Plasmas

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Cl<sub>2</sub>, HCl, and HBr added BCl<sub>3</sub>-based inductively coupled plasmas were used to etch (0001) sapphire wafers and their etch characteristics were investigated. The plasma characteristics were monitored in-situ by optical emission spectroscopy and a Langmuir probe. A photoresist was used as the etch mask and an etch selectivity greater than 1 with the etch rate of 3800 Å/min could be obtained with 20%HCl/80%BCl<sub>3</sub>. The most anisotropic etch profile could be observed in 10%HBr/90%BCl<sub>3</sub>. [DOI: 10.1143/JJAP.41.6206]

KEYWORDS: BCl<sub>3</sub>-based inductively coupled plasmas, sapphire etching, Cl<sub>2</sub>/BCl<sub>3</sub>, HCl/BCl<sub>3</sub>, HBr/BCl<sub>3</sub>, photoresist etch mask

### 1. Introduction

Sapphire (Al<sub>2</sub>O<sub>3</sub>) wafers have been widely used as substrates for growing GaN-based III-nitride epitaxial films for optoelectronic devices. However, there is difficulty in the etching or patterning due to the chemical and physical stability of sapphire. Recently, to etch sapphire, several etch techniques such as ion beam etching (IBE), chemical wet etching after ion implantation, reactive ion etching, and laser-assisted etching have been used.<sup>1–4</sup> BCl<sub>3</sub>, CCl<sub>4</sub>, SiCl<sub>4</sub>, and so forth have been used to etch sapphire, in general. In fact, these gases have been used in the case of aluminum etching to remove native oxide (Al<sub>2</sub>O<sub>3</sub>) on the aluminum surface.<sup>5,6</sup> Also, Cl<sub>2</sub>/BCl<sub>3</sub> and Ar/Cl<sub>2</sub>/BCl<sub>3</sub> gas combinations have been reported to have high etch rates in the case of sapphire etching but poor etch selectivities over a photoresist.<sup>4</sup> Therefore, to use a photoresist as the etch mask and to obtain more anisotropic etch profiles, gas combinations that have a greater etch selectivity over a photoresist are required. Some of the possible additive gases are hydrogen-containing halogen gases such as HCl and HBr which are used to realize a high selectivity over a photoresist and a vertical profile in silicon etching.<sup>7,8</sup>

In this study, sapphire etching was conducted in an inductively coupled plasma (ICP) etcher. The etch characteristics of sapphire were investigated with various BCl<sub>3</sub>-based gas combinations.

### 2. Experimental

In this study, sapphire wafers with (0001) orientation were used as the etch samples. AZ 9260 photoresist was used as the etch mask and a 24 μm thickness could be obtained by applying a double PR spin-on technique. Sapphire etching was performed in a laboratory-made planar ICP etcher with a spiral Ag-coated three-turn Cu antenna installed on the top of the chamber having a 2-cm-thick quartz dielectric. The internal size of the reactor was 210 mm × 210 mm. Cl<sub>2</sub>/BCl<sub>3</sub>, HCl/BCl<sub>3</sub>, and HBr/BCl<sub>3</sub> gas combinations were used to etch the sapphire. The total gas flow rate and working pressure were maintained at 100 sccm and 12 mTorr, respectively. Inductive power, bias voltage, and substrate temperature were fixed at 1200 W, –350 V, and 3°C, respectively.

To investigate the correlations of sapphire etch characteristic with gas combinations, optical emissions from the plasmas during the etch process were monitored in-situ by optical emission spectroscopy (OES: SC Tech. PCM402). A

single Langmuir probe (Hiden Inc. ESP) was also used to measure the ion densities in the plasmas. The probe tip was made of tungsten wire 10 mm in length and 0.15 mm in diameter and was positioned 15 mm above the substrate surface. The etch profiles were inspected using a scanning electron microscope (SEM: Hitachi S-2150).

### 3. Results and Discussion

Figure 1 shows the etch rates of sapphire and etch selectivities over PR for various BCl<sub>3</sub>-based gas combinations. The measured etch uniformity within a 10 cm diameter was less than ±6.8%. As shown in the figure, in Cl<sub>2</sub>/BCl<sub>3</sub> and HCl/BCl<sub>3</sub> gas combinations, sapphire etch rates were slightly increased with increasing Cl<sub>2</sub> and HCl up to 20–30% and the highest etch rate under these conditions was approximately 3800 Å/min. However, further increase of these additive gases (Cl<sub>2</sub>, HCl) decreased the etch rates rapidly. In the case of HBr/BCl<sub>3</sub> gas combinations, sapphire etch rates decreased almost linearly with increasing HBr in the gas mixture. The etch selectivities over PR decreased with the increase of Cl<sub>2</sub>, HCl, and HBr in general, however, for 10–30% gas mixtures with HBr or HCl, greater etch selectivities of 0.9 for HBr/BCl<sub>3</sub> and over 1 for HCl/BCl<sub>3</sub> could be obtained. In particular, the highest etch rate with an etch selectivity greater than 1 could be obtained with 20% of HCl in HCl/BCl<sub>3</sub> gas mixture.

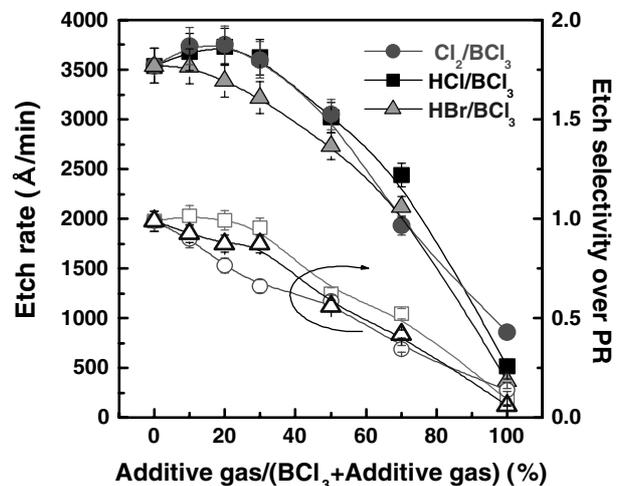


Fig. 1. Etch rates of sapphire and etch selectivities over PR for various BCl<sub>3</sub>-based etch gas combinations.

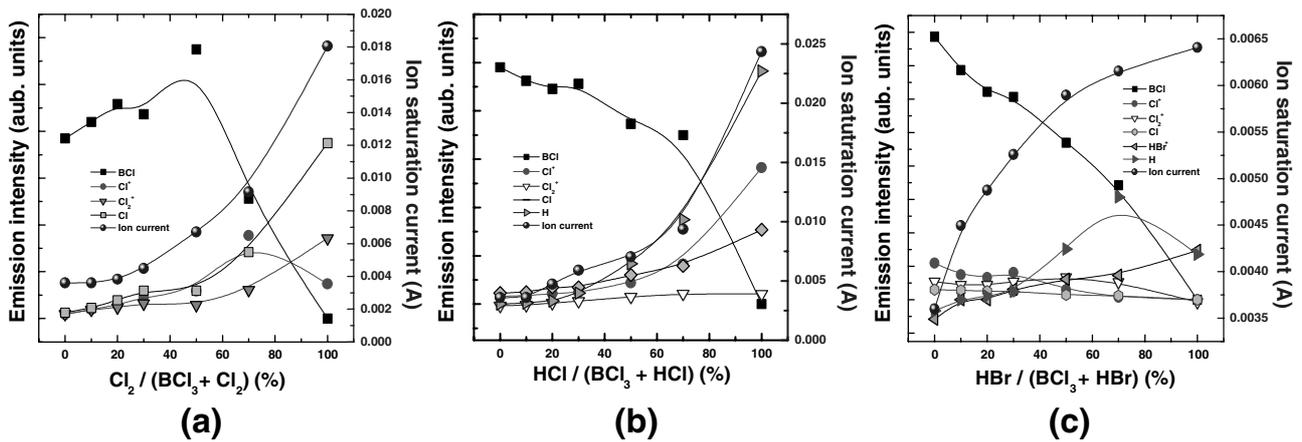


Fig. 2. Optical emission intensities measured by OES and ion saturation currents measured by a Langmuir probe for various  $\text{BCl}_3$ -based gas combinations. (a)  $\text{Cl}_2/\text{BCl}_3$  chemistry, (b)  $\text{HCl}/\text{BCl}_3$  chemistry and (c)  $\text{HBr}/\text{BCl}_3$  chemistry.

Figure 2 shows optical emission intensities of ions and radicals such as  $\text{BCl}$  (272.0 nm),  $\text{Cl}$  (754.7 nm),  $\text{H}$  (656.5 nm), chlorine ions ( $\text{Cl}^+$ : 384.4, 385.1, 386.1 nm,  $\text{Cl}_2^+$ : 430.0 nm), and  $\text{HBr}^+$  (358.1 nm) measured by OES and ion saturation currents measured by the Langmuir probe during the sapphire etching. Figures 2(a)–2(c) show these values for  $\text{Cl}_2/\text{BCl}_3$ ,  $\text{HCl}/\text{BCl}_3$ , and  $\text{HBr}/\text{BCl}_3$  plasmas, respectively. The addition and increase of  $\text{HBr}$  in  $\text{BCl}_3$  decreased the  $\text{BCl}$  radical intensities monotonically. However, the addition and increase of  $\text{Cl}_2$  or  $\text{HCl}$  in  $\text{BCl}_3$  up to 50% increased or slightly decreased  $\text{BCl}$  radical intensities, respectively, and the further increase of  $\text{Cl}_2$  or  $\text{HCl}$  decreased  $\text{BCl}$  radical intensities rapidly. In the case of Langmuir probe measurements, the increase of  $\text{Cl}_2$ ,  $\text{HCl}$ , and  $\text{HBr}$  in  $\text{BCl}_3$  increased the ion saturation currents monotonically. Also, the increase of optical emission intensities of the ions such as  $\text{Cl}_2^+$ ,  $\text{Cl}^+$ , and  $\text{HBr}^+$  was observed with increasing additive gases.

If the results obtained in Fig. 2 are compared with the sapphire etch rate results shown in Fig. 1, the variation of sapphire etch rates with the increase of  $\text{Cl}_2$ ,  $\text{HCl}$ , and  $\text{HBr}$  appears to be related to the abundance of  $\text{BCl}$  radicals acting as oxygen scavengers. The increase of ion bombardment with additive gases indicated by the increase of ion saturation currents appears not to be effective in increasing etch rates possibly due to the extremely low sputter yield of sapphire under these experimental conditions. Also, the change of  $\text{Cl}$  radicals with additive gases affected the photoresist etch rate but not the sapphire etch rate, and therefore, decreased the etch selectivity.

Figure 3 shows SEM micrographs of the sapphire etch profile for (a) 100% $\text{BCl}_3$ , (b) 20% $\text{Cl}_2/80\%\text{BCl}_3$ , (c) 20% $\text{HCl}/80\%\text{BCl}_3$ , and (d) 10% $\text{HBr}/90\%\text{BCl}_3$ . As shown in the figure, the most anisotropic etch profile was obtained with 10% $\text{HBr}/90\%\text{BCl}_3$ . The smallest etch profile angle was obtained with 20% $\text{Cl}_2/80\%\text{BCl}_3$  possibly due to the low etch selectivity over the photoresist. Even though 20% $\text{HCl}/80\%\text{BCl}_3$  showed a slightly greater etch selectivity compared to 10% $\text{HBr}/90\%\text{BCl}_3$ , a lower etch profile angle was observed in the figure. The larger etch profile angle for 10% $\text{HBr}/90\%\text{BCl}_3$  is probably related to the characteristics of  $\text{HBr}$  where etch products such as  $\text{AlBr}_x$  protect the sidewall of the photoresist mask better than  $\text{AlCl}_x$ .

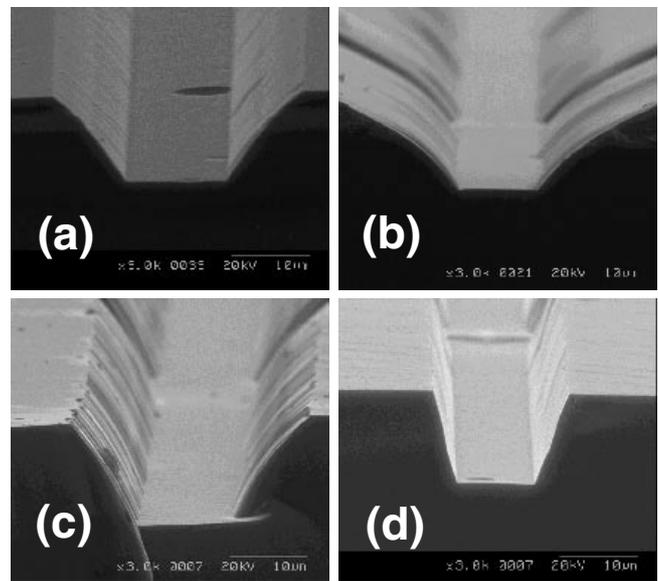


Fig. 3. SEM etch profiles of sapphire masked with a photoresist for various  $\text{BCl}_3$ -based gas combinations. (a) 100% $\text{BCl}_3$ , (b) 20% $\text{Cl}_2/80\%\text{BCl}_3$ , (c) 20% $\text{HCl}/80\%\text{BCl}_3$  and (d) 10% $\text{HBr}/90\%\text{BCl}_3$  chemistries.

#### 4. Conclusion

In this study,  $\text{BCl}_3$ -based inductively coupled plasmas were used to investigate the etch characteristics of photoresist-patterned sapphire wafers as a function of additive gases. The highest etch rate of 3800  $\text{\AA}/\text{min}$  was obtained with 20% $\text{Cl}_2/80\%\text{BCl}_3$  and the highest etch selectivity over a photoresist greater than 1 could be obtained with 20% $\text{HCl}/80\%\text{BCl}_3$ . Even though the etch selectivity over photoresist of 10% $\text{HBr}/90\%\text{BCl}_3$  was a little lower than that of 20% $\text{HCl}/80\%\text{BCl}_3$ , the largest etch profile angle could be obtained with 10% $\text{HBr}/90\%\text{BCl}_3$  for the investigated conditions. The etching of sapphire appeared to be controlled by the  $\text{BCl}$  radicals in the plasma through the reaction of  $\text{Al}_2\text{O}_3$  and scavenging oxygen in the plasma.

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