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Sapphire etching with BCl_3/HBr/Ar plasma

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Abstract

The etching of (0 0 0 1) sapphire wafer was studied in an inductively coupled plasma etcher using BCl_3/HBr/Ar plasmas. The qualitative relationship between etch rate and inductive power and d.c. bias voltage was studied to obtain high sapphire etch rate. The etch rate was increased almost linearly with the increase of inductive power and d.c. bias voltage. The etch selectivity over photoresist was remained similar for the investigated range of inductive power and d.c. bias voltage except for the low d.c. bias voltages. At the low d.c. bias voltages, the increase of d.c. bias voltage increased the etch selectivity. The highest sapphire etch rate obtained in BCl_3/HBr/Ar plasma was 550 nm/min with the etch selectivity over photoresist approximately 0.87 at 1400 W of inductive power and −800 V of d.c. bias voltage. In the etch conditions with the d.c. bias voltage over −600 V, the highly anisotropic sapphire etch profile and the sapphire surface composition similar to non-etched sapphire wafer (reference) could be obtained when observed by a scanning electron microscope and X-ray photoelectron spectroscopy, respectively. The surface roughness of the etched sapphire wafer was examined by atomic force microscopy and was remained similar regardless of d.c. bias voltage.

Keywords: Sapphire; Etch rate; BCl_3/HBr/Ar; DC bias voltage; Inductive power

1. Introduction

Sapphire wafer is widely used for GaN-based III-nitride device fabrication [1–3]. However, sapphire wafer is known to be difficult for other processing such as etching and device separation using mechanical cutting or scribing due to the high chemical and thermal stability, high hardness, and the differences in the crystal orientation of GaN with sapphire [1,3–9]. Even though the device size is less than $300\times300\ \mu m^2$, the width of the scribe line larger than 40 μm is required to separate the device using cutting or scribing. If the device separation can be replaced by dry etching technique, the width of the scribe line can be reduced to lower than 5 μm. Therefore, the yield of the device per wafer will be increased significantly. However, high sapphire etch rates with high etch selectivities over mask materials are required to replace the device separation by dry etching [10–15]. As a mask material, photoresist is preferred because of the simplicity of the processing.

In our previous works [10–12], sapphire wafer was etched using various BCl_3-based gas chemistries such as BCl_3/Cl_2, BCl_3/HCl and BCl_3/HBr. Among these gas combinations, the etch rate of approximately 380 nm/min with BCl_3/Cl_2 and etch selectivity over photoresist close to 1.0 with BCl_3/HCl could be obtained as the best conditions. In the case of etch profile, even though the etch selectivity over photoresist of BCl_3/HBr was a little lower than of BCl_3/HCl, the highest etch profile angle could be obtained with 90%BCl_3/10%HBr for the investigated conditions [11]. To apply the sapphire etching to device separation, high sapphire etch rate, high etch selectivity over photoresist, and highly anisotropic etch profile should be satisfied simultaneously.

For etching sapphire, due to the strong chemical bonding of the Al–O, high ion bombardment is essential for etching sapphire in addition to the effect of BCl to remove oxygen from Al–O and to remove the remaining Al by Cl or Br through $AlCl_x$ or $AlBr_x$. In the previous experiments, the effect of ion bombardment energy was not fully investigated. Etch selectivity can be changed by the differences in ion bombardment for etching sapphire and photoresist. Therefore, to improve the etch rate with etch selectivity and etch profile applicable to the device separation, the sapphire etching was performed as a function of d.c. bias voltage and inductive

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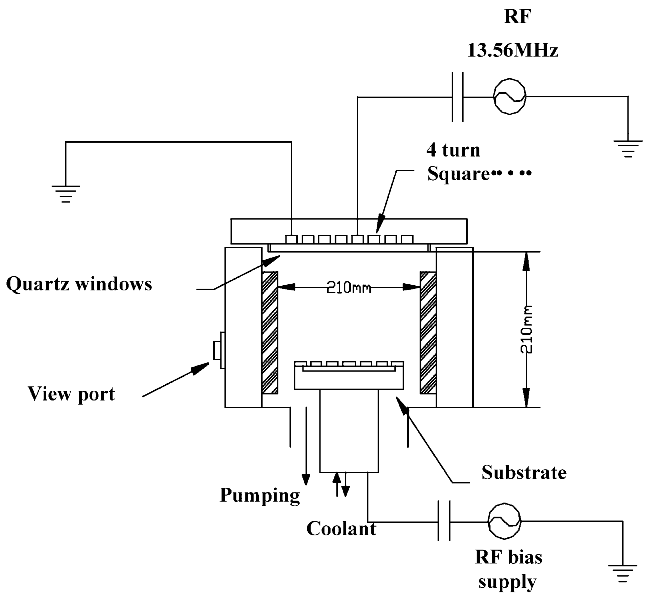


Fig. 1. Schematics of the ICP equipment used in the experiment.

power using an optimized planar inductively coupled 81%BCl_3/9%HBr/10%Ar plasma.

2. Experiment

Sapphire etching was performed in an inductively coupled plasma (ICP) etcher. A schematic view of the ICP equipment used in this study is shown in Fig. 1. The chamber is a square shape with the inner dimension of 210×210 mm^2 and was made of anodized aluminum. Radio frequency power (13.56 MHz, 2000 W) was supplied to the center of an Ag-coated four-turn square coil to generate plasma while different 13.56 MHz r.f. power was applied to the water cooled substrate to induce d.c. bias voltages to the wafer. A 15-mm quartz plate was used to separate the square coil from the plasma region. The substrate was maintained at 3 °C during the etching to prevent photoresist from reticulating. The operating pressure was kept at 1.33 Pa, the total flow rate at 100 sccm, and gas chemistry at 81%BCl_3/9%HBr/10%Ar while varying the d.c. bias voltage from −400 to −800 V at 1400 W of inductive power and varying the inductive power from 600 to 1800 W at −600 V of d.c. bias voltage.

The specimens were one-side polished sapphire wafers with (0 0 0 1) orientation. These wafers were patterned using a conventional photoresist (AZ9260) to measure the etch rates, etch selectivity, and etch profile. AZ9260 photoresist was used as the etch mask and 24 μm thick photoresist could be obtained by applying a double photoresist spin-on technique. The sapphire etch rates and the etch selectivities over photoresist were estimated from the depth of the etched features measured by a stylus profilometer. The profile of etched sapphire was evaluated with a scanning electron microscope (SEM) after the photoresist was stripped using a Piranha cleaning solution (H_2SO_4:H_2O_2=4:1, 90 °C) for 10 min. The surface composition and roughness of the etched sapphire were observed by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively.

3. Results and discussion

Sapphire wafers were etched as a function of inductive power and d.c. bias voltage to investigate a possibility to improve the etch rates and etch selectivities over photoresist while maintaining at 1.33 Pa of working pressure, 100 sccm of total flow rates, and 3 °C of substrate temperature using 81%BCl_3/9%HBr/10%Ar plasmas. The effect of inductive power on the sapphire and photoresist etch rates and their etch selectivity at −600 V of d.c. bias voltage is shown in Fig. 2. As shown in the figure, the increase of inductive power from 600 to 1600 W increased the etch rates of sapphire almost linearly. The photoresist etch rate also increased almost linearly, therefore, the etch selectivity remained similar near 0.85. The increase of sapphire etch rate with input power is believed to be not only from the increase of ion bombarding species such as BCl_x^+, Cl_x^+, Ar^+, etc. but also from the increase of reactive radical species such as BCl, Cl, Br, etc. which remove O and Al in Al_2O_3. The increase of photoresist etch rate with increasing input power appears to show the similar influence of fluxes of ion bombardment and reactive

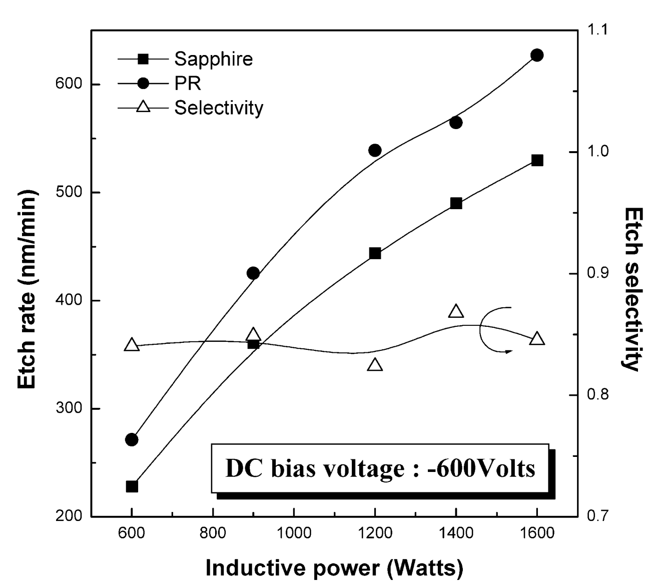


Fig. 2. Etch rates of sapphire and photoresist, and etch selectivities over photoresist as a function of inductive power. (Process condition: −600 V of d.c. bias voltage, 1.33 Pa of working pressure, 100 sccm of total flow rates, 3 °C of substrate temperature, and 81%BCl_3/9%HBr/10%Ar).

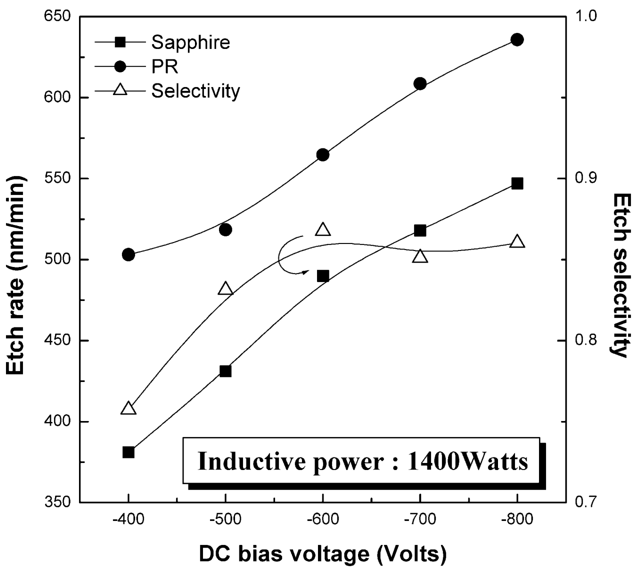
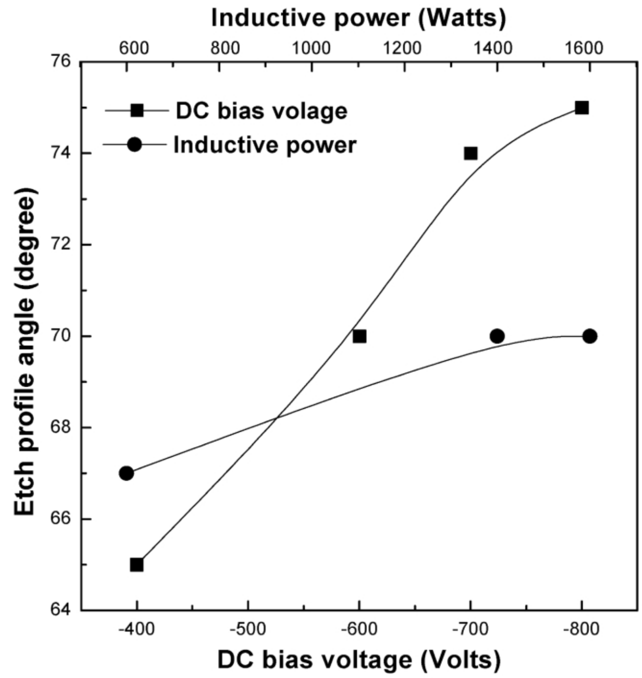


Fig. 3. Etch rates of sapphire and photoresist, and etch selectivities over photoresist as a function of d.c. bias voltage. (Process condition: 1400 W of inductive power, 1.33 Pa of working pressure, 100 sccm of total flow rates, 3 °C of substrate temperature, and 81%BCl_3/9%HBr/10%Ar.)

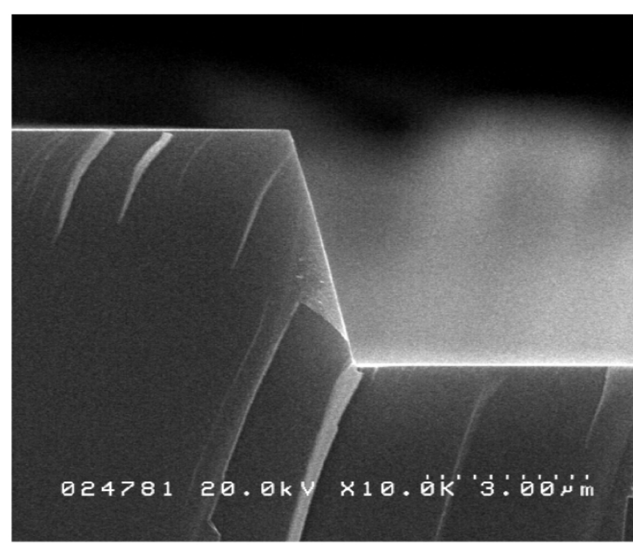
species on the photoresist etching similar to that of sapphire etch rate trends, even though the detailed reaction species and by products are different.

Fig. 3 shows the effect of d.c. bias voltage from −400 to −800 V at 1400 W of inductive power, 1.33 Pa of working pressure, 100 sccm of total flow rates, and 3 °C of substrate temperature using 81%BCl_3/9%HBr/10%Ar plasmas. The increase of d.c. bias voltage also increased the etch rates of sapphire and photoresist. However, at low bias voltages up to −600 V, the increase of sapphire etch rate was faster than that of photoresist etch rate. Therefore, the etch selectivity was increased until −600 V of d.c. bias voltage. The increase of d.c. bias voltage increases only the energy of the ions while the increase of input power increases fluxes of ions and radicals. Therefore, the increase in the etch rates of sapphire and photoresist with increasing d.c. bias voltage was believed to be caused by the increased sputter removal of the substrate material and reaction products formed on the surface. Also, in the case of sapphire etching, the bond breaking of Al−O appears to be important at low d.c. bias voltages. The highest sapphire etch rate obtained with −800 V of d.c. bias voltage was 550 nm/min with the etch selectivity over photoresist of 0.87. Even though the etch selectivity appeared to saturate at high bias voltages and high inductive powers, the sapphire etch rate increased continuously with d.c. bias voltage and inductive power for the investigated conditions, therefore, higher sapphire etch rate appeared to be possible than that obtained in our experiment.

The sapphire wafers were patterned using 24 μm thick photoresist and their etch profiles were observed as a function of d.c. bias voltage and inductive power for the investigated conditions (Figs. 2 and 3). Fig. 4a shows measured sapphire etch profile angles as a function of inductive power at −600 V d.c. bias voltage



(a)



(b)

Fig. 4. (a) Etch profile angle of photoresist masked sapphire as a function of d.c. bias voltage at 1400 W of inductive power and as a function of inductive power at −600 V. Remaining photoresist was stripped off. (Process condition: 100 sccm total flow rate, 1.33 Pa of working pressure, 3 °C of substrate temperature, and 81%BCl_3/9%HBr/10%Ar.) (b) One of the sapphire etch profiles observed by SEM for −700 V of d.c. bias voltage and 1400 W of inductive power.

Table 1
Variation of sapphire surface composition ratio (Al/O) and roughness for different d.c. bias voltages measured by XPS and AFM, respectively

Sample condition	Normalized Al/O ratio	RMS roughness (nm)
Reference	1.00	0.22
−400 V	0.81	0.38
−600 V	1.04	0.57
−700 V	1.05	0.46
−800 V	1.00	0.36

and as a function of d.c. bias voltage at 1400 W of inductive power. One of the sapphire etch profiles observed by SEM for −700 V of d.c. bias voltage and 1400 W of inductive power is shown in Fig. 4b. 1.33 Pa of working pressure, 100 sccm of total flow rates, and 3 °C of substrate temperature, and 81%BCl_3/9%HBr/10%Ar were also used. As shown in the figure, the increase of inductive power did not improve the etch profile significantly, however, the increase of d.c. bias voltage changed the etch profile more anisotropically. If the results of etch selectivities observed in Figs. 2 and 3 are compared with the sapphire etch profile angles in Fig. 4, the etch profile angles appeared to be related to the etch selectivity. In addition to the higher etch selectivity over photoresist, the removal of etch products accumulated at the sidewall of the photoresist and etched structure appeared to improve the etch profile by enhanced sputtering at the higher bombardment energy at the higher d.c. bias. Highest etch profile angle was approximately 75° with the etch rate of 550 nm/min and etch selectivity of 0.87.

The change in surface composition and roughness of sapphire by the etching was investigated as a function of d.c. bias voltage using XPS and AFM, respectively. The results are shown in Table 1. The etch conditions were the same as those in Fig. 3. The ratio of Al/O on the etched sapphire surface was normalized to the Al/O ratio measured for the non-etched sapphire (reference). As shown in the table, the surface composition of etched sapphire wafer was a little oxygen rich of 0.81 at −400 V of d.c. bias voltage. At the d.c. bias voltage higher than −600 V, the Al/O ratio was remained similar to the non-etched sapphire. The oxygen rich surface at −400 V might explain the remaining etch by-product at lower d.c. bias voltage resulting in lower etch profile angle as shown in Fig. 4. The ion bombardment of the sapphire surface can change the surface roughness by damaging the surface physically. The surface roughness measured by AFM after 5 μm of sapphire was etched is shown in Table 1. As shown in the table, the surface roughness appeared to increase from 0.22 nm before the etching to 0.36–0.57 nm after the etching at various d.c. bias voltages. However, the increase in surface roughness was not significant. In fact, pure ion bombardment tends to planarize any microscopic feature on the planar surface by enhancing the sputter rate for the material located at slanted angle. Therefore, no significant change in the surface roughness is shown in our experimental conditions for various bias voltages.

4. Conclusion

In this study, sapphire wafer was etched using planar inductively coupled 81%BCl_3/9%HBr/10%Ar plasmas. The effects of inductive power and d.c. bias voltage on the sapphire etch characteristics were investigated.

The increase of inductive power and d.c. bias voltage increased the sapphire and photoresist etch rates almost linearly. The etch selectivity over photoresist was remained similar for the investigated range of inductive power and d.c. bias voltage except for the low d.c. bias voltages. At the low d.c. bias voltages up to −600 V, the increase of d.c. bias voltage increases the etch selectivity possibly due to the increased sputter removal of reaction by-products formed on the surface and Al–O bond breaking in etching sapphire. The reaction product remaining on the etched sapphire surface at a low d.c. bias voltage showed lower Al/O ratio compared to that of the non-etched sample. The etch profile angle appeared to be related to the etch selectivity. Also, the removal of etch products accumulated at the sidewall of the photoresist and etched structure, appeared to improve etch profiles by sputtering at the higher d.c. bias voltage. Therefore, the etch profile angle was increased with increasing d.c. bias voltage. The sapphire etch rate obtained in the BCl_3/HBr/Ar plasma was 550 nm/min with the etch selectivity over photoresist approximately 0.87 and the etch profile angle of 75° at 1400 W of inductive power and −800 V of d.c. bias voltage. The surface roughness of the etched sapphire was remained similar regardless of d.c. bias voltage.

Acknowledgments

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References

[1] T. Egawa, T. Jimbo, J. Appl. Phys. 82 (11) (1997) 5816.
[2] W.S. Wong, T. Sands, Appl. Phys. Lett. 75 (10) (1999) 1360.
[3] S. Nakamura, T. Mukai, M. Senoh, Appl. Phys. Lett. 64 (1994) 1687.
[4] S. Nakamura, M. Senoh, N. Iwasa, S. Nagahama, T. Yamada, T. Mukai, Jpn. J. Appl. Phys. 34 (1995) L1332.
[5] T. Mukai, M. Yamada, S. Nakamura, Jpn. J. Appl. Phys. 37 (1998) L1358.
[6] T. Mukai, S. Nakamura, Jpn. J. Appl. Phys. 38 (1999) 5735.

[7] T. Egawa, H. Ishikawa, T. Jimbo, M. Umeno, Appl. Phys. Lett. 69 (6) (1996) 830.
[8] S. Nakamura, M. Senoh, S. Nagahama, et al., Jpn. J. Appl. Phys. 35 (1996) L74.
[9] S.D. Lester, F.A. Ponce, M.G. Craford, D.A. Steigerwald, Appl. Phys. Lett. 66 (1996) 1249.
[10] C.H. Jeong, D.W. Kim, J.W. Bae, et al., Mater. Sci. Eng. B 93 (2002) 60.
[11] C.H. Jeong, D.W. Kim, K.N. Kim, G.Y. Yeom, Jpn. J. Appl. Phys. 41 (2002) 6206.
[12] Y.J. Sung, H.S. Kim, Y.H. Lee, et al., Mater. Sci. Eng. B 82 (2001) 50.
[13] R. Lee, J. Vac. Sci. Technol. A 16 (1979) 164.
[14] J.W. Kim, Y.C. Kim, W.J. Lee, J. Appl. Phys. 78 (3) (1995) 2045.
[15] J.B. Fedison, T.P. Chow, H. Lu, I.B. Bhat, J. Electrochem. Soc. 144 (8) (1997) L221.