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A Study of Dry Etch Mechanism of the GaN using Plasma Mass Spectrometry

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Abstract

The characteristics of inductively coupled Cl_2/BCl_3 plasmas during the GaN etching were studied using plasma mass spectrometry by measuring the relative amounts of reactive ions, neutrals, and etch products. GaN etch rates increased with the increase of pressure and showed a maximum near 25mTorr for the pure Cl_2 and near 30mTorr for Cl_2/BCl_3. The addition of BCl_3 to Cl_2 also was increased GaN etch rates until 50%BCl_3 was mixed to Cl_2. The GaN etching with pure Cl_2 appears to be related to the combination of Cl_2^+ ion bombardment and the chemical reaction of Cl radicals. In the case of the GaN etching with Cl_2/BCl_3, in addition to the combined effect of Cl_2^+ ions and Cl radicals, BCl_2^+ ions appear to be responsible for some of GaN etching even though they do not have significant effect on the GaN etching compared to Cl_2^+ and Cl. Ga^+, $GaCl^+$, $GaCl_2^+$, and N_2^+ were observed as the positive ions of etch products, and the intensities of these etch products showed the same trends as those of GaN etch rate. Among the etch products, Ga and N_2 appear to be the main etch products.

Key words : *GaN, plasma etching, ICP, QMS, etch mechanism*

1. INTRODUCTION

Currently, although the dry etching of III-V compounds has received increasing attention recently, their chemical reactions and plasma characteristics have not yet been fully investigated. Among the various III-V compound semiconductors, only some of the studies on their respective dry etch mechanisms are reported such as for InP etching and GaAs chemical etching[1)-4)].

GaN etchings are widely applied to the fabrication of optoelectronic devices and electronic devices. Especially, mirror facet of GaN-based laser diode has been generally formed by dry etching methods. High density plasma source, ion beam etching, and advanced wet etching are used to mask mesa structures and laser facets. To etch GaN with the etch rates approaching 1000nm/min and smooth and high anisotropic etch profiles, high density plasma sources are gen-

erally used with chlorine-containing gases[5)-9)].

Cl_2/BCl_3 gas mixtures, used in this experiment, have been widely used in the etching of metal lines in microelectronic fabrications. Cl_2 is usually the primary etch gas while BCl_3 is added to remove the native oxide layer, to scavenge water vapor, and to enhance the anisotropic etching. These gas mixtures were also used to etch compound semiconductors such as GaAs and InP.10 The GaN etch rate close to 850nm/min was obtained using Cl_2-rich gas combinations of Cl_2/BCl_3, previously reported[7)].

In this study, the effects of the addition of BCl_3 to Cl_2 and the increase of pressure on the GaN etch rate were investigated by the mass spectrometer during the GaN etching.

2. EXPERIMENT

The GaN was etched by a home-made inductively coupled plasma (ICP) equipment using various combinations of Cl_2/BCl_3 at the operational pressures from 5 mTorr to 40mTorr while inductive power, bias voltage, and substrate temperature were fixed at 600 watts, -120 volts, and 70℃, respectively[7)]. The details of the ICP equipment and the GaN samples used in the experiments are described elsewhere[6),7)]. To understand the effects of plasma conditions on the GaN etch properties, a quarupole mass spectrometer (QMS ; Hiden Analytical Inc. PSM 500) located on the sidewall chamber have was used. The schematic diagram of ICP etcher with QMS system is shown in Fig. 1. The QMS used in the analysis of the plasmas was configured with ion optics, an energy filter, and an integral electron impact ion source.

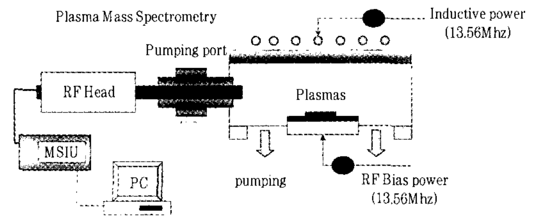


Fig. 1 Schematic diagram of inductively coupled plasma etcher with QMS

Neutral species such as radicals from the plasmas are ionized by an integrated electron impact ion source and are then detected. For the mass spectroscopic detection of radicals, it is difficult to distinguish the direct ionization of free radicals from the dissociative ionization of the parent molecule. Therefore, the appearance mass spectrometric (AMS) method[11)] was used to separate them because many of these processes have several eV differences in the threshold energies of their electron impact ionization. Some fundamental threshold ionization energy in Cl_2/BCl_3 plasmas are summarized in Table 1[12)-16)]. The threshold ionization energy can be also confirmed by scanning electron energy in the electron impact

Table 1. Summary of fundamental data of threshold ionization energy reported by other works[12)-16)].

Species	paths	E_{th} (eV)
Cl_2^+	Cl_2 + e	11.4-11.5
Cl^+	Cl + e Cl_2-- 2Cl +e	13.01 15.5
BCl_3^+	BCl_3 + e	11.64- 12.19
BCl_2^+	BCl_2 + e BCl_3 -- BCl_2 + e	9.68- 10.10 12.3-12.8
BCl+	BCl + e BCl_2 -- BCl + e BCl_3 -- BCl + e	13.15 15.73 18.37-20.2
B^+	B + e BCl_2 -- B + e	8.29 18.09

ion source with and without the plasma. For example, QMS output intensities of Cl and Cl_2 in the pure Cl_2 plasma at 600Watts of inductive power and 30mTorr of pressure as a function of electron energy are shown in Fig. 2.

Reactive ion densities in the plasmas were also measured using the QMS by turning off the filament and by the integration of the collected ions having different ion energies. At first, the ion mass was measured from 1 to 300 amu at 6eV of the ion energy. And then the intensity of each ions, detected by the previous basic mass scan, was scanned as a function of ion energy of -200 ~ +200eV and finally relative densities of ion species were estimated from the direct integration of the ion energy distribution. Fig. 3 shows ion energy distribution of Cl_2^+ in pure Cl_2 plasma at 600Watts of inductive power and 30mTorr of pressure. Total counts estimated from integration of ion energy distribution are 665900 counts

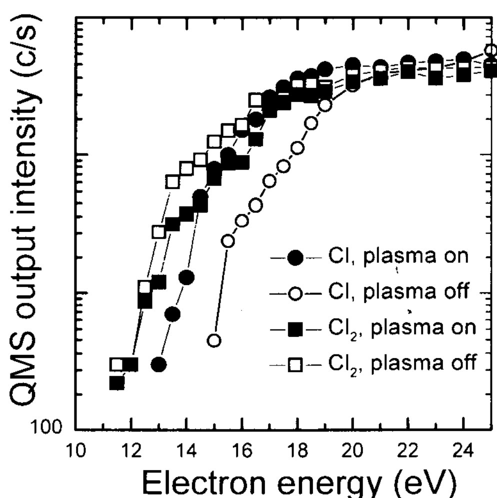


Fig. 2 QMS output intensities of Cl and Cl_2 as a function of electron energy in pure Cl_2 plasma at 600 Watts of inductive power and 20mTorr of pressure

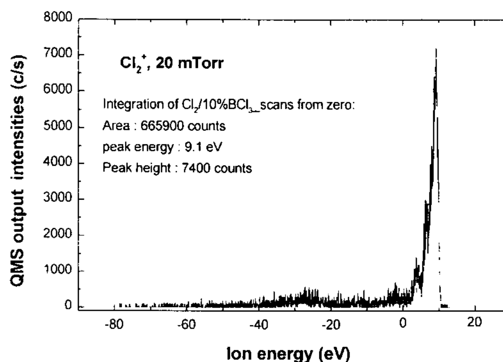


Fig. 3 Ion energy distribution of Cl_2^+ in pure Cl_2 plasma at 600Watts of inductive power and 20 mTorr of pressure

and peak energy is 9.1eV.

Etch products during the GaN etching by Cl_2/BCl_3 plasmas were also measured using positive ion measurements. Among these, Ga-containing etch products such as Ga^+, $GaCl^+$, and $GaCl_2^+$ were also verified by additionally etching GaAs with the same etching conditions for the GaN etching. To separate the residual etch products on the chamber wall or QMS ports and intrinsic N_2 from the actual etch products, the QMS intensities measured during the GaN etching were subtracted by the QMS intensities measured with the plasma without GaN. These results were compared with the etch products such as $GaCl_x$, Ga, and N_2 measured by OES. The detailed measurement method of OES and the measured results are described elsewhere[7].

3. RESULTS AND DISSCUSSION

GaN samples were etched with various Cl_2/BCl_3 combinations at the pressure from 5 to 40mTorr while keeping the inductive power at 600Watts, the bias voltage at -120Volts, and the substrate

temperature at 70℃, and some of the results are shown in Fig. 3. The GaN etch rate increased with the addition of BCl_3 to Cl_2 and the maximum etch rate was obtained with the Cl_2/10% BCl_3 mixture. Also, until 50% of BCl_3 was mixed to Cl_2, the GaN etch rates were higher than that etched with pure Cl_2. The GaN etch rate also increased with pressure and showed a maximum at 30mTorr for the Cl_2/10%BCl_3 mixture. In the case of pure Cl_2, the degree of GaN etch rate increase with pressure was smaller compared to the case of Cl_2/10%BCl_3, however, the GaN etch rate showed a maximum near 25mTorr which is similar to that etched with Cl_2/10%BCl_3.

Plasma species such as neutrals and ions were measured using QMS when 2 inch diameter GaN samples were etched at 600Watts of inductive power, -120 V of bias voltage, 70℃ of substrate temperature. To study the effect of BCl_3, neutrals and ions were measured as a function of Cl_2/10 %BCl_3 gas mixture at 30mTorr of operational pressure and the results are shown in Fig. 5 (a) for neutrals and (b) for ions. For pure Cl_2 inductively coupled plasmas, Cl_2^+ was the main ion species and Cl was the main neutral species. For Cl_2/BCl_3 plasmas, Cl was also main neutral species and Cl_2^+ was the main ion species until 50% BCl_3 was mixed to Cl_2. BCl_2^+ ions were the second main species for Cl_2/BCl_3 plasmas until 50% BCl_3 is mixed to Cl_2 and became the main species with the further increase of BCl_3 percent. The increase of pressure increased the densities of neutral species monotonically for both pure Cl_2 and Cl_2/BCl_3 gas mixtures while Cl_2^+ slightly decreased until 20mTorr for pure Cl_2, and while Cl_2^+ and BCl_2^+ increased until 30mTorr for Cl_2/BCl_3 (not shown). The trends of neutral and ions during the GaN etching were similar to the trends of those without GaN even though the absolute intensities of individual species were a little different.

As shown in Fig. 4, the GaN etch rates with the addition of BCl_3 (less than 50%) are higher than those with pure Cl_2 for all of the investigated pressure range even though Cl_2^+ appears to decrease continuously with the increase of BCl_3 and Cl are higher than that for pure Cl_2 only up to 20% BCl_3. The BCl_2^+, which exists as the second main ion (more than 15% at Cl_2/10%BCl_3), increases with the addition of BCl_3 even though BCl_2^+ appears not as effective as Cl_2^+ in the GaN etching. Therefore, in the case of GaN etching with Cl_2/BCl_3, not only Cl_2^+ and Cl but also BCl_2^+ appears to assist in the GaN etching. Total count of positive ions decreased continuously with the increase of BCl_3 percent ,therefore, rather than

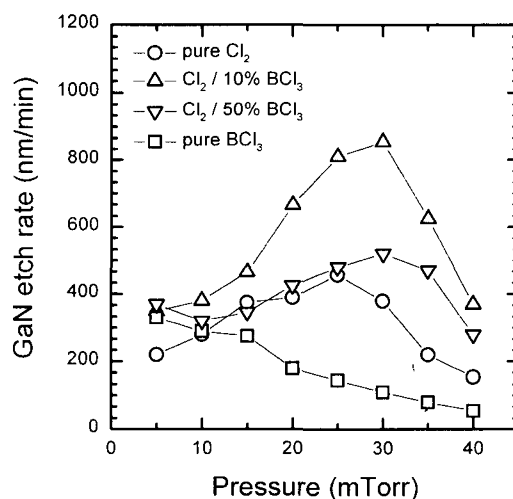
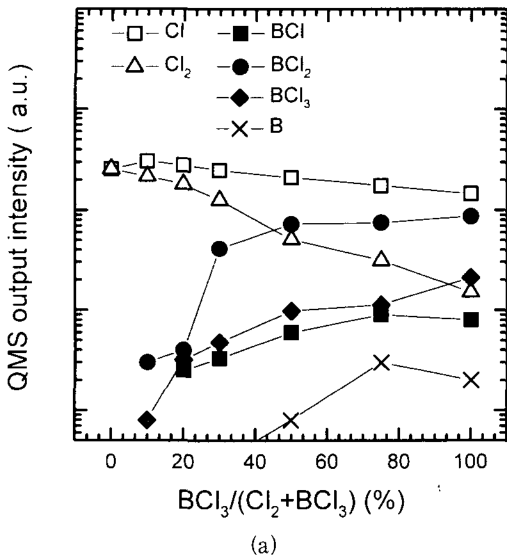
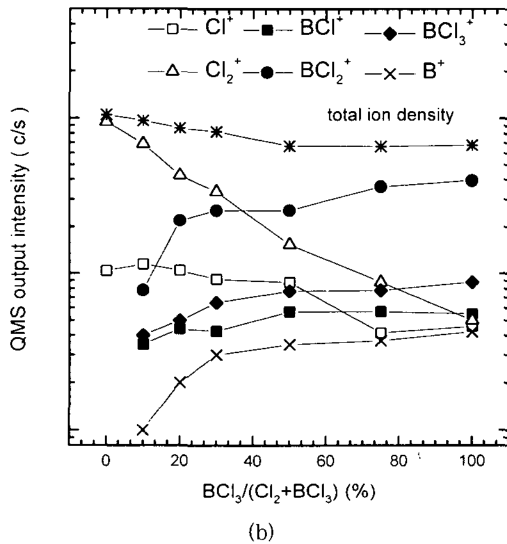


Fig. 4 GaN etch rates as a function of pressure for gas combination of Cl_2/BCl_3 plasmas at 600Watts of inductive power, -120 volts of bias voltage, and 70℃ of substrate temperature.



(a)

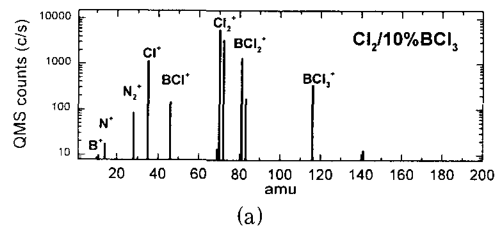


(b)

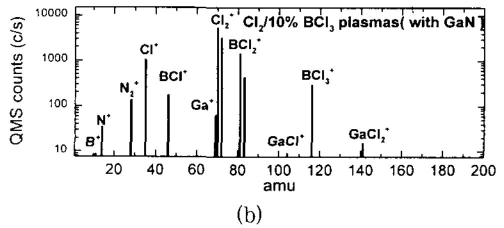
Fig. 5 QMS output intensities of (a) neutral species and (b) positive ion species as a function of gas combination of Cl_2/BCl_3 plasmas during the GaN etching at the same condition in Fig.4

the number of total ions, specific ions such as Cl_2^+ and BCl_2^+ appear to affect the GaN etch rate.

Etch products produced during the etching of 2-inch diameter GaN wafer were also investigated using the QMS. Fig. 6 shows ion mass spectra of Cl_2/10%BCl_3 plasma (a) with and (b) without GaN at 600Watts of inductive power, -120 volts of bias voltage, 70℃ of substrate temperature and 30mTorr of pressure. As a positive ion etch prosucts, Ga^+, $GaCl^+$, $GaCl_2^+$, and N_2^+ were observed as shown in this figure. The densities of positive ion species were integrated from ion energy distribution and the results are shown in Fig. 7 as a function of pressure for pure Cl_2 and for Cl_2/10%BCl_3. These etch products showed the maximum at 30mTorr similar to the case of GaN etch rate with pressure. Even though it is difficult to determine the main etch products only from positive ion products, Ga and N_2 appear to be the main etch products for both of the cases with pure Cl_2 and Cl_2/10%BCl_3 when compared with the data obtained with OES in the previous study[7]. Also, $GaCl_x^+$ (x=1,2) ions appear to be formed from the ionization of $GaCl_2$



(a)



(b)

Fig. 6 Ion mass spectra of Cl_2/10%BCl_3 plasma (a) with out and (b)with GaN at the same condition in Fig. 4.

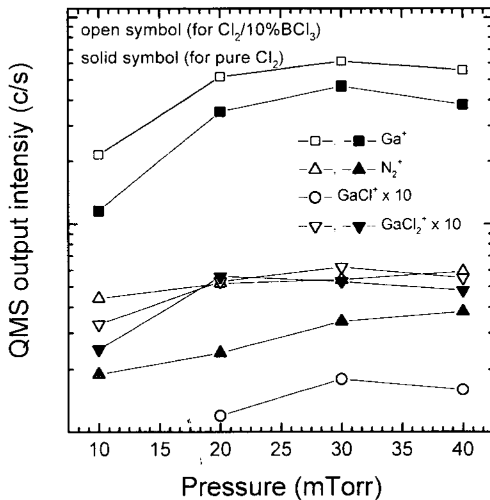


Fig. 7 QMS output intensities of ion etch products as a function of pressure during the GaN etching by the pure Cl_2 plasma (solid symbol) and the Cl_2/10%BCl_3 plasma (open symbol)at 600Watts of inductive power, -120 volts of bias voltage, and 70℃ of substrate temperature.

products, which is the primary fragment of $GaCl_3$ and is known to dominate the cracking pattern of $GaCl_3$ as reported by other' study[3),19)]. On the contrary, the intensity of Ga^+ appears not to be fully originated from the cracking of the GaClx, but to reflect physical sputtering of atomic species. In the previous study, we investigated etch products using OES and Ga and N_2 were observed as the main etch products similar to the QMS data obtained in Fig. 7. One of the possible etch product such as NCl_3 was not detected with our QMS. Also, N possibly from GaN was detected with a very low intensity.

4. CONCLUSIONS

In this study, neutrals and ions produced by inductively coupled Cl_2/BCl_3 plasmas were investigated as a function of pressure and Cl_2/BCl_3 mixture using the QMS and their relation to GaN etch rate were estimated.

The results showed that the enhancement of GaN etch rates for Cl_2/BCl_3 plasmas could be related to the formation of Cl radicals and reactive ions such as Cl_2^+ and BCl_2^+ measured by the mass spectrometry during the GaN etching. These Cl radicals are responsible for chemisorption and BCl_x^+ and Cl_2^+ for chemical and/or physical sputtering. Ion assisted chemical desorption seems to be generally enhanced by the addition of BCl_3 to Cl_2 and also with the increase of pressure. Also, the abundance of BCl_2^+ in the Cl_2/10%BCl_3 plasmas appears to be important in the GaN etching compared to the pure Cl_2 plasma. The Ga^+, $GaCl_2^+$, and N_2^+ were observed during the GaN etching as the etch products and the intensities of these ion etch products were correlated with the trend of GaN etch rate.

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