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Characteristics of inductively coupled Cl$_2$/BCl$_3$ plasmas during GaN etching

H. S. Kim$^a$ and G. Y. Yeom$^b$

Department of Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea

J. W. Lee and T. I. Kim

Photronics Laboratory, Samsung Advanced Institute of Technology, Suwon 440-660, Korea

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In this study, the characteristics of inductively coupled Cl$_2$/BCl$_3$ plasmas during GaN etching were estimated using plasma mass spectrometry by measuring the relative amounts of positive ions, neutrals, and etch products. 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$_3^+$ measured by the mass spectrometry during GaN etching. These Cl radicals are responsible for chemisorption and BCl$_3^+$ 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$_3^+$ in the Cl$_2$/10%BCl$_3$ plasmas appears to be important in GaN etching compared to pure Cl$_2$ plasma. Ga$^+$, GaCl$_2$ and N$_2^+$ were observed during GaN etching as the etch products and the intensities of these ion etch products were correlated with the trend of the GaN etch rate. © 1999 American Vacuum Society. [S0734-2101(99)07904-X]

I. INTRODUCTION

Many studies on the plasma characteristics during the dry etching of silicon and related materials have been reported. However, 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 studies of their respective dry etch mechanisms are reported such as for InP etching by CH$_4$/H$_2$, for GaAs chemical etching by Cl$_2$ and HCl, and for the surface reaction of GaAs with Cl$_2$ plasma or chlorine ion beams.

These days, the dry etching of GaN is obtaining particular attention for the fabrication of the laser facet of GaN laser diodes. To etch GaN with etch rates approaching 1000 nm/min and obtain smooth and highly anisotropic etch profiles, high density plasma sources are generally used with chlorine-containing gases (Cl$_2$, BCl$_3$, and ICl). In our previous work, a GaN etch rate close to 850 nm/min was also obtained using a Cl$_2$-rich gas combination of Cl$_2$/BCl$_3$. Optical emission spectroscopy (OES) was used to monitor some of the plasma species such as Cl, Cl$^+$, and BCl$_3$ and etch products such as Ga, N$_2$, and GaCl$_4$ in the plasmas. However, the effects of various species in the plasmas on the GaN etch properties and details of the etch products could not be observed.

In this study, to investigate the characteristics of the Cl$_2$/BCl$_3$ plasmas for GaN etching more closely, the relative amounts of positive ion species and neutral species were estimated by plasma mass spectrometric measurements. The effects of the addition of BCl$_3$ to Cl$_2$ and the increase of pressure on the GaN etch rate were also investigated by a mass spectrometer during GaN etching.

II. EXPERIMENT

The GaN was etched by homemade inductively coupled plasma (ICP) equipment using various combinations of Cl$_2$/BCl$_3$ at operational pressures of 5–40 mTorr while the inductive power, bias voltage, and substrate temperature were fixed at 600 W, −120 V, and 70 °C, respectively. The GaN sample was loaded manually after exposure to air. Details of the ICP equipment and the GaN samples used in the experiments are described elsewhere. To understand the effects of plasma conditions on the GaN etch properties, a quadrupole mass spectrometer (QMS) (Hiden Analytical Inc. PSM 500), optical emission spectrocope (SC Technology PCM 402), and a Langmuir probe (Hiden Analytical Inc., ESP) located on the sidewall chamber were used.

The QMS used in the analysis of the plasmas was configured with ion optics, an energy filter, and an integral electron impact ion source. To minimize the residual gas effect and contamination in the QMS, the pumping port was heated by a heating band and the filament of the ionizer was cleaned by O$_2$ plasma and degassed after every 20 min of glow discharge. Neutral species such as radicals from the plasmas are ionized by an integrated electron impact ion source and are then detected. For 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 was used to separate them because many of these processes have differences of several eV in the threshold...
energies of their electron impact ionizations. These threshold energy data can be obtained by the scanning electron energy in the electron impact ion source with and without plasma. The signal difference between the threshold energy \( E_{th} \) for direct ionization of radicals and the threshold energy for dissociative ionization of the parent molecules is a measure of the radical density in the plasmas. Threshold ionization energies of the various species could be obtained from these QMS measurements and the values obtained are similar to reference data previously reported.\(^{12-16}\) For example, to measure BCl\(_2\) radical species, an electron energy of 12 eV was used to measure BCl\(_2^+\) ionized directly from BCl\(_2\) \( (E_{th} = 10.5 \text{ eV}) \) without dissociative ionization of BCl\(_3\) \( (E_{th} = 12.5 \text{ eV}) \). Other species such as Cl \( (E_{th} = 13.0 \text{ eV}) \), Cl\(_2\) \( (E_{th} = 12.0 \text{ eV}) \), B \( (E_{th} = 10.5 \text{ eV}) \), BCl \( (E_{th} = 13.5 \text{ eV}) \), and BCl\(_3\) \( (E_{th} = 12.5 \text{ eV}) \) were measured using an electron energy of 14 eV.

It is impossible to measure significant negative ion densities by mass spectrometry in a continuously driven discharge.\(^{17,18}\) Because negative ions are caught by the plasmas potential, extraction of them is not very efficient. Extraction would only be efficient in the afterglow of the discharge after the electrons have vanished. In the actual GaN etching process, due to the negative bias voltage formed on the substrate, chemical etching by radicals and physical etching by positive ions incident to GaN by the potential developed in the sheath may affect GaN etching more significantly. Negative ions that remain within the bulk plasma during the most of the rf cycle are believed to have little effect on GaN etching especially because of the chemical inertness of GaN. Therefore, we measured only positive ion densities in the plasmas using the QMS by turning off the filament and by integrating collected ions having different ion energies. At first, the ion mass was measured from 1 to 300 amu at 8 eV of the ion energy. And then the intensity of each ion, detected by the previous basic mass scan, was scanned as a function of ion energy of \(-200—+200 \text{ eV}\) and finally relative densities of ion species were estimated from the direct integration of the ion energy distribution. The measured positive ion species generally showed energy distributions of 2–14 eV, and most ions had peak ion energies of 4–11.5 eV. The peak energy decreased with an increase of pressure, and was in a good agreement with the decrease of plasma potential energy measured by the Langmuir probe.\(^{19}\) Also, by inserting the Langmuir probe into the center of the chamber, total positive ion current densities were estimated by biasing the probe at \(-60 \text{ V}\) and electron densities were measured from the \(I-V\) characteristics of the probe.

The etch products during GaN etching by Cl\(_2\)/BCl\(_3\) plasmas were also measured using positive ion mass spectrometry. 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 used for the GaN etch. 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 GaN etching were subtracted from the QMS intensities measured with the plasma without GaN. These results were compared with etch products such as GaCl\(_x\), Ga, and N\(_2\) measured by OES. Details of the OES measurement method and the measured results are described elsewhere.\(^{27}\)

III. RESULTS AND DISCUSSION

GaN samples were etched with various Cl\(_2\)/BCl\(_3\) combinations at pressures from 5 to 40 mTorr while keeping the inductive power at 600 W, bias voltage at \(-120 \text{ V}\), and the substrate temperature at 70 °C, and some of the results are shown in Fig. 1. The GaN etch rate increased with an increased percent of BCl\(_3\) in the Cl\(_2\)/BCl\(_3\) gas mixture and the maximum etch rate was obtained with the Cl\(_2\)/10%BCl\(_3\) mixture. Also, until 50% of BCl\(_3\) was mixed into 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 30 mTorr 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 25 mTorr which is similar to that etched with Cl\(_2\)/10%BCl\(_3\), as shown in Fig. 1.

To study the GaN etching trends shown above, relative amounts of neutrals and ions in the Cl\(_2\)/BCl\(_3\) plasmas were investigated as a function of pressure and Cl\(_2\)/BCl\(_3\) gas mixture using the QMS described in Sec. II. Figure 2 shows the relative amounts of neutrals such as Cl and Cl\(_2\) and positive ions such as Cl\(^+\) and Cl\(_2^+\) measured by the QMS for the pure Cl\(_2\) as a function of pressure while the other process parameters were kept the same as the conditions in Fig. 1. The amounts of Cl and Cl\(_2\) generally increased with the pressure and the measured QMS intensity of Cl was higher than the Cl\(_2\) signal. Even though the electron ionization cross section of Cl\(_2\) is several times higher than that of Cl at the 14 eV of electron energy used to detect neutral signals, the detected Cl
signal is higher than Cl$_2$, therefore, Cl is expected to be the main radical of the pure Cl$_2$ plasmas used in the experiment.\textsuperscript{14–16,19} In the case of positive ions, the amount of individual ions was calculated by integration of the respective ion energy distribution described in Sec. II, and Cl$_2^+$ is expected to be the main positive ion as shown in Fig. 2. The Cl$_2^+$ showed an initial increase and a slight decrease with pressure until 20 mTorr and decreased rapidly after 30 mTorr while Cl$^+$ generally decreased more rapidly with the increase of pressure. When the GaN etch rates for pure Cl$_2$ were compared with the QMS results, the combination of Cl$_2^+$ ion bombardment and chemical etching by Cl radical appears to be responsible for the GaN etching.

Figures 3(a) and 3(b) show neutrals and positive ions as a function of pressure measured for Cl$_2$/10\%BCl$_3$, where the GaN etch rate was the highest. The other process parameters were also the same as those shown in Fig. 1. As shown in Fig. 3(a), the intensities of various BCl$_x$ ($x = 0, 1, 2, 3$) were lower than those from Cl and Cl$_2$. The electron ionization cross sections of BCl$_x$ species are similar to each other and are higher than those of Cl$_2$ and Cl.\textsuperscript{19,20} Therefore, we can confirm that Cl is the main neutral similar to the case of pure Cl$_2$. Among B, BCl, BCl$_2$, and BCl$_3$, BCl$_2$ and BCl$_3$ increase rapidly with pressure while B decreases and BCl increases only with pressure. The decrease of B and the only slight increase of BCl with pressure appear to be from the increased probability of recombination of the radicals and also from the decrease of electron energy which results in the decrease of gas dissociation. This tendency was more evident when BCl$_3$-rich gas combinations were used (not shown). Figure 3(b) shows the positive ion species measured directly for Cl$_2$/10\%BCl$_3$ as a function of pressure using the QMS. Most of the positive ions, except for B$^+$ and Cl$^+$, increased with pressure until 30 mTorr, which is consistent with the etch result shown in Fig. 1 for Cl$_2$/10\%BCl$_3$. The Cl$_2^+$ was the main ion species and BCl$_3^+$ was the secondmost prevalent species. These species were about 10 times higher than other ion species.

To study the effect of BCl$_3$, neutrals and positive ions were measured as a function of the Cl$_2$/10\%BCl$_3$ gas mixture at 30 mTorr of operational pressure and the results are shown in Figs. 4(a) and 4(b) for neutrals and for ions, respectively. As shown in Fig. 4(a), the intensity of Cl increased with the addition of 10\% BCl$_3$ and a further increase of BCl$_3$ decreased the intensity of Cl slightly. The intensity of Cl$_2^+$ decreased monotonically with the increase of the percent of BCl$_3$ while the intensities of BCl, BCl$_2$, and BCl$_3$ increased...
with the increase of the percent of BCl₃. Cl was the main neutral even with 100% BCl₃. In the case of ions, Cl²⁻ decreased with the increase of the percent of BCl₃ while BCl⁺, BCl₂⁺, and BCl₃⁺ increased with the increase of the percent of BCl₃. Until 30% BCl₃, Cl⁻ was the main positive ion and then BCl₂⁺ became the main positive ion with the further increase of the percent of BCl₃. In the case of Cl⁺, the increase of BCl₁ up to 20% increased the intensity of Cl⁺ and a further increase of the percent of BCl₃ decreased the intensity of Cl⁺. The intensity of BCl₃⁺ was not proportional to the increase of the percent of BCl₃, and is probably due to the lower dissociation threshold energy (4.6 eV) of BCl₃ into BCl₂ compared to the higher ionization threshold energy (12.19 eV) of BCl₃ into BCl₁⁺. Therefore, most of the added BCl₃ appears to be dissociated into BCl₂ or BCl₂⁺. The increase of Cl and Cl¹ with the addition of nearly 10%–20% BCl₃ is not clear, however, it appears to be related to both the additional source of Cl radicals from dissociation of BCl₃ and the decrease of recombination of Cl into Cl₂ on the chamber wall by the adsorbed BClₓ on the chamber as described by other researchers.¹⁹ The increase of Cl and Cl¹ with the addition of nearly 10%–20% BCl₃ was also observed from the OES measurement as described in the previous study.⁷

It is reported that the addition of BCl₃ into Cl₂ generally reduces the positive ion density and electron density because of the higher dissociation threshold energy of BCl₃, resulting in absorbing more energy for dissociation of the molecules and a higher electron affinity of BCl₃ compared to those of Cl₂.¹⁵,¹⁶,²⁰ Therefore, even though we did not measure the amount of negative ions in our study described in Sec. II, more negative ions will be formed with the increase of BCl₃, which results in the decrease of the electron density and positive ion density. When all of the positive ions measured in Fig. 4(b) were added, the decrease of total positive ion density could be observed. Using the Langmuir probe described in Sec. II, positive ion current density as a measure of total positive ion density and electron density were estimated. The results showed the decrease of ion current density and electron density with the increase of BCl₃, as shown in the bottom part of Fig. 5.

In fact, the QMS data described in Figs. 1–4 are obtained without loading GaN samples. We also measured neutrals and ions when GaN samples were etched with the conditions shown in Fig. 4 and also by biasing the substrate at −120 V and by heating it at 70 °C. The results are shown in Fig. 5 for the main species. The trends of neutrals and ions in the

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**Fig. 4.** QMS output intensities of (a) neutral species and (b) positive ion species as a function of gas combination of Cl₂/BCl₃ plasmas at 30 mTorr pressure and 600 W inductive power.

**Fig. 5.** Total positive ion current density and electron density measured by a Langmuir probe and a QMS of output intensities of Cl, Cl⁺, Cl²⁻, and BCl₃⁺ as a function of gas combination of Cl₂/BCl₃ plasmas during GaN etching at 30 mTorr pressure, 600 W inductive power, −120 V bias voltage, and 70 °C substrate temperature.
plasma when a 2 in. diam GaN deposited on the sapphire wafer was etched were similar to the trends of those without GaN even though the absolute intensities of individual species were a little different.

When GaN etch rates with BCl₃ addition are compared with the QMS data shown in Figs. 3 and 4, it can be concluded that GaN etch rates are mainly controlled by the combined effect of Cl₂⁺ ion bombardment and chemical reaction of Cl radicals. However, the GaN etch rates with the addition of BCl₃ (less than 50%) are higher than those with pure Cl₂ for all of the investigated pressure range even though Cl₂⁺ appears to decrease continuously with the increase of BCl₃ and Cl is higher than that for pure Cl₂ only up to 20%BCl₃, as shown in Fig. 4(b). The BCl₂⁺, which exists as the second most prevalent positive ion (more than 15% at Cl₂/10%BCl₃), increases with the addition of BCl₃ even though BCl₂⁺ appears to be not as effective as Cl₂⁺ in the GaN etching. Therefore, in the case of GaN etching with Cl₂/BCl₃, not only Cl₂⁺ and Cl but also BCl₂⁺ appear to assist in the GaN etching. Also, from the Langmuir probe data, the total number of positive ions and electrons appears to decrease continuously with the increase of BCl₃ even though GaN etch rates with the addition of BCl₃ (less than 50%) are higher than those with pure Cl₂. Therefore, rather than the number of total ions, specific ions such as Cl₂⁺ and BCl₂⁺ appear to affect the GaN etch rate.

Etch products produced during the etching of a 2 in. diam GaN wafer were also investigated using the QMS. Because we were not able to obtain all of the cracking patterns and threshold energies of the possible etch products, only the positive ion species were compared as a function of pressure and the results are shown in Fig. 6 for pure Cl₂ and for Cl₂/10%BCl₃. As the positive ions of etch products, Ga⁺, GaCl⁺, GaCl₂⁺, and N₂⁺ were observed, however, the intensities of these etch products including neutral etch products were detected as less than 1% of total plasma species. These etch products showed the maximum at 30 mTorr 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 N₂ appear to be the main etch products for both of the cases with pure Cl₂ and Cl₂/10%BCl₃ when compared with the data obtained with OES in the previous study. Also, GaClₓ⁺ (x = 1, 2) ions appear to be formed from the ionization of GaCl₂ products, which is the primary fragment of GaCl₃ and is known to dominate the cracking pattern of GaCl₃ as reported in studies by others. On the other hand, the intensity of Ga⁺ appears not to fully originate from the cracking of the GaCl₂, but to reflect physical sputtering of atomic species. In the previous study, we investigated etch products using OES and Ga and N₂ were observed as the main etch products similar to the QMS data obtained in Fig. 6. One of the possible etch products, for example, NCl₃, was not detected by our QMS. Also, N possibly from GaN was detected with a very low intensity.

FIG. 6. QMS output intensities of positive ion etch products as a function of pressure during GaN etching by the pure Cl₂ plasma (closed symbol) and by the Cl₂/10%BCl₃ plasma (open symbol) at 600 W inductive power, −120 V bias voltage, and 70 °C substrate temperature.

IV. CONCLUSIONS

In this study, neutrals and positive ions produced by inductively coupled Cl₂/BCl₃ plasmas were investigated as a function of pressure and Cl₂/BCl₃ mixture using a QMS and their relation to the GaN etch rate was estimated.

The GaN etch rates increased with the increase of pressure and showed a maximum near 25 mTorr for the pure Cl₂ and near 30 mTorr for Cl₂/BCl₃. The addition of BCl₃ to Cl₂ also increased the GaN etch rates until 50% BCl₃ was mixed into Cl₂. The GaN etch rate with Cl₂/BCl₃ showed a maximum at Cl₂/10%BCl₃.

For pure Cl₂ inductively coupled plasmas, Cl₂⁺ was the main positive ion species and Cl was the main neutral species. For Cl₂/BCl₃ plasmas, Cl was also main neutral species and Cl₂⁻ was the main positive ion species until 50% BCl₃ was mixed into Cl₂. Cl₂⁻ ions were the second most prevalent species for Cl₂/BCl₃ plasmas until 50% BCl₃ is mixed into Cl₂ and became the main species with a further increase of the percent of BCl₃.

The increase of pressure increased the densities of neutral species monotonically for both pure Cl₂ and Cl₂/BCl₃ gas mixtures while Cl₂⁺ slightly decreased until 20 mTorr for pure Cl₂; Cl₂⁺ and BCl₂⁺ increased until 30 mTorr for Cl₂/BCl₃. The GaN etching with pure Cl₂ appears to be related to the combination of Cl₂⁺ ion bombardment and the chemical reaction of Cl radicals. In the case of the GaN etching with Cl₂/BCl₃, in addition to the combined effect of Cl₂⁺ ions and Cl radicals, BCl₂⁺ ions appear to be responsible for some of GaN etching even though they do not have a significant effect on the GaN etching compared to Cl₂⁺ and Cl.

Ga⁺, GaCl⁺, GaCl₂⁺, and N₂⁺ were observed as the positive ions of the etch products, and the intensities of these...
products showed the same trends as those of the GaN etch rate. Among the etch products, Ga and N_2 appear to be the main etch products. No NCl_3 was observed and only a trace of N was detected.