JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY A

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Citation: J. Vac. Sci. Technol. A **18**, 1390 (2000); doi: 10.1116/1.582360
View online: http://dx.doi.org/10.1116/1.582360
View Table of Contents: http://avspublications.org/resource/1/JVTAD6/v18/i4
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Additional information on J. Vac. Sci. Technol. A

Magnetized inductively coupled plasma etching of GaN in Cl_2/BCl_3 plasmas*

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(Received 20 January 2000; accepted 17 April 2000)

In this study, Cl_2/BCl_3 magnetized inductively coupled plasmas were used to etch GaN, and the effects of magnetic confinements of inductively coupled plasmas on the GaN etch characteristics were investigated as a function of Cl_2/BCl_3. Also, the effects of Kr addition to the magnetized Cl_2/BCl_3 plasmas on the GaN etch rates were investigated. The characteristics of the plasmas were estimated using a Langmuir probe and quadrupole mass spectrometry (QMS). Etched GaN profiles were observed using scanning electron microscopy. The small addition of BCl_3 (10%–20%) in Cl_2 increased the GaN etch rates for plasmas both with and without magnetic confinements. The application of magnetic confinements to the Cl_2/BCl_3 inductively coupled plasmas increased the GaN etch rates and changed the Cl_2/BCl_3 gas composition of the peak GaN etch rate from 10% BCl_3 to 20% BCl_3. It also increased the etch selectivity over the photoresist, while slightly reducing the selectivity over SiO_2. The application of the magnetic field significantly increased positive BCl_2^+ measured by QMS and total ion saturation current measured by the Langmuir probe. Other species such as Cl, BCl, and Cl^+ increased, whereas species such as BCl_2 and BCl_3 decreased with the application of the magnetic field. Therefore, it appears that the increase of the GaN etch rate in our experiment is related to the increased dissociative ionization of BCl_3 by the application of the magnetic field. The addition of 10% Kr in an optimized Cl_2/BCl_3 condition (80% Cl_2/20% BCl_3) with the magnets increased the GaN etch rate about 60%. A more anisotropic GaN etch profile was obtained with the application of the magnetic field, and a vertical GaN etch profile was obtained with the addition of 10% Kr in an optimized Cl_2/BCl_3 condition with the magnets. © *2000 American Vacuum Society.* [S0734-2101(00)16404-8]

I. INTRODUCTION

III-nitride semiconductors such as GaN have great potential for the fabrication of optoelectronic devices such as light-emitting diodes and laser diodes, UV detectors, and microwave-power and ultra-high-power switches.[1–4] In the case of GaN-based optoelectronic devices, fabricating the devices successfully requires reproducible etching processes with high etch rate, vertical, and smooth etch profile.[3,5–11]

To obtain high GaN etch rates, high-density plasmas such as electron cyclotron resonance plasmas and inductively coupled plasmas (ICPs) have been used recently by many researchers.[7–16] The application of a magnetic field to inductively coupled plasmas is known to further increase plasma densities, but also to increase the plasma uniformity if adequate combinations of permanent magnetic cusping and Helmholtz-type axial magnets are used.[17]

In this study, GaN etch rate characteristics and plasma characteristics were studied in Cl_2/BCl_3 gas mixtures for a magnetized inductively coupled plasma configuration, which is made of a permanent magnet bucket and Helmholtz-type axial electromagnets. The results were compared with the conventional nonmagnetized inductively coupled plasma configuration by removing the magnetic field.

II. EXPERIMENT

The specimen was undoped GaN epitaxial layers grown on *c*-axis Al_2O_3 substrates using metal–organic chemical-vapor deposition; before etching, the GaN was patterned by SiO_2 masks deposited by plasma-enhanced chemical-vapor deposition. To etch GaN, a specially designed inductively coupled plasma unit was fabricated that can hold a permanent magnetic bucket inside the chamber and Helmholtz-type axial electromagnets around the chamber wall. The chamber was square shaped, with an inner size of 210 mm×210 mm, and was made of anodized aluminum. A square array of magnet housing made of anodized aluminum was used to install 3000 G permanent magnets around the inner wall of the chamber. Two square-shaped (500 mm×500 mm) Helmholtz-type axial electromagnets (separated by 20 cm and having 20 G inside the chamber by the application of 32 A to the coils) were also positioned outside the chamber. By using a suitable combination of permanent magnets and Helmholtz-type axial magnets with the conventional inductively coupled plasmas, an increase of plasma density and improved plasma uniformity compared to previous studies could be obtained.[17] The details of the characteristics of the plasmas and the magnet configurations used in this experiment can be found elsewhere.[17]

The undoped GaN was etched as a function of gas ratio of

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Cl_2/BCl_3 at 600 W of inductive power, −200 V of dc self-bias voltage, 10 mTorr of operational pressure, and 70 °C substrate temperature. The GaN was also etched as a function of Kr (0–30 sccm) added to the optimized Cl_2/BCl_3 chemistry of 80% Cl_2 (24 sccm)/20% BCl_3 (6 sccm) with magnets. The GaN etch rates were measured from the depth of the etched features with a stylus profilometer after removing the SiO_2 mask layer in a buffered oxide etchant. To obtain etch selectivities, patterned SiO_2 and photoresist were also etched, and the etch rates were obtained by measuring the remaining steps before and after the etch using the step profilometer.

Ion saturation current and plasma species such as Cl, Cl^+, Cl_2^+, and BCl_2^+ were monitored by a single Langmuir probe (Hiden Analytical Ltd.; model ESP) and quadrupole mass spectrometry (Hiden Analytical Ltd.; QMS) as functions of with/without magnets and gas composition of Cl_2/BCl_3. A single Langmuir probe inserted in the center of the chamber and bias voltage from −60 to +40 V to collect ion currents were used to measure the ion saturation current of the chlorine-based plasma as a measure of total positive ions. The profiles of the etched GaN were evaluated with a scanning electron microscope (SEM) after removing the SiO_2 mask layers.

III. RESULTS AND DISCUSSION

To investigate the effects of magnetic confinements on the etch properties of GaN, undoped GaN thin films were etched in the inductively coupled plasma equipment with both the magnetized ICP (MICP) configuration and the conventional nonmagnetized ICP configuration. Figures 1(a) and 1(b) show GaN etch rates and their etch selectivities over photoresist and SiO_2 as a function of gas combination of BCl_3/Cl_2 for 600 W of rf power, −200 V of dc self-bias voltage, and 10 mTorr of operational pressure for ICP and MICP, respectively. As shown in Fig. 1, with the conventional ICP configuration, the GaN etch rate showed the highest etch rate near 10% of BCl_3 and the highest etch rate with this ICP was about 3500 Å/min. The further increase of BCl_3 in Cl_2 decreased the GaN etch rate continuously. The etch selectivity over the photoresist increased slowly with the increase of BCl_3 from 1.1 to 1.4, and the etch selectivity over SiO_2 was the highest near 20% of BCl_3 and was in the range of 1.6–2.4. By applying the magnetic field (MICP) at the same etching condition, the GaN etch rate increased in general, and the highest GaN etch rate above 5000 Å/min was obtained near 20% of BCl_3. Also, by applying the magnetic field, the GaN etch selectivity over the photoresist increased in general, whereas the etch selectivity over SiO_2 decreased slightly.

To understand these changes in the etch behaviors by the application of a magnetic field, the characteristics of plasmas with and without the magnetic-field strength were studied. Figures 2(a) and 2(b) show the results of the species detected using quadrupole mass spectrometry (QMS) as a function of BCl_3/Cl_2 for the same conditions shown in Fig. 1 and for the ICP and MICP, respectively. The quadrupole mass spectrometer was located at the sidewall of the chamber. The total ion

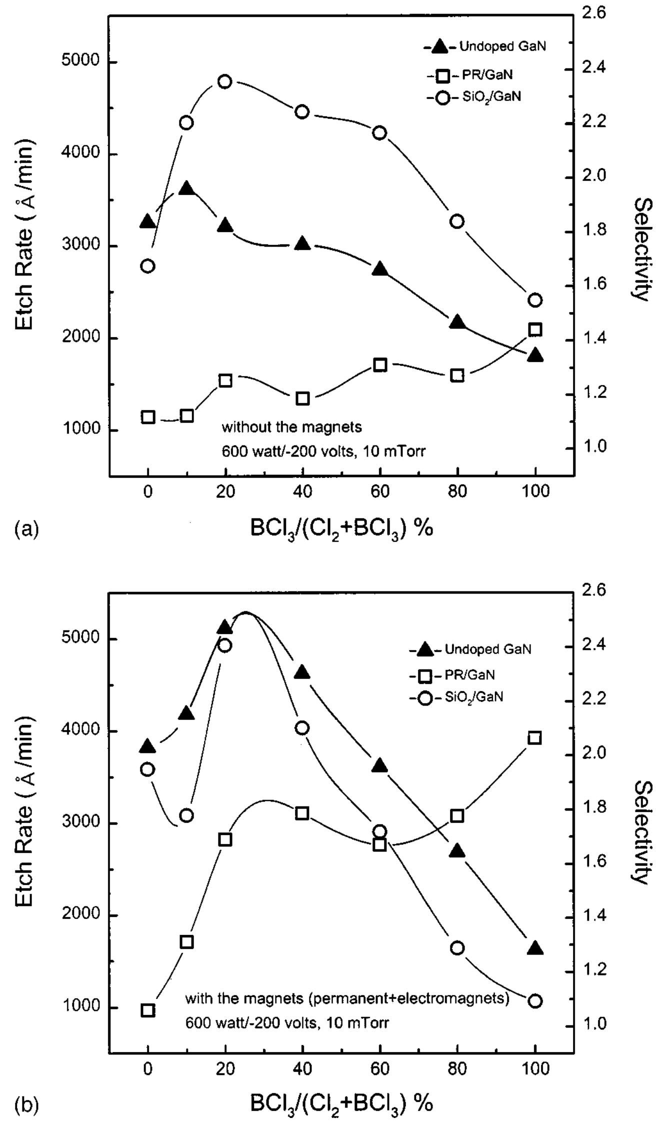

FIG. 1. GaN etch rates and selectivities as a function of gas combination of Cl_2/BCl_3 plasmas at 10 mTorr, 600 W inductive power, −200 V bias voltage, and 70 °C substrate temperature. Without the magnetic field (a) and with the magnetic field (permanent+electromagnets) (b).

saturation current measured using a Langmuir probe was also included in Fig. 2. From the quadrupole mass spectrometry, the most abundant positive ion species were Cl_2^+ and BCl_2^+, and the most abundant radical species was Cl for both with and without the magnets. Without the magnets, Cl_2^+ ions showed a maximum at 10% of BCl_3, and BCl_2^+ ions showed a maximum at near 40% of BCl_3. Cl radicals showed a maximum near 20% of BCl_3. The total ion current measured using the Langmuir probe showed a maximum at 10% BCl_3. By applying the magnetic field as shown in Fig. 2(b), the maximum of BCl_2^+ and the total ion current changed to 20% of BCl_3 and the maximum of Cl radical changed to 10% of BCl_3. Also, Cl^+ showed a maximum at 20% BCl_3. The position of the peak of the abundant species as well as the peak intensities was changed by the application of the magnetic field. As shown in Fig. 2, the application of the magnetic field especially increased the intensities of

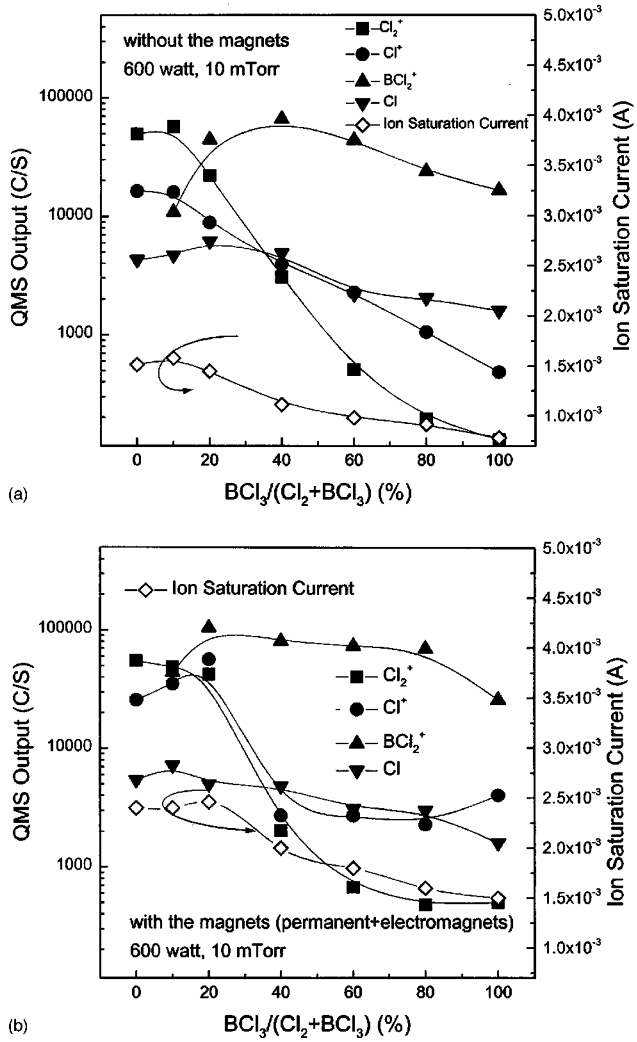

FIG. 2. Total positive ion saturation current measured by a Langmuir probe and QMS output intensities of Cl, Cl^+, Cl_2^+, and BCl_2^+ as a function of Cl_2/BCl_3 at 10 mTorr and 600 W inductive power. Without the magnetic field (a) and with the magnetic field (permanent+electromagnets) (b).

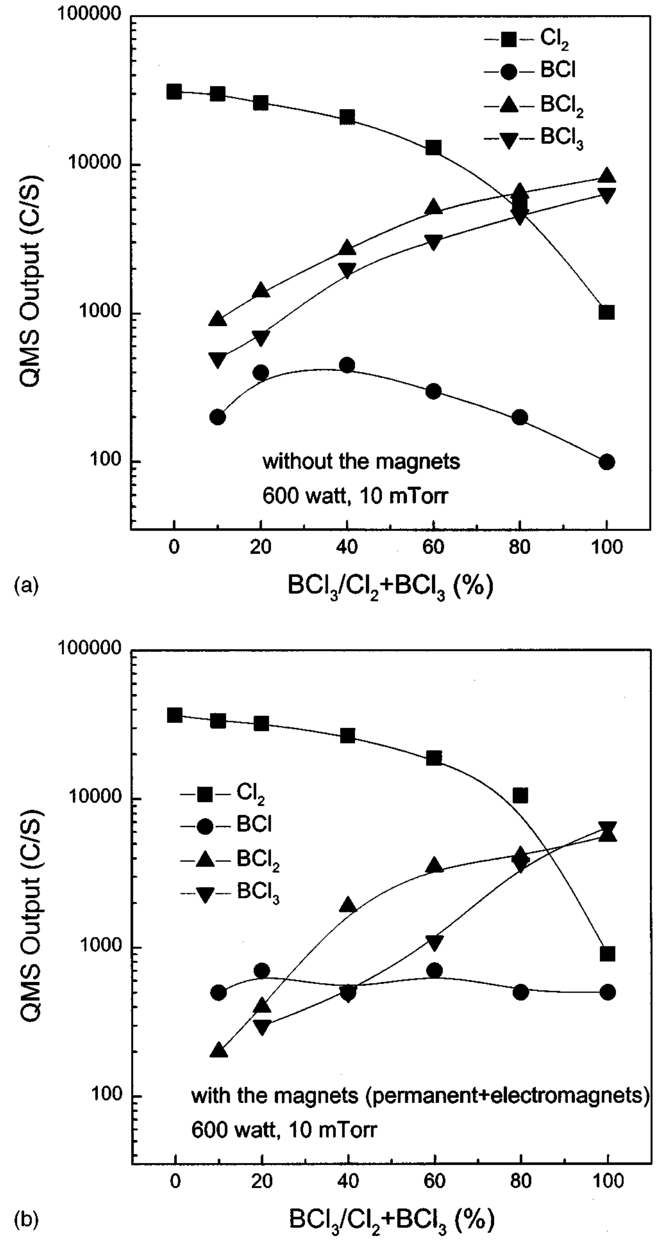

FIG. 3. QMS output intensities of neutral species such as Cl_2, BCl, BCl_2, and BCl_3 as a function of gas combination of Cl_2/BCl_3 plasmas at 10 mTorr and 600 W inductive power. Without the magnetic field (a) and with the magnetic field (permanent+electromagnets) (b).

BCl_2^+ and the total ion saturation current. A small increase of intensities was observed for the Cl radical and Cl^+ ion. In the case of Cl_2^+, no significant change of intensity was observed.

The total ion saturation current measured using the Langmuir probe is related to the increase of reactive major ions such as Cl_2^+ and BCl_2^+ measured by the quadrupole mass spectrometer. When the major ions were added together and plotted as a function of gas combination of BCl_3/Cl_2, similar trends as the total ion saturation current were obtained. Also, as was discussed in a previous article by our group,[9] in the etching of GaN, radicals such as Cl and reactive ions such as Cl_2^+ and BCl_2^+ appeared to play important roles by chemical reaction and physical/chemical reactions with Ga in GaN because the peak intensities of Cl, Cl_2^+, BCl_2^+, and Cl^+ appear to be close to the peak GaN etch rates. There was a significant increase of BCl_2^+ and the total ion saturation current with application of the magnetic field; therefore, the increased dissociative ionization of BCl_3 with application of the magnetic field appears to be responsible for the increase of the GaN etch rate.

Other neutral species such as BCl, BCl_2, BCl_3, and Cl_2 were also measured using the quadrupole mass spectrometer, and the results are shown in Figs. 3(a) and 3(b) for the same conditions shown in Fig. 2. As shown in Fig. 3, by application of the magnetic field, there is an increase of BCl with the decrease of BCl_2 and BCl_3; therefore, increased dissociation was observed. The increase of dissociation may have to increase Cl radicals significantly; however, as shown in Fig. 2(b), only a small increase of Cl radicals was observed. As shown in Fig. 3(b), somewhat higher Cl_2 peak intensities were observed by application of the magnetic field, and it

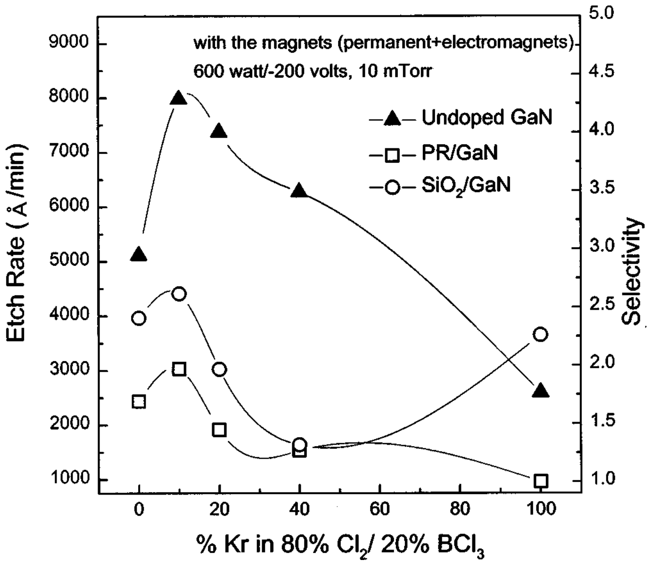

FIG. 4. GaN etch rate and selectivities as a function of Kr addition in the optimized Cl_2/BCl_3 composition of 80% Cl_2/20% BCl_3 with the magnets.

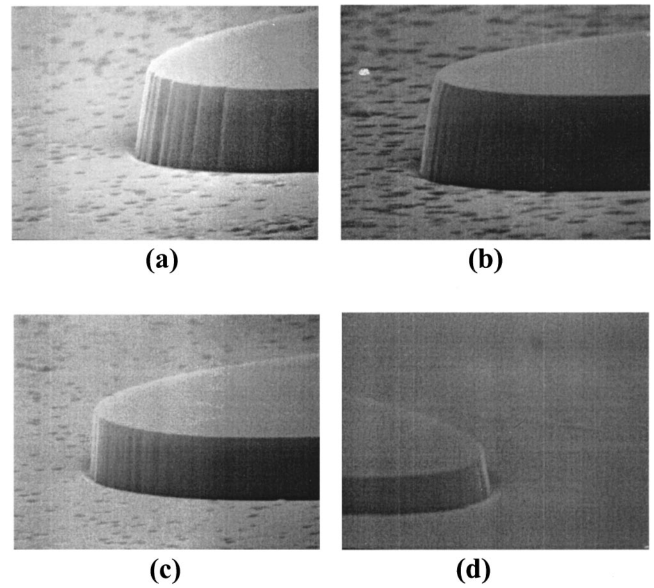

FIG. 5. SEM micrographs of GaN etch profiles; a conventional ICP configuration without the magnetic field (a) and no Kr (b), 10% Kr (c), and pure Kr (d) for a MICP configuration with the magnetic field; 10 mTorr, 80% Cl_2/20% BCl_3 gas combination, 600 W inductive power, −200 V bias voltage, and 70 °C substrate temperature.

might be from the recombination of dissociated Cl radicals. Therefore, some of the dissociated Cl radicals appeared to recombine into Cl_2; only a small increase of Cl radicals resulted.

The increase of BCl_2^+ can increase the GaN etch rate by the increased momentum transfer with the large mass to the substrate at a given dc self-bias condition used in this experiment. The increase of borochloride species in the plasma such as BCl_2^+ and BCl can also decrease the photoresist etch rate by the formation of BCl_xO_y in the plasma by removing oxygen in the plasma. (In our experimental configuration, oxygen originating from the quartz ICP window erosion is present during the operation of inductively coupled plasmas.) The increase of borochloride in the plasma also appears to help in removing oxygen on SiO_2 under sufficient ion bombardment. Therefore, the increase of GaN etch selectivity over the photoresist both with the increase of BCl_3 and with the application of the magnetic field appears to be related to the relative increase of borochloride such as BCl_2^+ and/or BCl. The decrease of the selectivity over SiO_2 both with the increase of BCl_3 (in general, except for the initial high Cl_2^+ and Cl^+ regions compared to BCl_2^+) and with the application of magnetic field also might be partially related to the relative abundance of borochloride in that region.

To investigate the effect of pure ion bombardment on the GaN etch rate, Kr, which has a similar molecular mass to BCl_2^+, was added to the gas composition (80% Cl_2/20% BCl_3), which has the highest GaN etch rate with the magnets. The GaN etch rates and etch selectivities over SiO_2 and the photoresist were then measured, and the results are shown in Fig. 4. The addition of 10% Kr increased the GaN etch rate from 5300 to 8200 Å/min (about a 60% increase), and the selectivities over the photoresist and SiO_2 were also increased. However, the further increase of Kr in 80% Cl_2/20% BCl_3 generally decreased both the GaN etch rates and etch selectivities. Currently, the reason for the increase of the GaN etch rate with the addition of 10% Kr is under study; however, the decrease of the GaN etch rate and the decrease in the etch selectivities of both the photoresist and SiO_2 with the further increase of Kr to the 80% Cl_2/20% B Cl_3 plasma appear to suggest the importance of chemical reactants in addition to the pure physical ion bombardment in the etching of GaN.

The GaN samples masked with patterned SiO_2 were etched using the magnetized inductively coupled plasma equipment with and without the magnets at 80% Cl_2/20% BCl_3 of the gas composition, the other etch parameters were kept the same as before. The results are shown in Fig. 5(a) for the conventional ICP configuration (without the magnets) and in Fig. 5(b) for the MICP configuration (with the magnets). As shown in Fig. 5, a slightly more anisotropic GaN etch profile was obtained by applying the magnets. Also, the effect of Kr addition to the Cl_2/BCl_3 plasma on the GaN etch profile was investigated, and the results are shown in Fig. 5(c) for 10% Kr in 80% Cl_2/20% BCl_3 and in Fig. 5(d) for pure Kr with the magnets, while the other etch parameters were kept the same. If Fig. 5(b) (no Kr addition) and Fig. 5(c) (10% Kr addition) are compared to each other, the addition of 10% Kr appears to produce a more anisotropic etch profile; however, in the case of etching with pure Kr [Fig. 5(d)], a sloped GaN etch profile was obtained with the decreased etch selectivity over SiO_2.

IV. CONCLUSIONS

In this study, the effects of magnetized inductively coupled plasmas on the etch properties of GaN and the characteristics of their plasmas were investigated as a function of Cl_2/BCl_3 and with/without magnetic field. The magnetic-field configuration was composed of both magnetic cusping using permanent magnets and an axial magnetic field using Helmholtz-type axial electromagnets. The characteristics of the plasmas were studied using a quadrupole mass spectrometer and a Langmuir probe. Also, the effects of Kr addition to a magnetized ICP on the GaN etch properties were investigated. The GaN etch profiles were observed using SEM.

The application of the magnetic field generally increased the GaN etch rate and increased the etch selectivity over the photoresist, while decreasing the selectivity over SiO_2. The application of a magnetic field also changed the Cl_2/BCl_3 composition of the maximum GaN etch rate from 10% to 20% BCl_3. When the species in the plasma were measured using the QMS, the significant increase of BCl_2^+ ions was observed with the application of the magnetic field. Using a Langmuir probe, a significant increase of total positive ion current was also measured with the magnets. In addition, the increase of Cl, BCl, and Cl^+ with the decrease of BCl_2 and BCl_3 was observed with QMS by application of the magnetic field. The GaN etch rates appear to be controlled by major species such as Cl_2^+, BCl_2^+, and Cl radicals observed using QMS. The increase of the GaN etch rate by application of the magnetic field appears to be related to the increase of BCl_2^+, which is possibly formed by the increased dissociative ionization of BCl_3. The addition of 10% Kr in the optimized Cl_2/BCl_3 composition of 80% Cl_2/20% BCl_3 with the magnets showed the maximum GaN etch rate of 8200 Å/min and also increased the etch selectivities over the photoresist and SiO_2. However, the further increase of Kr addition decreased the GaN etch rates and the etch selectivities. When GaN etch profiles masked with patterned SiO_2 were observed for the optimized 80% Cl_2/20% BCl_3 gas composition with/without the magnets and with/without Kr addition, more anisotropic etch profiles could be obtained by application of the magnetic field and also by addition of 10% Kr.

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