Etch characteristics of GaN using inductively coupled Cl_2/Ar and Cl_2/BCl_3 plasmas

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In this study, Cl_2/Ar and Cl_2/BCl_3 inductively coupled plasmas were used to etch GaN and the effects of etch parameters such as gas combination and operation pressure on the characteristics of the plasmas and etch properties of GaN were investigated. The characteristics of the plasmas were estimated using a Langmuir probe and optical emission spectroscopy. Surface residue remaining after the etch was investigated using x-ray photoelectron spectroscopy (XPS). The increase of Ar and BCl_3 in Cl_2 generally reduced GaN etch rates except for the small addition of Ar or BCl_3. With the addition of 10% Ar or 10% BCl_3 to Cl_2, the GaN etch rates showed the maximum etch rates. Also, the increase of operational pressure up to 30 mTorr increased the GaN etch rates. By optimizing etch process parameters, etch conditions having smooth and nearly vertical etch profiles with the etch rates close to 8500 A/min and the selectivity over SiO_2 higher than 3.5 could be obtained with Cl_2-rich Cl_2/BCl_3 gas combinations. The change of Cl radical density measured by optical emission spectroscopy as a function of gas combination showed the same trend as the change of GaN etch rates, therefore, chemical reactions between Ga in GaN and Cl from Cl_2 appear to be one of the most important factors controlling the GaN etch rates. Ga/N ratios of the etched GaN surfaces measured by angle resolved XPS were less than 1 for all of the etch conditions used in the experiment. However, when Ar was added to Cl_2, Ga/N ratio increased and, when BCl_3 was added, the Ga/N ratio decreased from that of the GaN surface etched using pure Cl_2. © *1998 American Vacuum Society.* [S0734-2101(98)60703-X]

I. INTRODUCTION

To fabricate GaN-based light emitting diodes and laser diodes, the development of GaN dry etching techniques with high etch rates, high selectively over mask materials, highly anisotropic etch profiles, and smooth sidewalls are required.[1–3] To meet these requirements, dry etching techniques using electron cyclotron resonance (ECR) plasmas, inductively coupled plasmas, and chemically assisted ion beam plasmas have been used with various gas combinations.[4–12] In general, Cl_2-based gases were the main etch chemistries for III–V compound semiconductors including GaN due to the higher volatility of III chlorides compared to other halogen-based or hydrocarbon-based gases.[2,3,12]

In this study, planar inductively coupled Cl_2/Ar and Cl_2/BCl_3 plasmas were used to etch *n*-GaN, and the effects of process parameters such as gas combination and gas pressure on the characteristics of the plasmas and the etch characteristics of GaN were studied. The change of gas chemistry can also induce surface change of the chemistry of the etched GaN. Therefore, the variation in the surface composition of GaN depending on the process parameters were also investigated.

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II. EXPERIMENT

Si-doped *n*-GaN epitaxial layers were grown on (0001) sapphire substrates using metalorganic chemical vapor deposition (MOCVD). The GaN was patterned using a plasma enhanced chemical vapor deposited (PECVD) SiO_2 mask.

The inductively coupled plasmas (ICP) were generated with a 13.56 MHz rf power which was applied to a planar spiral Cu coil separated by a 1-cm-thick quartz window located on the top of the process chamber. A separate 13.56 MHz rf power was also applied to the bottom electrode to generate dc self-bias voltages measured using a high voltage probe (Tektronix P6015A). The GaN was etched using various combinations of Cl_2/BCl_3 and Cl_2/Ar at operational pressures from 10 to 30 mTorr while inductive power, bias voltage, and substrate temperature were fixed at 600 W, −120 V, and 70 °C, respectively. The 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.

A single Langmuir probe inserted in the center of the chamber and biased at −40 V to collect ion currents was used to measure ion current densities of the chlorine-based inductively coupled plasmas as a measure of total positive ion densities. Optical emission spectroscopy [(OES) SC Tech. PCM402] was used to monitor plasma species such as Cl, Cl^+, and BCl and etch byproducts such as Ga, N_2, and $GaCl_x$ in the plasmas during the GaN etching. 2-in. diameter

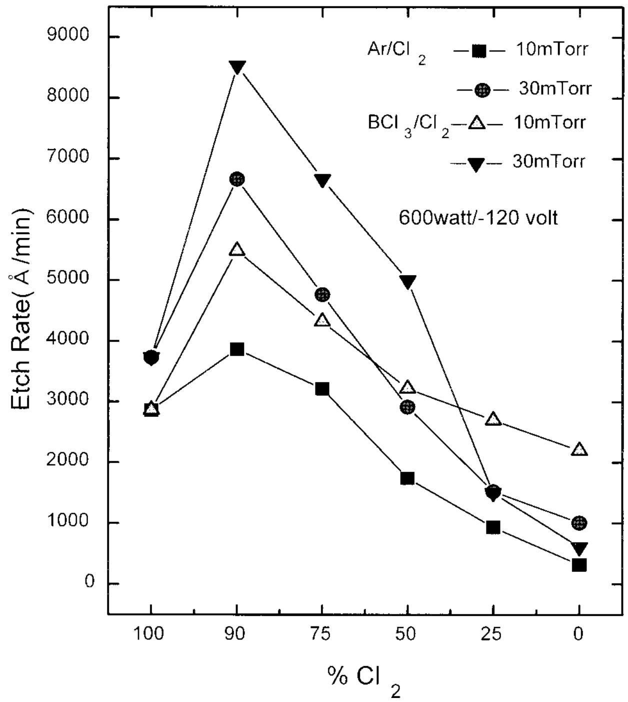

FIG. 1. GaN etch rates as a function of gas combination of Cl_2/Ar and Cl_2/BCl_3 plasmas for the operational pressure of 10 and 30 mTorr at 600 W of inductive power, −120 V of bias voltage, and 70 °C of the substrate temperature.

blank GaN/sapphire wafers were used to enhance the signals of the byproducts. Surface morphology, etch anisotropy, and sidewall undercutting of the etched GaN were evaluated with a scanning electron microscope (SEM). Surface composition of the variously etched GaN was investigated using angle resolved XPS (Fisons Instruments Surface Systems; ESCALAB 220i) after the etching.

III. RESULTS AND DISCUSSION

Figure 1 shows the effects of gas composition of Cl_2/Ar and Cl_2/BCl_3 on the GaN etch rates at 600 W of inductive power, −120 V of dc-self bias voltage, 70 °C of substrate temperature, and operational pressure of 10 and 30 mTorr. The inductive power, bias voltage, and the substrate temperature used in this experiment was chosen from the previous experiment to give optimal process conditions.[6] The increase of inductive power, bias voltage, and substrate temperature generally increased the GaN etch rates while reducing the etch selectivity. As shown in the figure, the increase of Ar percent to 10% increased GaN etch rates to 4000 Å/min at 10 mTorr, however, the further increase of Ar percent in chlorine plasmas reduced the GaN etch rates monotonically. The same trend was observed when the operational pressure was increased to 30 mTorr and the GaN etch rate increased to 6500 Å/min at 10% Ar. The addition of BCl_3 instead of Ar enhanced the GaN etch rates as shown in the figure. Also, the same trend as the Ar addition was obtained, therefore, the highest GaN etch rates were obtained at 10% BCl_3 and the increase of operational pressure to 30 mTorr generally improved the GaN etch rates even though GaN etch rates at 10 mTorr were higher than those at 30 mTorr at the high BCl_3 percentages. At the condition of 10% BCl_3 and 30 mTorr, a GaN etch rate close to 8500 Å/min was obtained. The etch selectivities over SiO_2 were also measured for some of the etch conditions, and the etch selectivity was 3.7 at the condition of 10% BCl_3 and 30 mTorr. The highest etch selectivities were observed at 30 mTorr and were 5.2 for 25% BCl_3 and 4.8 for 25% Ar. In general, the change of additive gas from Ar to BCl_3 increased the etch selectivity.

To understand the effects of the gas combination and the pressure on the GaN etch rates, plasma characterization tools such as a Langmiur probe and optical emission spectroscopy were used and the results are shown in Fig. 2(a) for Cl_2/Ar and Fig. 2(b) for Cl_2/BCl_3 at 30 mTorr. Using the Langmuir probe, ion current densities were measured as an estimation of total positive ion densities in the plasmas and, using optical emission spectroscopy, estimates of Cl radical peak intensity and Cl^+ ion peak intensity were obtained. As shown in Fig. 2(a), the addition of Ar to chlorine increased ion current density, that is, total positive ion density. The increase of Ar also increased Cl^+ ion peak intensity measured by optical emission spectroscopy. (The increase of Cl^+ ion peak intensity with the increase of Ar is not clear, however, the variation of ion densities with gas combinations are currently under investigation with an ion mass spectrometer, and will be published in the near future.) However, the addition of Ar generally decreased chlorine radical density except for the small addition of chlorine near 10% Ar. The addition of 10% Ar to chlorine increased the chlorine radical density. The addition of BCl_3 in Fig. 2(b) also decreased Cl radical density except for the addition of 10% BCl_3 similar to Ar addition. However, the increase of BCl_3 decreased the ion current density and Cl^+ ion density even though Cl^+ ion density measured by the optical emission spectroscope appeared to show a slight increase near 10% BCl_3. A peak corresponding to BCl radical was also observed and increased with the increase of BCl_3. Reducing pressure to 10 mTorr also showed the same trend as that at 30 mTorr, however, the intensities of each species were smaller (not shown).

When the etch results shown in Fig. 1 are compared with the characteristics of the plasmas shown in Fig. 2(a) and 2(b), the increase of GaN etch rates near the 10% Ar and 10% BCl_3 appears to be mostly related to the increase of Cl radical density near 10% of the additives. The increase of total positive ion densities with the increase of the additive gases shown in Fig. 2(a) did not increase the GaN etch rates. Therefore, in our GaN etching, chemical reactions between Cl radical and GaN appears to be one of the most important factors governing GaN etch rates.

Using optical emission spectroscopy, the peaks emitted from etch byproducts were measured and are shown in Fig. 3 for the Cl_2/BCl_3 gas combination. 2-in. diameter blank and 3-μm-thick GaN deposited sapphire wafers were used to enhance the signal intensities during the etching and the etch time used to monitor the optical emission signals was less

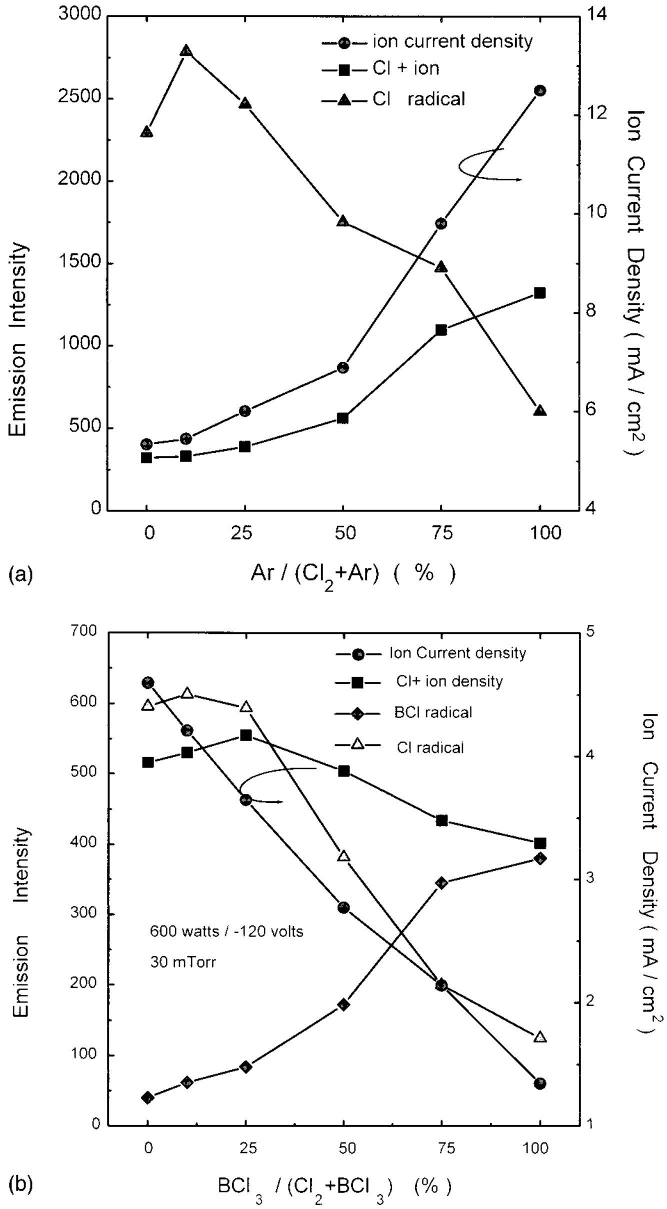

FIG. 2. Ion current density and relative OES signal intensities as a function of gas composition of (a) Cl_2/Ar and (b) Cl_2/BCl_3 at 600 W of inductive power, −120 V of bias voltage, 30 mTorr of operational pressure, and 70 °C of substrate temperature.

than 4 min. Figure 3(a) shows the measured optical emission spectra of the plasmas from 250 to 450 nm for different Cl_2/BCl_3 gas combinations at 30 mTorr. To identify the peaks from the byproducts, an optical emission spectrum from the plasma for 50%Cl_2/50%BCl_3 without loading the GaN wafer was measured and included in the figure, and the identified peaks with GaN wafers were Ga(403 nm), GaCl(337 nm), and N_2(358 nm). Figure 3(b) shows the effects of the gas pressure on the emission intensities from Ga, GaCl, and N_2 at the condition of 90% Cl_2/10% BCl_3, 600 W of inductive power, and −120 V of dc bias voltage. The emission peaks were normalized to the relative peak intensities from pure Cl_2. As shown in the figure, the peak intensities increased with the increase of operational pressure, which is consistent with the increase of Cl radical density and ion density with gas pressure as also shown in Fig. 3(b), and which may imply the increase of both chemical etching effect and physical sputtering effect with the increase of operational pressure. Figure 3(c) shows the effects of gas composition, and also the signal intensities from each species were normalized to those from pure Cl_2, respectively. The intensities showed the maximum values at 10% BCl_3 similar to the trends of GaN etch rates. The maximum emission intensity from GaCl intensity and possibly that from N_2 could also be also understood from the enhanced chemical etching effect between Ga in GaN and Cl from Cl_2 gas due to the maximum Cl radical intensity at 10% BCl_3. The maximum intensity of Ga at 10% BCl_3 was possibly originated not only from the physical sputtering effect, but also from the dissociation of $GaCl_x$ ($x=1,2,3$) emitted from the GaN surface especially for high density plasma conditions, because the ion density measured using a Langmuir probe which is responsible for the physical sputtering effects monotonically with the increase of BCl_3 as shown in Fig. 2(b). Therefore, the increase of the Ga intensity near the 10% BCl_3 may also be related to the increased chemical etching at the etching condition.

Figure 4 shows the effects of gas composition on the etch profiles for 10% Ar and 10% BCl_3 at 30 mTorr. 1-μm-thick SiO_2 mask was used to investigate GaN etch profiles. Figures 4(a) and 4(b) show the etch anisotropy and sidewall etch profile for 10% Ar, and Figs. 4(c) and 4(d) for 10% BCl_3, respectively. Anisotropic etch profiles and smooth sidewall profiles could be obtained for both conditions. In fact, more anisotropic etch profiles close to 90° and smoother sidewall could be obtained with pure Cl_2. The addition of Ar and BCl_3 to 100% generally decreased the etch anisotropy, increased the trenching near the bottom edge possibly due to the ion reflection from the sidewall and enhanced sputtering at the bottom edge by those ions, and rougher sidewall surface (not shown). Rougher sidewall was obtained with the addition of Ar instead of BCl_3 at the same percent of the additive gas. The loss of the anisotropy with the increase of BCl_3 appears to be related to the deposition of sidewall residues possibly consisting of a mixture of low vapor pressure $GaCl_x$ and SiO_x, however, the rougher sidewall surface with the addition of Ar compared to that with the addition of BCl_3 appears to be more related to the enhanced mask erosion.

Angle resolved x-ray photoelectron spectroscopy was carried out to investigate the variation of Ga/N ratio of the etched GaN surface for different gas combinations of Cl_2/BCl_3 and Cl_2/Ar at 30 mTorr, and some of the results are shown in Fig. 5. The lower takeoff angle represents the detection of XPS signals from the shallower position of the etched GaN surface. As a reference, x-ray photoelectron spectroscopic data for the nonetched (control) GaN surface was included. As shown in the figure, all of the GaN surfaces etched in our experimental conditions showed nitrogen-rich surfaces. The addition and increase of Ar to Cl_2 increased the

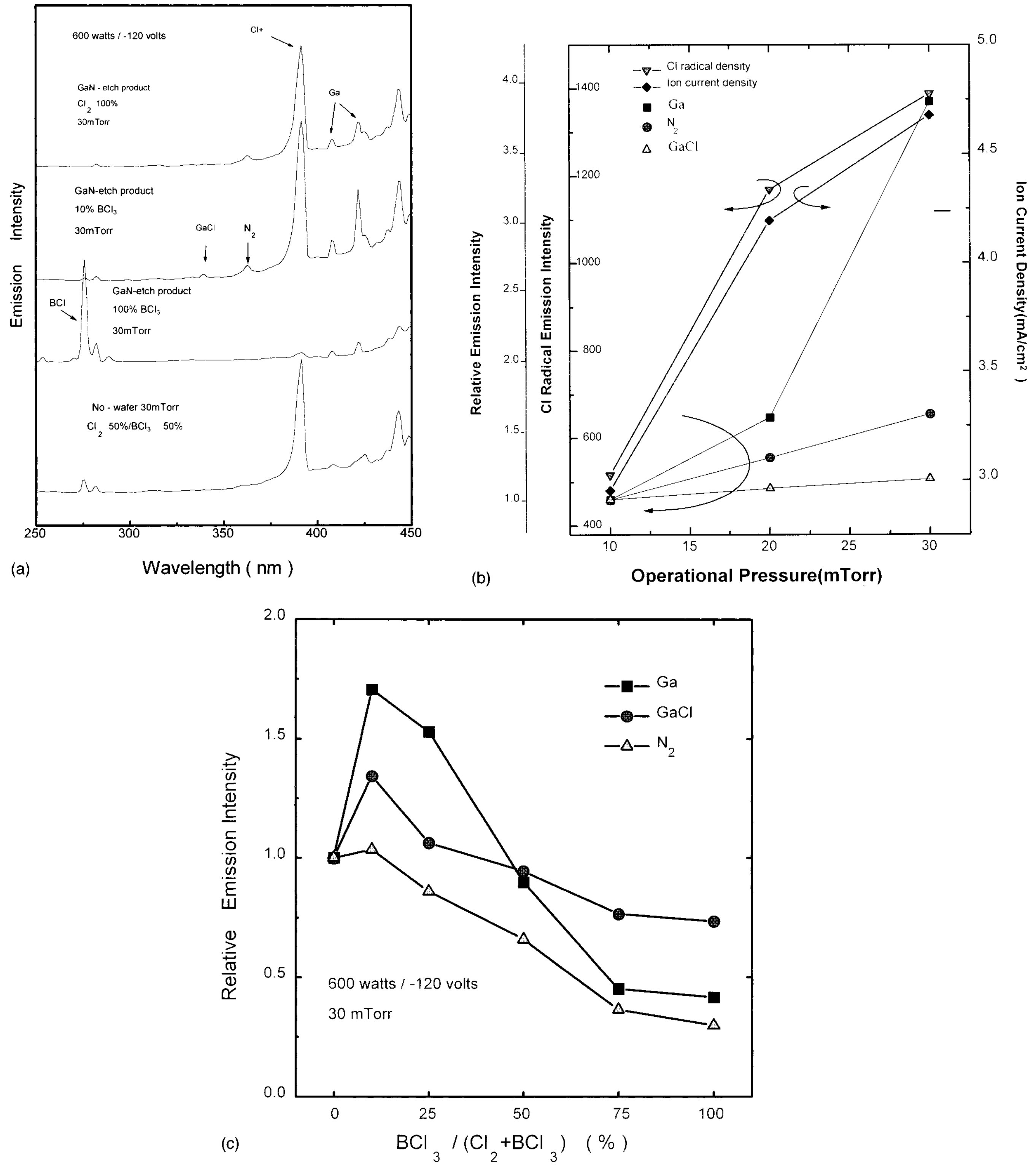

FIG. 3. OES results on GaN etching using Cl_2/BCl_3; (a) OES spectra showing etch byproducts as a function gas composition, (b) the relative emission intensities of byproducts, Cl radical emission intensity, and ion current density as a function of operational pressure, and (c) relative emission intensities as a function of gas composition.

Ga/N ratio of the etched surface toward the stoichiometric Ga/N ratio of 1.0, however, the addition and increase of BCl_3 reduced the Ga/N ratio lower than that etched in pure chlorine. This altered GaN surface could give an impact on the resistance of ohmic contact which will be formed on the etched GaN surface after the etching.

IV. CONCLUSIONS

In this study, the effects of gas addition such as Ar and BCl_3 to Cl_2 and operational pressure on the GaN etch characteristics were investigated using inductively coupled plasma equipment.

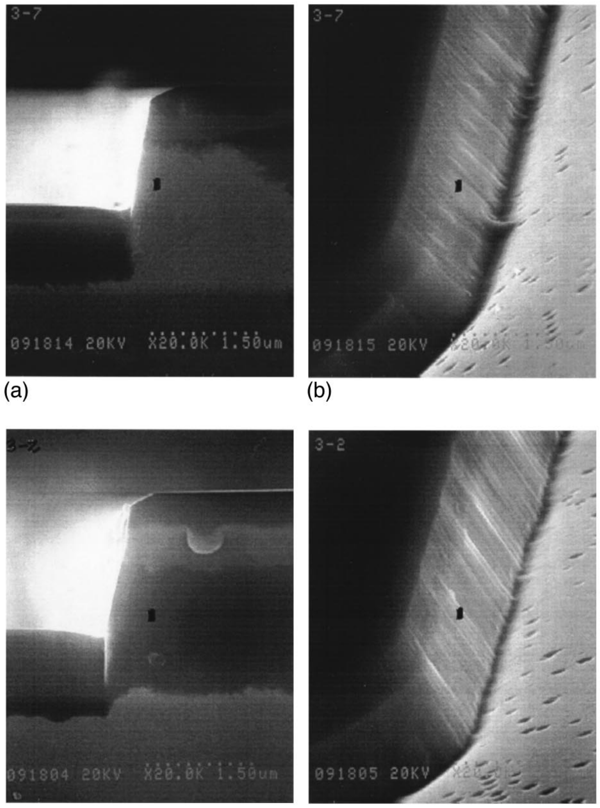

FIG. 4. SEM micrographs of PECVD-SiO_2 masked GaN etch profiles; the etch anisotropy (a) and sidewall roughness (b) for 10% Ar, and the etch anisotropy (c) and sidewall roughness (d) for 10 BCl_3.

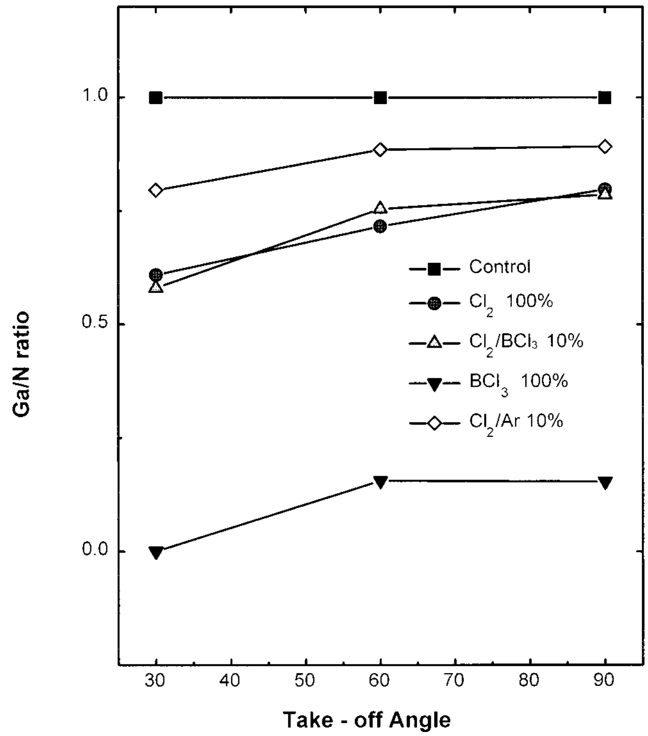

FIG. 5. Ga/N ratios of the etched GaN surfaces for different gas combinations of Cl_2/BCl_3 and Cl_2/Ar measured using angle resolved XPS.

The increase of Ar or BCl_3 in Cl_2 generally reduced GaN etch rates except for the small addition of Ar or BCl_3. With the addition 10% Ar and 10% BCl_3 in Cl_2 at 30 mTorr, the GaN etch rates showed the maximum etch rates of 6500 and 8500 Å/min, respectively. Etch selectivity of 3.7 could be obtained at the highest etch rate condition of 10% BCl_3. The highest etch selectivity was obtained near 25% of additive gases. Etch profiles were less vertical and showed rougher sidewalls with the increase of Ar and BCl_3 possibly due to the deposition of low pressure sidewall residue, however, acceptable etch profiles and smooth sidewalls were obtained with the addition of 10% Ar or 10% BCl_3. The change of Cl radical density as a function of gas combination showed the same trend as that of the GaN etch rate, therefore, chemical reactions between Ga in GaN and Cl from Cl_2 appeared to be one of the most important factors controlling the GaN etch rates. Angle resolved x-ray photoelectron spectroscopy showed that Ga/N ratios were less than 1 for all of the etch conditions used in the experiment. However compared to the Ga/N ratio of the GaN surface etched using pure Cl_2, the addition of Ar to Cl_2 increased the Ga/N ratio and the addition of BCl_3 reduced the Ga/N ratio.

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