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Effects of plasma conditions on the etch properties of AlGaN

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Abstract

In this study, etchings of III-nitrides such as GaN, AlGaN, and InGaN were performed using planar inductively coupled Cl_2/BCl_3 plasmas. Especially, etch properties of $Al_xGa_{1-x}N$ were investigated as a function of inductive power, bias voltage, substrate temperature, and pressure. Etch rates of GaN were higher than those of AlGaN and InGaN regardless of plasma conditions for the Cl_2-rich plasmas. The increase of the Al composition in the AlGaN decreased the etch rate because of higher bond strength between Al and N and Al-oxidation. The enhancement of AlGaN etch rates could be obtained by the addition of BCl_3 to Cl_2 gas and the decrease of the pressure. Plasma diagnostics and surface analysis were performed to understand the etch mechanism of AlGaN. The effective removal of Al from the surface of AlGaN during the etching appears to be important in increasing the AlGaN etch rates.

Keywords: Etching; AlGaN; Laser diode; Inductively coupled plasmas (ICP); QMS; Cl_2/BCl_3

1. Introduction

Generally, diverse chemistries of the group III-nitrides and differences in the physical properties of their compounds make optimization of their etching processes difficult. Optimization is further complicated by the fact that many applications impose their own unique requirements on the etching processes. In the fabrication of GaN-based laser diodes, the mesa sidewalls should be smooth and striation-free, and it is beneficial to design a process to etch through InGaN and AlGaN alloys with a simple etch recipe. Therefore, it is necessary to develop dry etching conditions which can effectively cover the entire composition range of $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ alloys since GaN-based devices are based on the heterostructure with a variety of compositions.

In our previous works, the etch properties of GaN were investigated using Cl_2/BCl_3 plasmas and GaN etch rate close to 850 nm/min was obtained using a 90% Cl_2/10% BCl_3 plasma. The effects of various species in the plasmas on the GaN etch properties could be estimated using quadrupole mass spectrometry (QMS) and optical emission spectroscopy (OES) [1–3]. In this study, to optimize the etch condition of GaN-based LD(laser diode), III-nitride etchings were performed using planar inductively coupled Cl_2/BCl_3 plasmas. Especially, the etch properties of AlGaN, which is the etch rate limiting layer of general optoelectronic device structures, were investigated using the plasma diagnostic tools and surface analysis.

2. Experimental

In this study, a planar inductively coupled plasma (ICP) equipment has been used to etch III-nitrides a function of gas combination of Cl_2/BCl_3, inductive power, bias voltage, substrate temperature, and operational pressure. III-nitrides such as *p*-GaN, *n*-GaN, InGaN, AlGaN, and AlN with 100–1000 nm in thickness were deposited using metal–organic vapor deposition (MOCVD). The blue LD device made of these materials showed a pulse-mode operation in a separate experiment [4]. When these materials were etched, patterned SiO_2 was used as etch mask, and the etch depth was measured using a step profilometer after removing the SiO_2 etch mask.

To investigate the characteristics of the plasmas more closely, the relative amounts of positive ion species and

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neutral species were estimated by quadrupole mass spectrometry (QMS: Hiden Analytical Inc. PSM 500). The mass resolution of the QMS system used in this experiment was 0.01 amu. The details of the ICP equipment and QMS tools used in the experiments are described elsewhere [3]. The total ion current densities and electron densities were measured using an electrostatic probe (Hiden Analytical Inc. ESP). Surface composition on the etched AlGaN were investigated using X-ray Photoelectron Spectroscopy (XPS:ESCA Lab 220I-XL) after the etchings. The inaccuracies of QMS, electrostatic probe, and XPS used in this experiment were about 5, 1, and 0.1%, respectively.

3. Results and discussion

3.1. Etch rates of III-nitrides

Fig. 1 shows the etch rates of *n*-GaN, *p*-GaN, InGaN, and AlGaN as a function of Cl_2/BCl_3 mixtures. The etchings were performed at the condition of 600 W of inductive power, − 120 V of bias voltage, 30 mTorr of operational pressure, and 70°C of substrate temperature. This etch condition used in the study was the highest GaN etch rate condition we obtained from the previous study [1]. As shown in the figure, with the increase of BCl_3 in Cl_2, all of the III-nitrides showed a maximum etch rate in a certain mixture of Cl_2/BCl_3, however, the etch rates of AlGaN and InGaN were lower than those of *n*-GaN and *p*-GaN, in general. The etch rates of *p*-GaN and *n*-GaN were similar each other and showed a maximum at 90% Cl_2/10% BCl_3. In the case of AlGaN, the maximum etch rate was about 500 nm/min at 70%/30% BCl_3, and the further increase of BCl_3 decreased the etch rate, however, the AlGaN etch rate was similar to those of *n*-GaN and *p*-GaN in this region. The maximum etch rate of InGaN showed at 20% of BCl_3, and the etch rates of InGaN were lower than the etch rates of AlGaN, therefore, they showed the lowest etch rates among the III-nitrides investigated.

In the mesa structure of laser diode device, the thickness of InGaN active layer is only a few nm in thickness, therefore, the etch rate of InGaN is relatively unimportant compared to the etch rates of AlGaN which has a few hundred nm in thickness on both sides of InGaN. Therefore, for the etching of the above mesa structure, the etch condition with 70% Cl_2/30% BCl_3 which shows the highest AlGaN etch rate of 500 nm/min and the lowest etch selectivity among the III-nitride layers has been chosen for the next experiment.

To improve the AlGaN etch rates which control the overall etch rate of the mesa structure, AlGaN, AlN, and GaN were etched with 70% Cl_2/30% BCl_3 while varying the inductive power, bias voltage, operational pressure, or the substrate temperature, and the results are shown in Fig. 2. The increase of inductive power (a), bias voltage (b), and substrate temperature (c) increased the etch rates of AlGaN, AlN, and GaN, however, the increase of Al in GaN decreased the etch rate for all of the cases, in general. Etch rates of AlGaN and AlN were decreased with the increase of Al in the film appears to be from the higher binding energy of AlN (11.5 eV) compared to those of GaN (8.9 eV). That is, Al of AlGaN which contains AlN binding could be removed by the formation of highly volatile $AlCl_x$, however, $AlCl_x$ can not be easily formed due to the strong binding energy of AlN. The increase of etch rates of GaN, AlGaN, and AlN with the increase of inductive power and bias voltage appears to be from the increase of reactive ion density and energy respectively similar to the cases of other materials. The increase of etch rates of GaN, AlGaN, and AlN with the increase of substrate temperature appears to be from the increase of removal rates of byproducts such as $GaCl_x$ and $AlCl_x$ formed on the substrate surfaces. The increase of operational pressure (d) generally decreased the AlGaN etch rates except for GaN, where the increase of operational pressure showed a maximum etch rate of GaN at 30 mTorr. By decreasing operational pressure, non-selective etch condition between AlGaN and GaN with the etch rate of about 500 nm/min could be obtained at 15 mTorr as shown in Fig. 2(d). Even selective AlGaN and AlN etching condition over GaN could be also obtained with the further decrease of operational pressure. To investigate the effect of operational pressure on the etch rates of GaN, AlGaN, and AlN more closely, QMS, electrostatic probe, and XPS were employed.

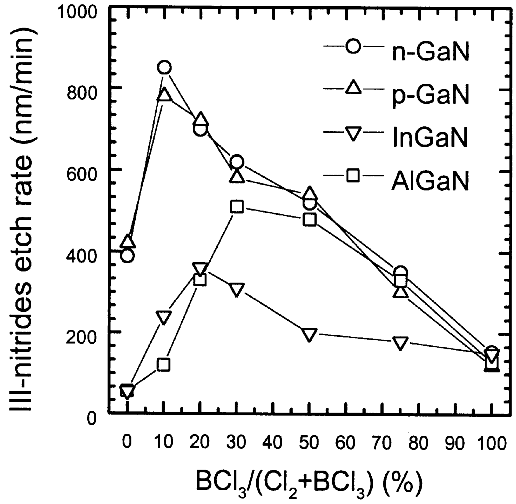

Fig. 1. Etch rates of *p*-GaN, *n*-GaN, AlGaN, and InGaN as a function of gas combination of Cl_2/BCl_3 plasmas at 600 W of inductive power, − 120 V of bias voltage, 30 mTorr of pressure, and 70°C of substrate temperature.

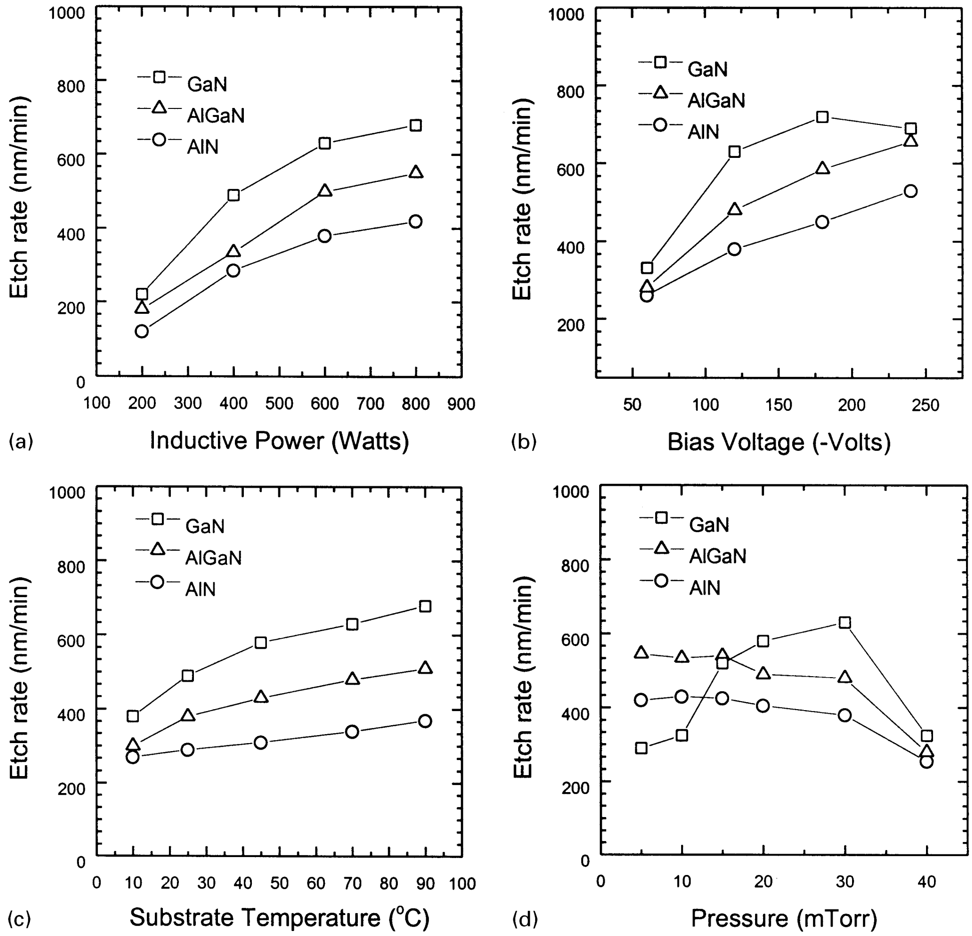

Fig. 2. Etch rates of GaN, AlGaN, and AlN as a function of (a) inductive power, (b) bias voltage, (c) substrate temperature, and (d) pressure for 70% Cl_2/30% BCl_3 plasmas at the same conditions shown in Fig. 1.

3.2. Plasma diagnostics

Fig. 3(a) and (b) shows the radical and reactive ion intensities measured as a function of operational pressure using QMS for the condition shown in Fig. 2(d). Higher radical intensity measured using QMS does not necessarily show the higher radical density in the plasma because ionization and dissociation cross-sections of the species detected by QMS are different each other. However, using a technique described elsewhere [3], the radical densities from the detected QMS output intensities could be estimated, and the results showed that Cl is the main radical in the plasma similar to the QMS output intensity, and it increased with the increase of operational pressure. The rest of radical species such as BCl_x ($x = 1, 2, 3$) also increased with the increase of pressure even though their radical densities were lower for the more highly dissociated BCl_x (lower x). In the case of reactive ion intensities, the detected output intensities are proportional to ion densities and no corrections are needed. As shown in the figure, the main ion species in the plasma were Cl_2^+ and BCl_2^+, and these species showed a maximum at 30 mTorr of operational pressure similar to the etch rates of GaN as a function of operational pressure shown in Fig. 2(d).

Ion current densities were measured using the electrostatic probe as a measure of total ion densities in the plasma for pure Cl_2, pure BCl_3, and 70% Cl_2/30% BCl_3 mixture and the results are shown in Fig. 3(c). The ion current densities also showed a maximum at 30 mTorr of pressure similar to the GaN etch rates as a function of operational pressure. Therefore, the amounts of reactive species in the plasmas as a function of pressure appear to be related to the GaN etch rates. However, the change of reactive ion densities or radical densities as a function of pressure appears not to be directly related to the etch rates of AlGaN and AlN.

3.3. XPS analysis

Fig. 4(a) and (b) shows the surface composition of AlGaN etched as a function of Cl_2/BCl_3 mixture and

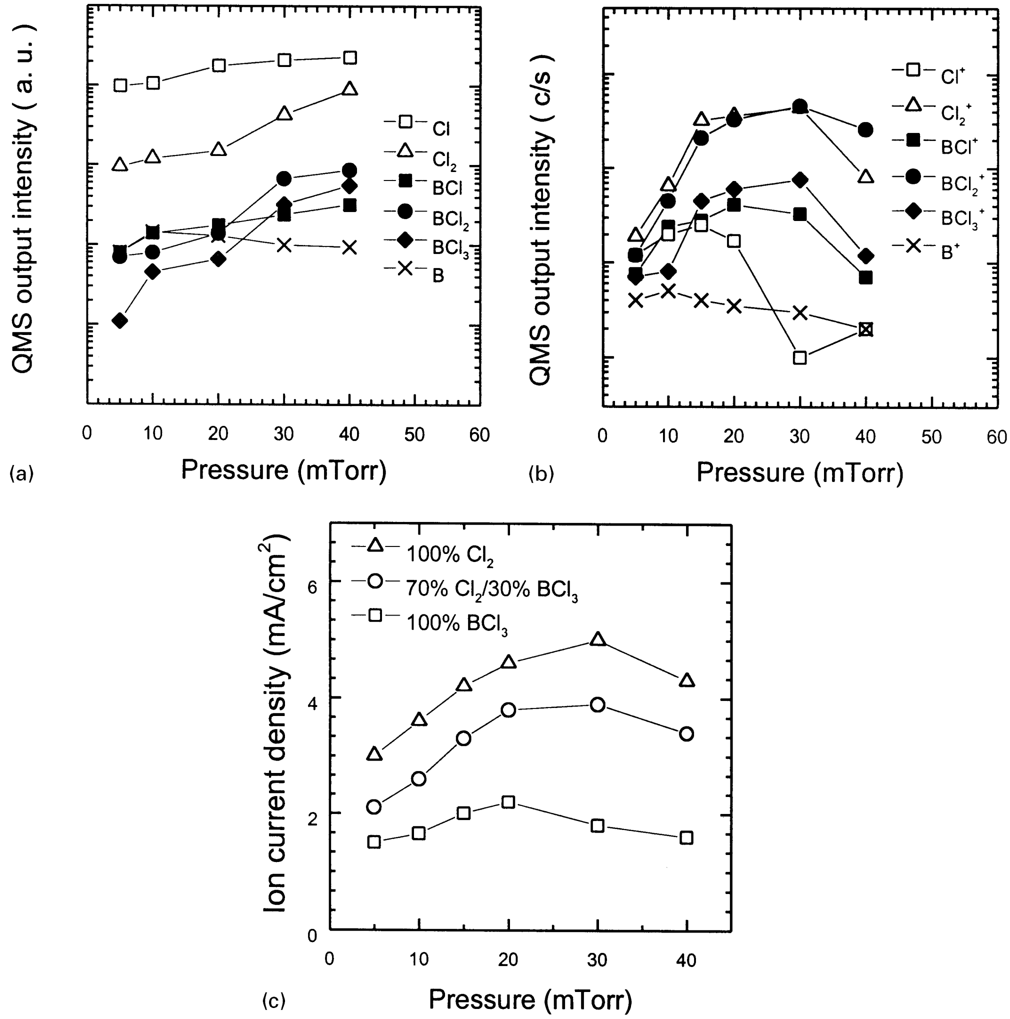

Fig. 3. QMS output intensities of (a) neutral species and (b) positive ion species as a function of pressure for 70% Cl_2/30% BCl_3 plasmas and (c) ion current densities as a function of pressure at 600 Watts of inductive power, $-$ 120 V of bias voltage, and 70°C of substrate temperature.

operational pressure, respectively. The surface composition was measured by XPS. Al, Ga, N, and O were detected on the etched AlGaN and the surface composition of non-etched AlGaN was also measured as a reference and the ratio of Ga : Al : N : O was 36.0 : 10.7 : 46.7 : 6.6. As shown in Fig. 4(a), when AlGaN was etched using pure Cl_2, O and Al contents on the etched AlGaN surface were increased while Ga was decreased. The increase of oxygen was about 8% and the relative increase of Al/(Al + Ga) was 5% (from 23 to 28%). Therefore, from the above XPS data, it turns out that removing Al is relatively more difficult compared to removing Ga when pure Cl_2 is used to etch AlGaN. This difficulty in removing Al appears to be from the stronger binding energy related to AlN compared to GaN and is also possibly from the formation of aluminum oxide. The oxygen which is responsible for the formation of aluminum oxide appears to be from the erosion of quartz window [5] and the erosion of SiO_2 etch mask used in our experiment during the operation of planar inductively coupled plasmas. The addition of BCl_3 in Cl_2 decreased oxygen content on the etched AlGaN surface and also decreased the ratio of Al/(Al + Ga) as shown in Fig. 4(a). In addition, the decrease of operational pressure also decreased oxygen content and Al relative amount on the etch surface as shown in Fig. 4(b). The decrease of oxygen on the etched AlGaN with the increase of BCl_3 can be explained by the formation of $B_xCl_yO_z$ in the plasma as explained by other researchers [6,7]. The lower oxygen content on the surface at lower pressures is cannot fully understood, however, it could be related to the decrease in the redeposition of eroded SiO_2 etch mask.

If the results from Fig. 1 and Fig. 2(d) are compared with the data in Fig. 4(a) and (b), respectively, it can be concluded that the etch rates are related to the remaining oxygen on the etched AlGaN surface. Therefore, the etch rates of AlGaN in our experimental conditions are

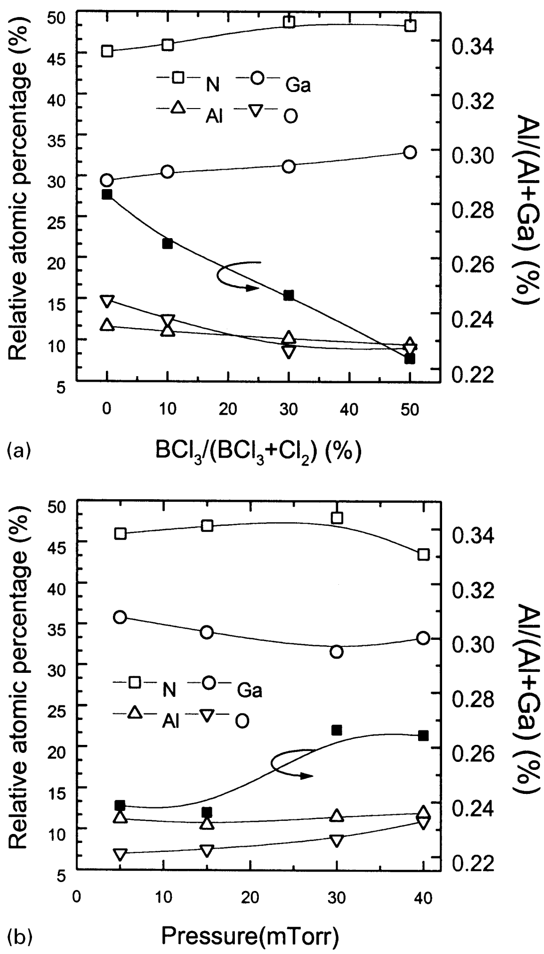

Fig. 4. Composition and Al/(Al + Ga) percentage of the etched AlGaN surface as functions of (a) gas combination of Cl_2/BCl_3 plasmas at 30 mTorr of pressure and (b) operational pressure for 70% Cl_2/30% BCl_3 plasmas. Other etch conditions are same as shown in Fig. 3.

appeared to be strongly related to the removal of AlO_x on the etched AlGaN surface rather than the abundance of specific radicals and ions in the plasmas. Etchant and ion species cannot easily react with the AlO_x on the AlGaN surface from the chemical stability and higher bonding strength.

4. Conclusions

In this study, III-nitrides such as *p*-GaN, *n*-GaN, InGaN, AlGaN, and AlN were etched using Cl_2/BCl_3 plasmas and their characteristics of plasmas and surface compositions were investigated to optimize etching conditions for the formation of a mesa structure of GaN laser diode. The etch rates of AlGaN and InGaN were lower than those of GaN and the etch rates of *p*-GaN were similar to those of *n*-GaN. The increase of Al in AlGaN decreased the AlGaN etch rates. The etch rates of AlGaN increased with the increase of BCl_3 in Cl_2 and with the decrease of pressure. The etch rates of AlGaN were related to oxygen on the etched surface. The effective removal of Al from the surface of AlGaN during the etching appears to be important in increasing the rtch rates of AlGaN and AlN. Finally, by optimizing Cl_2/BCl_3 mixtures and pressures, a reasonable etch condition which has high etch rates for both AlGaN and GaN could be obtained.

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