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Etch Properties of Gallium Nitride Using Chemically Assisted Ion Beam Etching (CAIBE)

Weon-Jeong LEE, Hyeon-Soo KIM, Jae-Won LEE[1], Tae-Il KIM[1] and Geun-Young YEOM
Department of Materials Engineering, Sungkyunkwan University, Suwon, Kyunggi-do, 440-746, Korea
[1]*Photonics Semiconductor Lab. Samsung Advanced Institute of Technology, Suwon, Kyunggi-do, 440-660, Korea*

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Dry etching properties of GaN were investigated using chemically assisted ion beam etching (CAIBE) with Cl_2, BCl_3, and HCl gases. The measured GaN etch rate with increasing tilt angle showed the maximum at a 30° tilt angle, similar to the effect of tilt angle on sputter yield. The GaN etch rate was the highest with Cl_2 and the lowest with BCl_3. In the case of GaN etching with BCl_3, the GaN etch rate was even lower than that in the case of GaN etched with Ar ion source only. The lower etch rate appears to be related to the higher binding energy of BCl_3 and high degree of condensation on the substrate maintained at 0°C. A highly anisotropic etch profile with smooth sidewalls could be obtained with Cl_2. The addition of Cl_2 to BCl_3 did not improve GaN etch profile. The lowest roughness value of about 10 Å was obtained for the etching with Cl_2. The GaN surface etched by Cl_2 and BCl_3 showed an N-rich surface possibly due to the removal of Ga preferentially by forming $GaCl_x$, and GaN surface etched by HCl showed near-stoichiometric surface possibly due to the removal of Ga by forming $GaCl_x$ and N by forming NH_x.

KEYWORDS: GaN, CAIBE, XPS, AFM, etch rate, etch profile, selectivity, gas-flow rate

1. Introduction

III–V nitride materials such as gallium nitride (GaN) have a wide band gap, chemical inertness, and high temperature stability. Therefore, GaN can be used for the fabrication of wide band gap semiconductors including blue and ultraviolet (UV) optoelectronic devices. However, the hexagonal structure of GaN prevents conventional cleaving of mirror facets required in the solid-state laser devices. To make mesa structures or laser facets, dry etching techniques such as reactive ion etching (RIE),1) reactive ion beam etching (RIBE),2,3) chemically assisted ion beam etching (CAIBE),4,5) high-density plasma etching such as inductively coupled plasma (ICP)6,7) and electron cyclotron resonance (ECR) plasma8) etching are required. It is not possible to form anisotropic sidewalls and deep etched structures by wet etching9,10) due to the chemical inertness of GaN, low etch rate, and the isotropic etch characteristics of wet etching. Therefore, dry etching processes are important for well-controlled pattern definition. For the fabrication of GaN laser facets for optoelectronic devices, a high etch rate, high selectivity over mask layers, and a vertical etch profile with smooth sidewalls are necessary. CAIBE is a technique in which the physical and chemical etching components are controlled independently. By varying the ion beam energy and current, chemically resistant layers can be etched physically by sputtering effects and the reactive gas causes the formed volatile products to be removed from the substrate surface. The CAIBE system has been applied to obtain a high etch rate and vertical profile in various materials such as GaAs and InP.11,12)

CAIBE is also suitable for obtaining a vertical profile with smooth sidewalls for mirror facets. Currently, a few studies are reported on GaN etching using CAIBE, which studies used only a 0° tilt angle and hard masks such as SiO_2 or Ni/SiO_2 to prevent the loss of mask layers.4,5,13) If a conventional photoresist can be used as a GaN etch mask, the process steps in masking optoelectronic devices can be reduced and the throughput can be increased. Therefore, in this study, the effects of tilt angle and gas chemistry on the GaN etch characteristics were investigated using a conventional photoresist.

2. Experiment

GaN samples used in the experiment were grown by metalorganic chemical vapor deposition (MOCVD) on sapphire substrates. GaN samples were masked and patterned using a conventional photoresist (PR Shipley 1400-37) or SiO_2. GaN etching was performed using a chemically assisted ion beam etching system having a 210-mm-diameter ion beam etch source, a Meissner trap, and a load-lock chamber. As the ion beam etch source, a filamentless radio frequency inductively coupled plasma (rf-ICP) ion source with 3 optically aligned Mo grids was used. A plasma bridge neutralizer used to ignite the rf-ICP source was also used to avoid positive charge buildup on the substrate and to prevent beam spreading. The current and voltage of the ion beam etch source used in the experiment were fixed at 300 mA and 500 V, respectively. 6 sccm of Ar was introduced into the ion source while reactive gases were distributed around the substrate through the nozzle. Reactive gases used in this experiment were Cl_2, BCl_3, HCl, and their mixtures, and their gas-flow rates were in the range of 1 sccm to 8 sccm. The substrate was kept at 0°C or room temperature while rotating the samples. The substrate was tilted from 0° to 60°. The tilt angle was measured between the surface normal of the the substrate and the axis of the ion beam. Etch depths were determined from the Dektak profilometer measurement. Etch profiles were observed by scanning electron microscopy (SEM). Surface composition and roughness of etched GaN samples were investigated using X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM), respectively.

3. Results and Discussion

Effects of ion beam energy and current on the GaN etch rates for the CAIBE system have been reported by other researchers.4,5) These studies show that GaN etch rates increase with the increase in ion beam energy and ion beam current. In our study, the effects of ion beam energy and ion beam current were also studied and we obtained similar results. Also, in our study, the effects of tilt angle on the etch rate, etch selectivity over PR, and etch profile were investigated. Figure 1 shows the effects of the substrate tilt angle on the GaN etch rate and etch selectivity. The tilt angle was varied from 0° to 60° and

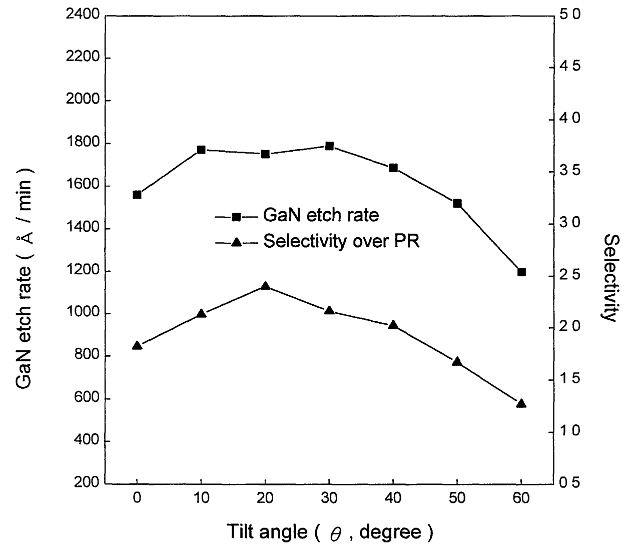

Fig. 1. The angular dependency of GaN etch rate and etch selectivity over photoresist for Cl_2 flow rate of 6 sccm. The angle was measured between the surface normal of the substrate and the axis of the ion beam. Ar Ion beam voltage and current were 500 V and 300 mA, respectively, and the substrate temperature was fixed at 20°C.

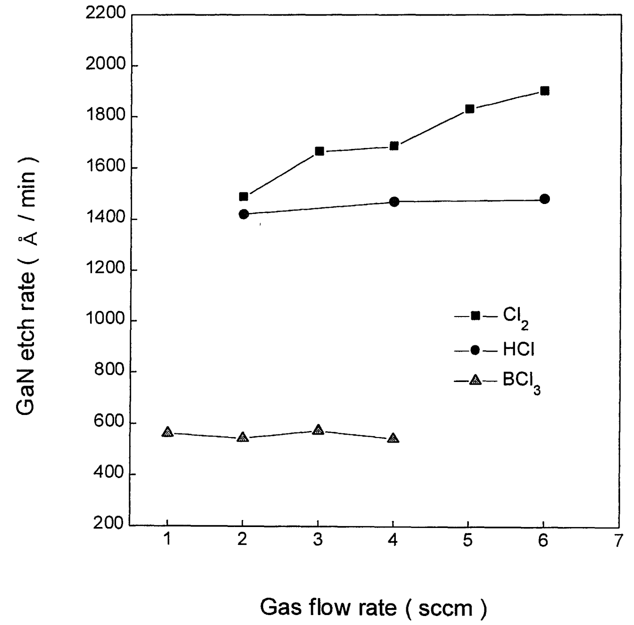

Fig. 2. GaN etch rates as a function of gas-flow rate for Ar ion beam voltage/current 500 V/300 mA, tilt angle 30°, and substrate temperature 0°C.

6 sccm of Cl_2 was fed to the gas nozzle in addition to 6 sccm of Ar to the ion beam source. The ion beam energy and current were fixed at 500 V and 300 mA, respectively. As shown in the figure, as the tilt angle was increased to near 30°, the GaN etch rate increased to the maximum value of 1800 Å/min and a further increase in the tilt angle decreased the GaN etch rate. The dependence of GaN etch rate on tilt angle was similar to the dependence of the sputter yield on the tilt angle. GaN etch selectivity over PR also showed a maximum value of 2.5 near 20°. The effect of tilt angle on the etch profile was also investigated (not shown), and the result showed that, from 0° to 20°, the GaN etch profile showed sidewall trenching due to the enhanced ion etching of the sidewall bottom area by the scattered ions at the sidewall. When the tilt angle was greater than 45°, the etch selectivity decreased due to the increase in mask erosion and an etch tail developed near the GaN-etched structure possibly due to the shadowing effect and sidewall redeposition of the etched materials. These effects of tilt angle on the etch rates and etch profiles were also reported by other researchers for ion beam etching and reactive ion beam etching.[14] On comparing our results with theirs, the effects of tilt angle appear to be related more to the physical sputtering effect than to the chemical etching effect. Therefore, a 30° tilt angle was chosen for other experimental conditions in our study.

By fixing the tilt angle at 30°, gas-flow rates and the effects of various reactive gases in addition to Ar, on the GaN etch rates were investigated and are shown in Fig. 2. The substrate temperature was maintained at 0°C. As reactive gases, chlorine-containing gases such as Cl_2, HCl, and BCl_3 were used. To maintain the chamber pressure in the range of 10^{-4} Torr, gas flow rates varing from 1 sccm to 4 sccm for BCl_3, and 2 sccm to 6 sccm for Cl_2 and HCl were used. As shown in Fig. 2 different reactive gases showed different GaN etch rates. Cl_2 showed the highest GaN etch rate and BCl_3 showed the lowest etch rate. An increase in Cl_2 flow rate increased GaN etch rates from 1500 Å/min to 2000 Å/min, however, no dependence of gas-flow rate on GaN etch rate was seen for HCl and BCl_3. The GaN etch rates for HCl were about 1400 Å/min and those for BCl_3 were about 600 Å/min. When no reactive gas was used, and therefore, when the Ar ion milling condition was used, a GaN etch rate of 1200 Å/min was obtained. Therefore, in the case of BCl_3, the addition of the reactive gas suppressed the GaN etch rates more than the GaN sputtering rate by Ar. The enhancement of the GaN etch rate due to the introduction of a reactive gas should be accompanied by the dissociation of the reactive gas, the formation of etch products such as $GaCl_x$ on the GaN surface, and the vaporization of these products from the surface. In the case of BCl_3, the dissociation of BCl_3 is difficult due to the high binding energy of B–Cl (536 KJ/mole at 298 K) compared to dissociation of other gases such as Cl_2 (Cl–Cl 242.58 KJ/mole at 298 K) and HCl (431.62 KJ/mole at 298 K).[15] In addition, BCl_3 has the lowest and Cl_2 has the highest vapor pressure among these gases. Therefore, BCl_3 dissociation is difficult and it easily condenses on the cold surface. The suppression of the GaN etch rate using BCl_3 may be related to the insufficient dissociation of BCl_3 and condensation of BCl_3 on the GaN wafer, because the substrate was maintained at 0°C in order to use the photoresist as an etch mask, which shields GaN from the sputtering. A similar argument could be applied to HCl, however, HCl is more easily dissociated and condensed to a lesser degree on the wafer compared to BCl_3, therefore, only a slightly higher GaN etch rate than the Ar ion milling rate may be obtained. The lack of dependence on the BCl_3 and HCl flow rates may be related to the saturation of condensation at the substrate temperature and gas-flow rate used in the experiment. A higher GaN etch rate and an increase in the GaN etch rate with the increase in the reactive gas flow rate for Cl_2 appear to be due to not only the easier dissociation of Cl_2 and absence of condensation on the substrate but also due to the easier vaporization of the formed $GaCl_x$ by Ar ion bombardment at the substrate temperature.[4,6,7]

Figure 3 shows the effects of various gases on the GaN etch profile. Figure 3(a) shows the GaN etch profile for only a supply of 6 sccm Ar to the ion beam source without supplying any reactive gas to the gas nozzle and (b) for 6 sccm Cl_2, (c) for 4 sccm BCl_3, and (d) for 4 sccm HCl supplied to the gas nozzle in addition to 6 sccm Ar to the ion source. The substrate temperature was maintained at 0°C, tilt angle at 30°, and ion beam voltage/current at 500 V/300 mA. The GaN etch profile with Ar ion milling reveals a more positively sloped etch profile showing the effect of mask erosion due to physical sputtering. Near the sidewall bottom of etched GaN, an etch tail is also observed possibly due to the reason described above. In the case of the GaN etch profile for BCl_3 and HCl, the etched sidewall was rough and an etch tail similar to that in the case of Ar milling was observed. The etch tail was very rough and this rough surface was confined near the GaN etched structure. A similar rough etch tail was observed when an oxide etch mask was used instead of the PR mask, however, no such rough surface was observed when blank GaN was etched. When the substrate temperature was increased, the etch tail and roughness were significantly reduced. Therefore, this roughness may be related to the micromasking of condensed BCl_x (or HCl) due to shadowing effect or $GaCl_x$ redeposited from the sidewall during the etching. The best etch profile was obtained for Cl_2, in which case a smoother etch profile with a smaller a etch tail was obtained as compared to other gas conditions.

To study the effects of a gas mixture, the GaN etch rate and etch selectivity over PR were investigated using gas mixtures of Cl_2 and BCl_3 and are shown in Fig. 4. The total reactive gas flow in addition to 6 sccm of Ar was maintained at 4 sccm and the rest of the etch parameters were kept the same as the conditions in Fig. 2. As shown in Fig. 4, the Cl_2 percentage in BCl_3 increased up to 50%, and a further increase in the Cl_2 percentage saturated the GaN etch rate or decreased the GaN etch rate slightly. The etch selectivity over PR was also the highest at 50% Cl_2. The maximum etch rate for 50% Cl_2 and no further increase in GaN etch rate with the increase of Cl_2 percentage are possibly due to the saturation of $GaCl_x$ formation on the GaN surface because the maximum etch rate (1800 Å/min) at 50% Cl_2 (Cl_2 = 2 sccm) is higher than the GaN etch rate (1400 Å/min) at 2 sccm 100% Cl_2 in Fig. 2 and is close to the etch rate (1900 Å/min) for 6 sccm of 100% Cl_2. Therefore, Cl radicals required to form $GaCl_x$ may have been

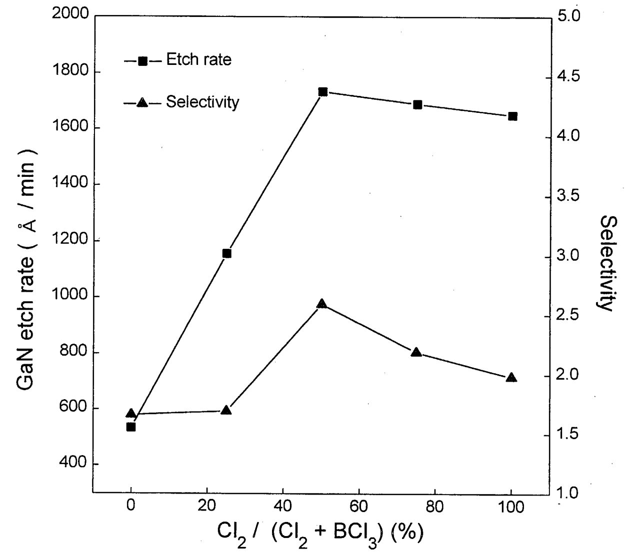

Fig. 4. GaN etch rates and selectivities as a function of Cl_2/BCl_3 ratio for Ar ion beam voltage/current 500 V/300 mA, tilt angle 30°, and substrate temperature 0°C.

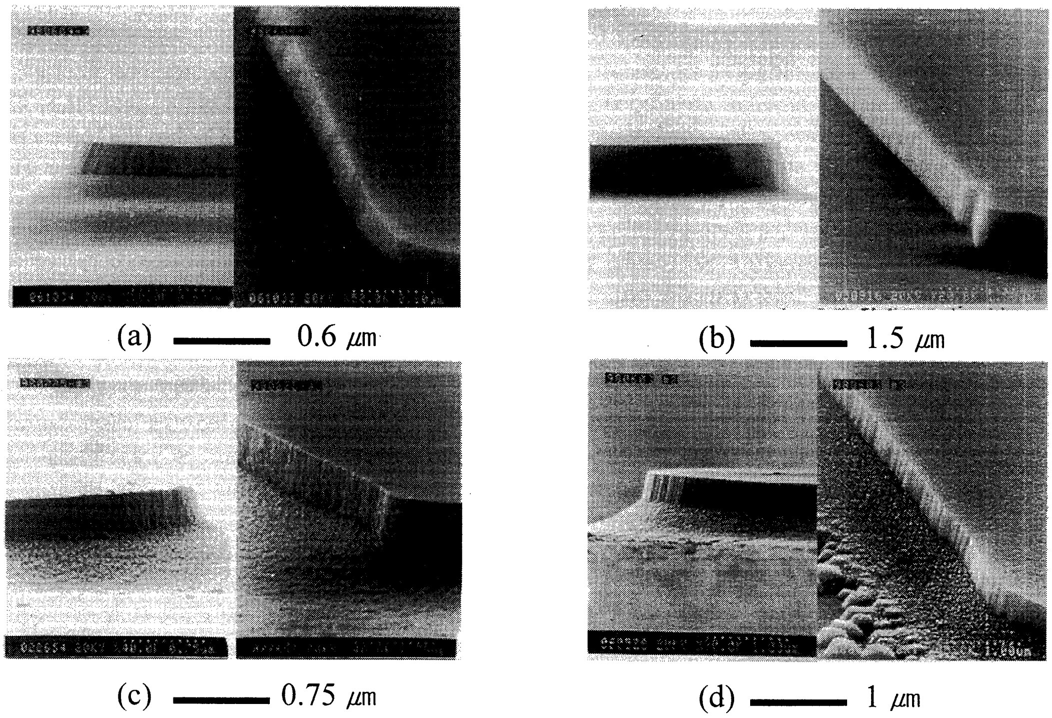

Fig. 3. GaN etch profiles etched with Ar ion beam condition 500 V/300 mA, tilt angle 30°, and substrate temperature 0°C; (a) Ar ion milling, (b) Cl_2 flow rate 6 sccm (c) BCl_3 flow rate 4 sccm, and (d) HCl flow rate 8 sccm.

Table I. The Ga/N ratio by XPS analysis and average roughness by AFM of the etched GaN surface with ion beam voltage/current 500 V/300 mA, tilt angle 30°, and substrate temperature 0 °C.

	Ga/N ratio	RMS roughness (Å)
Control	1.00	5.6
Cl_2 6 sccm	0.80	14.3
BCl_3 4 sccm	0.96	50.0
HCl 8 sccm	1.01	20.2

sufficiently dissociated from Cl_2 and BCl_3 to saturate the GaN surface even though the data is not conclusive. Etch profiles for those gas mixtures were also investigated (not shown). A rough etch tail was observed whenever BCl_3 was included in the gas mixture, however, the roughness and size of the etch tail decreased with the increase of Cl_2 percentage in the gas mixture.

Using XPS and AFM, the effects of different reactive gases on the surface stoichiometry and surface roughness of etched GaN were investigated and are shown in Table I. Blank GaN wafers were used instead of patterned GaN wafers. The Ga/N ratio of nonetched GaN was 1.0 and the average roughness was 5.6 Å. The average roughness of GaN etched with BCl_3 was the highest (50 Å) and that with Cl_2 was the lowest (14.3 Å) even though it is higher than the control (nonetched GaN wafer). The degree of roughness for different reactive gases was related to the GaN etch rate, therefore, the lower the etch rate, the higher the roughness. Therefore, the roughness of the GaN etched surface obtained in our experiment appears to be related to the micromasking by condensed and redeposited species such as BCl_x, HCl, and $GaCl_x$ on the GaN surface. Ga/N of etched GaN was also varied depending on the reactive gas used in the experiment. In the case of GaN etched with Cl_2 and BCl_3, nitrogen-rich GaN was obtained and more nitrogen-rich GaN was obtained for Cl_2. However, in the case of GaN etched with HCl, near-stoichiometric GaN was obtained. Nitrogen-rich GaN for Cl_2 and BCl_3 is believed to be due to the removal of Ga preferentially by forming $GaCl_x$ from the GaN surface. Stoichiometric GaN for HCl is believed to be due to the removal of Ga by forming $GaCl_x$ and that of N by forming NH_x.[6] However, whether $GaCl_x$ and NH_x are formed during the etching is not currently conclusive, and requires more detailed investigation.

4. Conclusions

In this study, GaN was etched using a CAIBE system and the effects of tilt angle and reactive gas species on the GaN etch properties such as etch rate, etch selectivity, and etch profile were investigated. Also, the effects of gas chemistry on the etched GaN surface roughness and GaN surface stoichiometry were investigated. A conventional photoresist was used as an etch mask, therefore, the substrate temperature was maintained lower than room temperature.

When GaN etching was performed with Cl_2 by tilting the substrate, the maximum GaN etch rate was observed near a 30° tilt angle and the etching trend was similar to the effect of tilt angle on the sputter yield. Tilting the substrate lower than 20° resulted in trenching and higher than 45° resulted in etch tailing. By maintaining the tilt angle at 30°, the effects of reactive gases such as Cl_2, BCl_3, and HCl on the GaN etch rate and etch profile were investigated and the highest etch rate was obtained in the case of Cl_2. The GaN etch rate with BCl_3 was even lower than that etched with Ar ions only, and only slightly higher with HCl. The lower etch rates for BCl_3 and HCl compared to Cl_2 appear to be due to the difficulty in dissociation of molecules and the condensation of BCl_x and HCl on the substrate maintained at 0°C. The etch profile etched with a 30° tilt angle and substrate temperature of 0°C showed an etch tail and roughness possibly related to the shadowing effect and micromasking by the condensation of gas species, in addition to the redeposition of etch byproducts, respectively. A mixture of reactive gases did not improve the GaN etch profile. The best etch profile with high anisotropy, minimum etch tail, and low roughness was obtained with Cl_2.

The Ga/N ratio of the etched GaN surface was believed to be related to the degree of formation of volatile $GaCl_x$ and NH_x. Therefore, nitrogen-rich GaN was obtained with Cl_2 and BCl_3 and near stoichiometric GaN was obtained with HCl. The surface roughness of etched GaN appeared to be related to the degree of the condensation of gas species and the redeposition of etch byproducts on the substrate. The lowest roughness was obtained with Cl_2. Therefore, using a CAIBE system, an optimized GaN etch process using PR as the etch mask could be obtained with Cl_2, by keeping the tilt angle at 30° and maintaining the substrate temperature at 0°C, even though GaN surface stoichiometry was not maintained. The addition of hydrogen to Cl_2 may improve the surface stoichiometry of etched GaN.

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