

PLASMA CHEMISTRY DEPENDENT ECR ETCHING OF GaN

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ABSTRACT

Electron cyclotron resonance (ECR) etching of GaN in Cl₂/H₂/Ar, Cl₂/SF₆/Ar, BCl₃/H₂/Ar and BCl₃/SF₆/Ar plasmas is reported as a function of percent H₂ and SF₆. GaN etch rates were found to be 2 to 3 times greater in Cl₂/H₂/Ar discharges than in BCl₃/H₂/Ar discharges independent of the H₂ concentration. In both discharges, the etch rates decreased as the H₂ concentration increased above 10%. When SF₆ was substituted for H₂, the GaN etch rates in BCl₃-based plasmas were greater than those for the Cl₂-based discharges as the SF₆ concentration increased. GaN etch rates were greater in Cl₂/H₂/Ar discharges as compared to Cl₂/SF₆/Ar discharges whereas the opposite trend was observed for BCl₃-based discharges. Variations in surface morphology and near-surface stoichiometry due to plasma chemistries were also investigated using atomic force microscopy and Auger spectroscopy, respectively.

INTRODUCTION

Wide band-gap group-III nitrides continue to attract interest as blue and ultraviolet emitters and detectors, high temperature electronics, and passivation layers¹⁻⁵. Recent advances in the growth of GaN films have resulted in device demonstrations of GaN light emitting diodes (LEDs)^{6,7} and metal semiconducting field effect transistors (MESFETs)^{5,8}. Although progress has also been reported in dry patterning these materials, rapid development of material growth and advanced device structures including lasers and heterojunction bipolar transistors (HBTs) has increased the need for anisotropic, smooth, high-rate etching. A variety of plasma etch chemistries have been reported in a reactive ion etch (RIE) system using chlorine-^{10,11} and bromine-¹² based plasma chemistries. Etch rates for GaN up to approximately 650 Å/min have been reported at dc biases of -400 V. Significantly higher etch rates have been reported in electron cyclotron resonance (ECR) etch systems where the plasma is confined by a magnetic field to provide a high density plasma at low pressure and low ion energies. Most ECR etching of GaN has been performed using Cl₂/H₂-based plasmas.¹³⁻¹⁵ Highly anisotropic GaN etching was obtained at dc-biases ranging from -150 to -250 V with etch rates exceeding 2800 Å/min.

In this paper, we report ECR etching of GaN as a function of plasma chemistry using Cl₂/H₂/Ar, Cl₂/SF₆/Ar, BCl₃/H₂/Ar, and BCl₃/SF₆/Ar plasmas. These discharge chemistries are expected to etch GaN due to the high volatility of the Ga-chlorides and the formation of volatile NH_x or NF_x etch products with the addition of H₂ or SF₆ to the plasma.

EXPERIMENT

The GaN films were grown using Metal Organic Molecular Beam Epitaxy (MO-MBE) on GaAs substrates in an Intevac Gen II system described previously.¹⁶ The group-III source was triethylgallium and the atomic nitrogen was derived from an ECR Wavemat source operating at 200 W forward power. The layers were single crystal with a high density of stacking faults and microtwins and were resistive as-grown.

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The GaN samples were patterned using a photoresist mask. The ECR plasma reactor used in this study was a load-locked Plasma-Therm SLR 770 etch system with an ECR source operating at 2.45 GHz. Energetic ion bombardment was provided by superimposing an rf-bias (13.56 MHz) on the sample. Samples were mounted using vacuum grease on an anodized Al carrier that was clamped to the cathode and cooled with He gas. Etch gases were introduced through an annular ring into the chamber just below the quartz window. To minimize field divergence and to optimize plasma uniformity and ion density across the chamber, an external secondary collimating magnet was located on the same plane as the sample and a series of external permanent rare-earth magnets were located between the microwave cavity and the sample. ECR etch parameters held constant in this study were: 30°C electrode temperature, 1 mTorr total pressure, 30 sccm total gas flow, 5 sccm of Ar, 850 W of applied microwave power, and 150 W rf-power with a corresponding dc-bias of -150 ± 10 V.

Etch rates were calculated from the depth of etched features measured with a Dektak stylus profilometer after removing the photoresist mask. Samples etched in the ECR were approximately 1 cm^2 and depth measurements were taken at a minimum of three positions. Error bars for the etch rates were $\pm 10\%$ across the sample. Limited sample supply precluded multiple runs at each condition. The gas phase chemistry of the plasma was studied using a quadrupole mass spectrometer (QMS). Surface morphology, anisotropy, and sidewall undercutting were evaluated with a scanning electron microscope (SEM). The root-mean-square (rms) surface roughness was quantified using a Digital Instruments Dimension 3000 atomic force microscope (AFM) system operating in tapping mode with Si tips. Auger electron spectroscopy (AES) was used to investigate the near-surface stoichiometry of GaN before etch and after exposure to several plasma conditions.

RESULTS AND DISCUSSIONS

The etch rate for GaN is plotted in Figure 1 as a function of percent hydrogen concentration for the $\text{Cl}_2/\text{H}_2/\text{Ar}$ and $\text{BCl}_3/\text{H}_2/\text{Ar}$ plasma discharges. The GaN etch rates were consistently greater

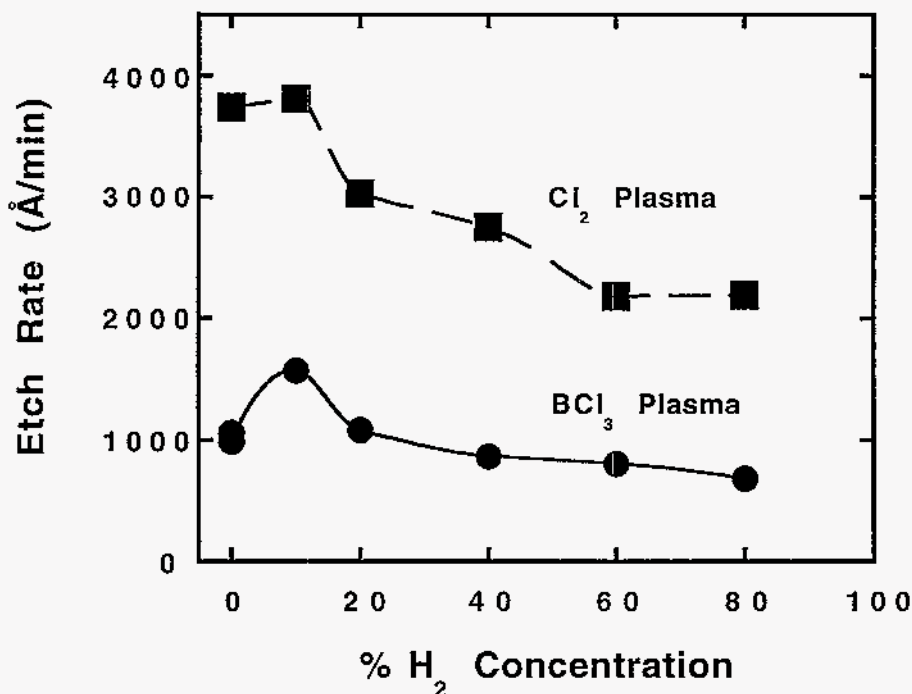


Figure 1. GaN etch rates as a function of %H₂ concentration for $\text{Cl}_2/\text{H}_2/\text{Ar}$ and $\text{BCl}_3/\text{H}_2/\text{Ar}$ plasmas.

in the Cl_2 -based plasma as compared to BCl_3 by a factor of 2 to 3 due to the higher concentration of active Cl species. The trends were similar for both plasmas as the H_2 concentration was increased, however, the increase in etch rate at 10% H_2 was much more significant in the BCl_3 -plasma. The increase in etch rate observed at 10% H_2 concentration in BCl_3 correlated with an increase in the reactive Cl concentration indicated by $m/e = 35$ peak intensity. In the Cl_2 -based plasma, the GaN etch rate and Cl concentration remained relatively constant at 10% H_2 . As the H_2 concentration was increased further, the Cl concentration decreased and the HCl concentration increased as the GaN etch rates decreased in both plasmas, presumably due to the consumption of reactive Cl by hydrogen.

In Figure 2, GaN etch rates are shown for the $\text{Cl}_2/\text{SF}_6/\text{Ar}$ and $\text{BCl}_3/\text{SF}_6/\text{Ar}$ plasmas. With the substitution of SF_6 for H_2 in the Cl_2 -based plasma, the GaN etch rate was typically a factor of 2 lower. As the concentration of SF_6 was increased the etch rate decreased up to 30% SF_6 followed by a slight increase at 40%. As the % SF_6 was increased from 0 to 20, the Cl concentration ($m/e = 35$) decreased but remained significant; GaN etching at 20% SF_6 might be expected based on the Cl concentration alone. However, formation of SCl ($m/e = 67$) was observed at 20% SF_6 . Consumption of the reactive Cl by S may be responsible for the reduced GaN etch rate. At 30 and 40% SF_6 , the Cl concentration was greatly reduced and low GaN etch rates result. The opposite trend was observed for BCl_3 , where the GaN etch rates were significantly greater when SF_6 was substituted for H_2 . The GaN etch rate increased up to 30% SF_6 and then decreased sharply at 40% SF_6 . The Cl concentration ($m/e = 35$) also increased as the SF_6 increased to 30% and then decreased at 40%. As with the Cl_2 -based plasma, there appeared to be a competitive reaction of sulfur with chlorine as the SCl concentration increased above 30% SF_6 . Under most etch conditions, the trend of the Cl concentration correlated with the trends observed for the GaN etch rate. However, a higher concentration of Cl was observed at 40% SF_6 than 0% SF_6 while the GaN etch rate was greater at 0% SF_6 . Studies are planned to elucidate the chemistry involved.

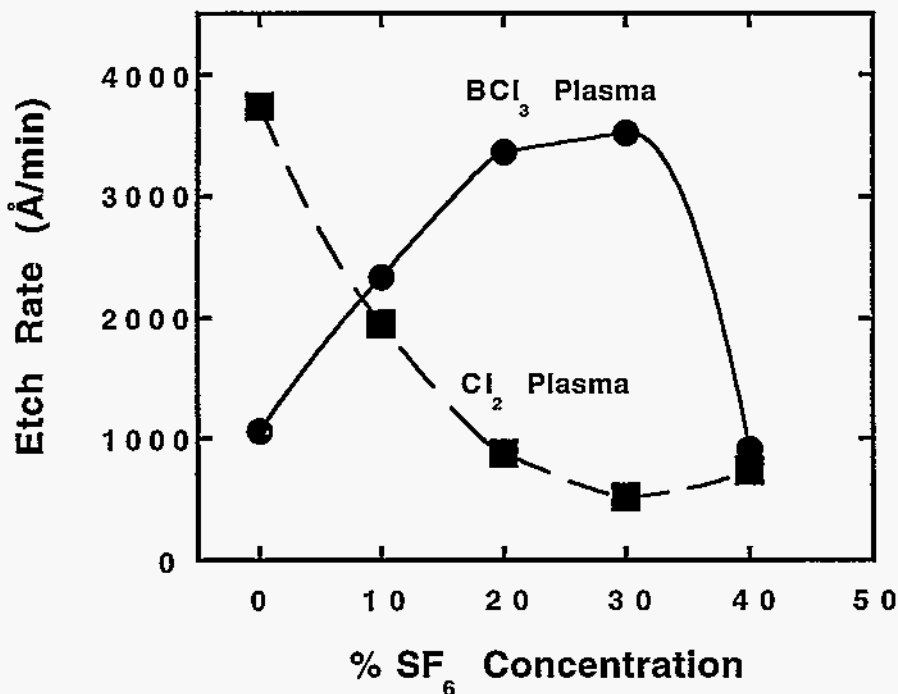


Figure 2. GaN etch rates as a function of % SF_6 concentration for $\text{Cl}_2/\text{SF}_6/\text{Ar}$ and $\text{BCl}_3/\text{SF}_6/\text{Ar}$ plasmas.

The root-mean-square (rms) roughness of the etched surfaces were quantified using AFM. In Figure 3 the rms roughness is plotted as a function of % H_2 for the Cl_2 -based and BCl_3 -based

plasmas. The rms roughness for the as-grown GaN was 6.4 ± 0.5 nm. The rms roughness for GaN etched in $\text{Cl}_2/\text{H}_2/\text{Ar}$ increased as the $\% \text{H}_2$ increased from 0 to 10 and then decreased as the H_2 concentration was increased further. The roughest surface was observed at 10% H_2 where the etch rate was greatest. In the $\text{BCl}_3/\text{H}_2/\text{Ar}$ plasma the rms roughness increased slightly as the $\% \text{H}_2$ increased, but remained relatively smooth. Pattern transfer into GaN was very smooth in $\text{Cl}_2/\text{SF}_6/\text{Ar}$ and $\text{BCl}_3/\text{SF}_6/\text{Ar}$ discharges with rms roughness ranging from 7.5 to 3.6 nm.

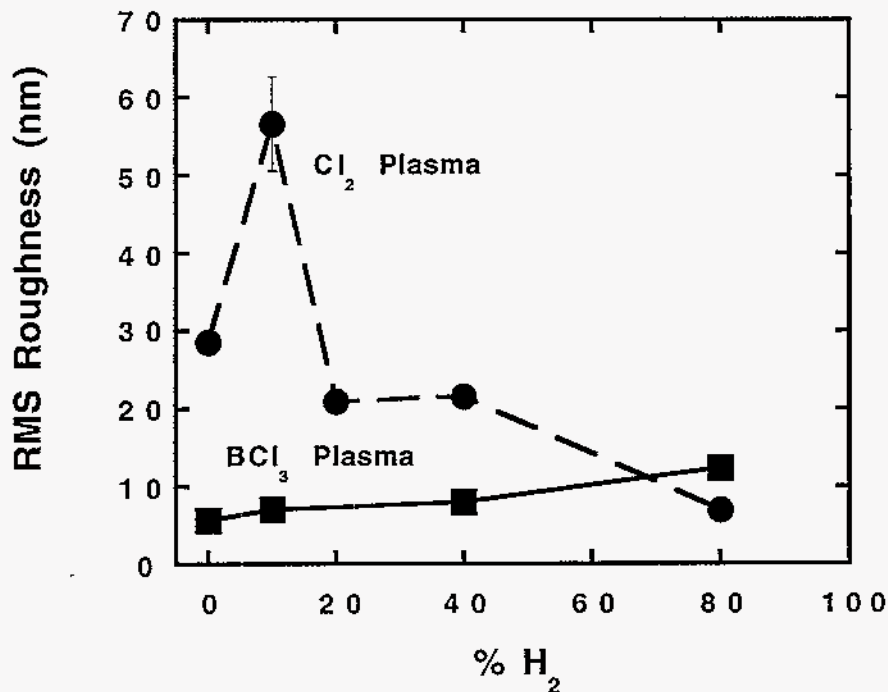


Figure 3. GaN rms roughness as a function of $\% \text{H}_2$ concentration for $\text{Cl}_2/\text{H}_2/\text{Ar}$ and $\text{BCl}_3/\text{H}_2/\text{Ar}$ plasmas. The rms roughness for the as-grown GaN is 6.4 ± 0.5 nm.

The etch profiles showed a strong dependence on the discharge chemistry (Figure 4). The etched surface was quite rough (Figure 4a) in the Cl_2/Ar plasma possibly due to preferential removal of the GaCl_x etch products. The foot observed at the edge of the etched feature may be attributed to mask-edge erosion due to the aggressive attack of photoresist by reactive Cl. As the H_2 concentration was increased to 20% the etch became smooth and very anisotropic (Figure 4b).

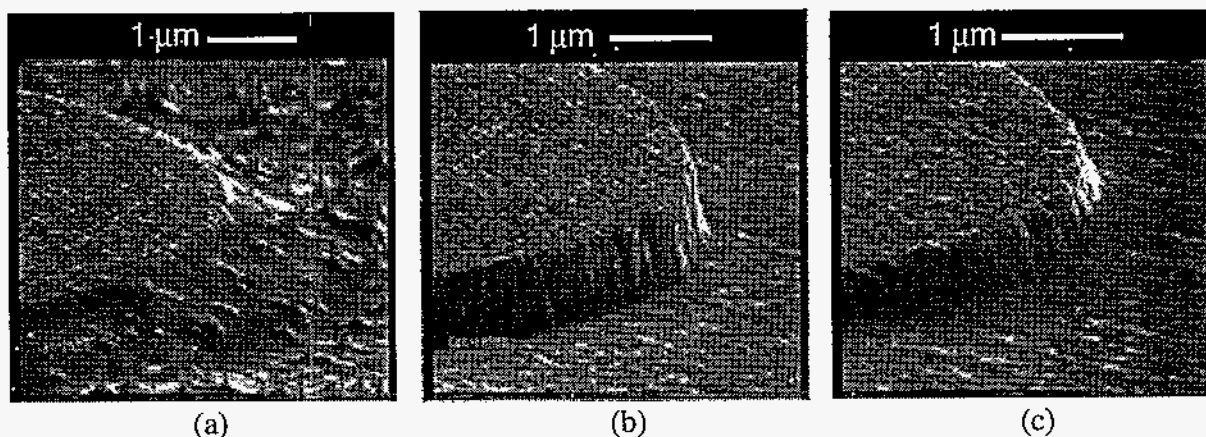


Figure 4. SEM micrographs of GaN samples ECR etched in (a) Cl_2/Ar plasma, (b) 20% H_2 $\text{Cl}_2/\text{H}_2/\text{Ar}$ plasma, and (c) 60% H_2 $\text{Cl}_2/\text{H}_2/\text{Ar}$ plasma. The photoresist mask has been removed.

However, the SEM micrograph showed a lower density of surface roughness near the etched feature than AFM images scanned in open $10 \times 10 \mu\text{m}$ areas. This may be attributed to a proximity effect of the etch where redeposition is worse in the open areas. It may also explain the smooth etch observed in Figure 4b where the rms roughness measured in the field was approximately 21 nm. At 60% H_2 , the etch remained smooth and anisotropic with a slight foot at the base of the feature (Figure 4c). The GaN etch profiles in Cl_2/SF_6 plasmas were anisotropic with relatively smooth sidewalls and etched surfaces. Etching GaN in BCl_3/H_2 or BCl_3/SF_6 resulted in anisotropic profiles with etched surface morphologies similar to the as-grown samples. The anisotropic profiles may have been improved in the BCl_3 -based plasmas due to the higher physical component of the etch mechanism as compared to Cl_2 -based plasmas.

Auger spectra for GaN samples etched under several different plasma conditions were taken to determine the near-surface stoichiometry. Prior to exposure of the GaN to the plasma, the Auger spectrum for the as-grown GaN showed a Ga:N ratio of 1.5 with normal amounts of adventitious carbon and native oxide on the GaN surface. The Auger spectra showed virtually no Ga or N for GaN samples exposed to the Cl_2/Ar plasma or the 80% H_2 $\text{Cl}_2/\text{H}_2/\text{Ar}$ plasma. This is not understood since the GaN was grown on GaAs and showed a minimum of 2500 Å of GaN remaining after etch. Since the Auger spectra were near-surface and did not include any depth profiling, redeposition during etch may have prevented the observation of the Ga and N peaks. Further surface analysis are underway. For GaN samples etched in $\text{Cl}_2/\text{SF}_6/\text{Ar}$, the Ga:N ratio increased as the SF_6 concentration increased implying that the N is effectively removed as NF_x . In the BCl_3/Ar plasma the Ga:N ratio increased from 1.5 for the as-grown sample to 1.9 following exposure to the plasma. This may be attributed to the preferential removal of the lighter N atoms due to the strong physical component of the etch mechanism in BCl_3 plasmas. As the H_2 or SF_6 concentration was increased in the BCl_3/Ar plasma, the Ga:N ratio increased to 6.3 for 80% H_2 and 4.2 for 40% SF_6 . Within experimental error, these trends imply that the GaN film is being depleted of N perhaps due to preferential chemical etching of the N atoms with the addition of H_2 or SF_6 to either Cl_2 - or BCl_3 -based plasmas.

CONCLUSIONS

In summary, ECR etching of GaN is reported as a function plasma chemistry. GaN etch rates were greatest in Cl_2/Ar and $\text{Cl}_2/\text{H}_2/\text{Ar}$ at 10% H_2 . Etch rates were a factor of 2 to 3 times higher in Cl_2/H_2 plasmas than BCl_3/H_2 plasmas due to higher concentrations of reactive Cl. As the hydrogen concentration was increased above 10%, the GaN etch rate decreased in both plasmas possibly due to consumption of the reactive Cl by hydrogen. When SF_6 was substituted for H_2 , the GaN etch rates were greater in the BCl_3 -based plasma. The GaN etch rate increased as SF_6 was added to the BCl_3/Ar plasma up to 30% and then dropped sharply at 40% SF_6 . This trend correlated qualitatively with the concentration of reactive Cl. In general, GaN etch rates increased as the concentration of reactive Cl increased. Surface morphologies were evaluated and quantified using AFM. Very smooth pattern transfer was obtained for a wide range of plasma chemistries; however, the etched surface morphology was rougher in Cl_2/Ar and $\text{Cl}_2/\text{H}_2/\text{Ar}$ plasmas at low H_2 concentrations. Etch profiles were more anisotropic with the addition of H_2 or SF_6 to Cl_2 . The etch profiles were typically more anisotropic with BCl_3 -based plasmas due to the physical nature of the etch while the etch rates were slower due to less reactive Cl present in the plasma. Using Auger spectroscopy, we have observed a general trend where the Ga:N ratio increased as the concentration of H_2 or SF_6 increased implying a substantial chemical etch mechanism to remove N atoms from the GaN film.

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