HIGH RATE DRY ETCHING OF GaN, AlN AND InN IN ECR Cl$_2$/CH$_4$/H$_2$/Ar PLASMAS

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ABSTRACT

Etch rates for binary nitrides in ECR Cl$_2$/CH$_4$/H$_2$/Ar are reported as a function of temperature, rf-bias, microwave power, pressure and relative gas proportions. GaN etch rates remain relatively constant from 30 to 125 °C and then increase to a maximum of 2340 Å·min^{-1} at 170 °C. The AlN etch rate decreases throughout the temperature range studied with a maximum of 960 Å·min^{-1} at 30 °C. When CH$_4$ is removed from the plasma chemistry, the GaN and InN etch rates are slightly lower, with less dramatic changes with temperature. The surface composition of the III-V nitrides remains unchanged over the temperatures studied. The GaN and InN rates increase significantly with rf power, and the fastest rates for all three binaries are obtained at 2 mTorr. Surface morphology is smooth for GaN over a wide range of conditions, whereas InN surfaces are more sensitive to plasma parameters.

INTRODUCTION

The III-V nitrides are attracting considerable attention for blue and ultraviolet light emitting diodes (LEDs) and lasers as well as high temperature electronics due to their wide band gaps and high dielectric constants.[1,2] Although a great deal of work has been concentrated in this area, the existing processing techniques for these materials are unsuitable for many device applications. The lack of lattice matched substrate for epitaxial growth, poor ohmic and Schottky contacts, and unsuitable patterning techniques have prevented the fabrication of high performance reliable photonic and electronic devices more sophisticated than LEDs. Wet etch techniques have proven impractical due to the low chemical reactivity of the III-V nitrides, however, dry etch results have been much more promising. Relatively low etch rates for GaN (~ 500 Å·min^{-1}) have been reported in reactive ion etch systems,[3,4] however significantly higher etch rates (1000 to 3500 Å·min^{-1})[5] have been obtained in high density etch systems under moderate dc-bias conditions.

In this paper we report on a detailed study of ECR plasma etching of the nitrides in Cl$_2$/CH$_4$/H$_2$/Ar discharges. The surface morphology of the etched samples was examined by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), and the near-surface stoichiometry measures by Auger Electron Spectroscopy (AES). The Cl$_2$/CH$_4$/H$_2$/Ar chemistry is found to provide high etch rates and smooth, anisotropic pattern transfer over a wide range of conditions.

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Experimental

The GaN, InN and AlN films were grown using Metal Organic Molecular Beam Epitaxy (MO-MBE) on either GaAs or Al_2O_3 substrates in a Intevac Gen II system. The group-III sources were trigallium, triethylindium or triethylamine alane, respectively, and the atomic nitrogen was derived from an ECR Wavemat source operating at 200 W forward power. The layers are single crystal with a density of stacking faults and microtwins. The GaN and AlN are resistive as grown, while the InN is highly auto-doped n-type ($>10^{20}$ cm^{-3}) due to the presence of native defects.

The group-III nitrides were patterned using a PECVD Si_3N_4 mask due to the high etch temperatures studied. The ECR plasma reactor used in this study was a load-locked PlasmaTherm SLR 770 etch system with an ECR source operating at 2.45 GHz.[6] Ion energies were 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 heated with He gas. ECR etch parameters used in this study were: 10 sccm Cl_2, 15 sccm of H_2, 10 sccm of Ar, 3 sccm of CH_4, 30 to 170 °C electrode temperature, 1 to 10 mTorr total pressure, 125 to 850 W applied power, and 0 to 250 W rf-power.

Etch rates were calculated from the depth of the etched features measured with a Dektak stylus profilometer. The Si_3N_4 masking material was removed in a SF_6/O_2 RIE plasma. 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 represent the standard deviation across the sample. Several plasma conditions were repeated with better than ± 10% sample to sample variation.

Results and Discussion

GaN did not show a large variation in etch rate over the temperature range 30-170 °C, being ~ 2000 Å·min^{-1} at 850 W microwave power, 180 V dc-bias and 1 mTorr. AlN decreased in etch rate under the same conditions from ~ 1000 Å·min^{-1} at 30 °C to ~500 Å·min^{-1} at 170 °C.

In Figure 1 the InN etch rates are shown as a function of temperature for the same plasma chemistries. The InN etch rate decreases by more than 60% as the temperature is increased to 150 °C for the $Cl_2/CH_4/H_2/Ar$ plasma chemistry, however the etch rate increases rapidly above 150 °C to a maximum of 2300 Å·min^{-1} at 170 °C. A similar trend is observed in the $Cl_2/H_2/Ar$ plasma chemistry at etch rates 20 to 50 % lower than those obtained with CH_4 in the plasma. The higher GaN and InN etch rates observed with the presence of CH_4 in the plasma chemistry, regardless of the temperature, may be attributed to the additional formation of the group III-methyl etch product which appears to be more volatile than the group III-chlorides below ~ 150 °C or an etch mechanism which is enhanced by the CH_4. The initial InN etch rate decrease observed in the $Cl_2/CH_4/H_2/Ar$ plasma chemistry may be due to competitive reactions between Cl_2 and CH_4 with InN to form either $InCl_x$ or $In(CH_x)_y$.

Figure 2 shows characteristic Auger spectra for GaN samples before and after ECR etching at 30 and 170 °C in a $Cl_2/CH_4/H_2/Ar$ plasma. Prior to exposure of the GaN to the plasma, the Auger spectrum shows normal amounts of carbon and native oxide on
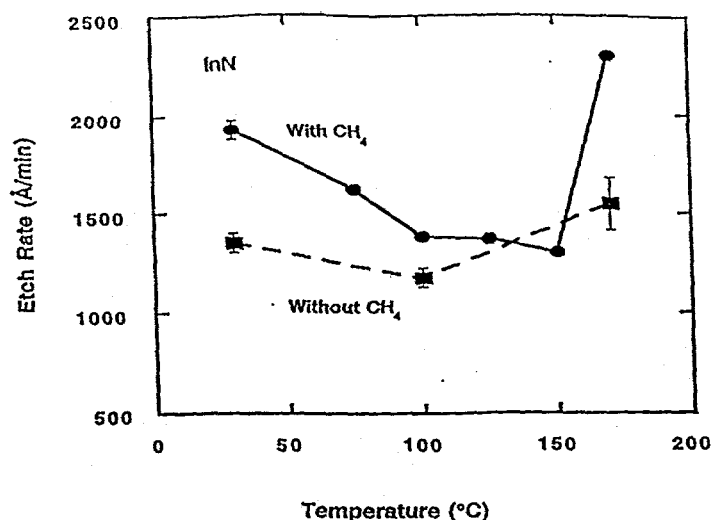
Figure 1. Etch rates of InN as a function of temperature for ECR generated $Cl_2/CH_4/H_2/Ar$ or $Cl_2/H_2/Ar$ plasma chemistries.

the surface. Following exposure to the plasma, within experimental error, there is no change in the stoichiometry of the GaN surface at either 30 or 170 °C and some residual atomic Cl is present. Similar results were observed for the InN and AlN samples.

There was slight dependence of nitride etch rate on pressure over the range 1-10 mTorr, with the fastest rates obtained at 2 mTorr. In Figure 3 etch rates are plotted as a function of rf-power for GaN, InN and AlN. As the rf- power is increased the etch rates increase monotonically for GaN and InN due to the higher ion energies. Without rf-biasing, the dc-bias is approximately -10 to-15 V and the GaN and InN samples do not etch during a two minute exposure; however, when 75 W of re-power is applied the GaN etches at a rate of 817 $Å·min^{-1}$ and the InN etches at 363 $Å·min^{-1}$. This suggests that either the etch products ate not desorbed efficiently at low ion energy or the presence of a thin film which must be sputter removed before chemical etching can occur. High etch rates for GaN, 3840 $Å·min^{-1}$, and InN, 2850 $Å·min^{-1}$, have been achieved at 275 W rf-power. The etch rate for AlN is essentially constant, 240 $Å·min^{-1}$, at 0 and 75 W rf- power, and increases to 1245 $Å·min^{-1}$ at 225 W rf-power and then decreases at 275 W. The rates also increased with microwave power, as expected.

The surface morphology as a function of plasma etch conditions is evaluated using AFM. The RMS roughness for GaN and InN as-grown is 3.21±0.56 and 8.35±0.50 nm respectively. In Figure 4 the RMS roughness is shown as a function of pressure. The GaN RMS roughness remains virtually unchanged at approximately 4 nm over the pressure range studied, very similar to the as-grown RMS roughness. The InN RMS roughness is consistently higher than the GaN and shows a monotonic increase as the pressure is increased.

Figure 5 shows characteristic Auger spectra for GaN samples before and after ECR etching at 125 and 625 W applied microwave power. Prior to exposure of the GaN to the plasma, the Auger spectrum shows normal amounts of adventitious carbon and native oxide on the GaN surface. Following exposure to the plasma, there is a reduction in N content within the top 100 Å of the surface. Therefore, the changes in RMS roughness
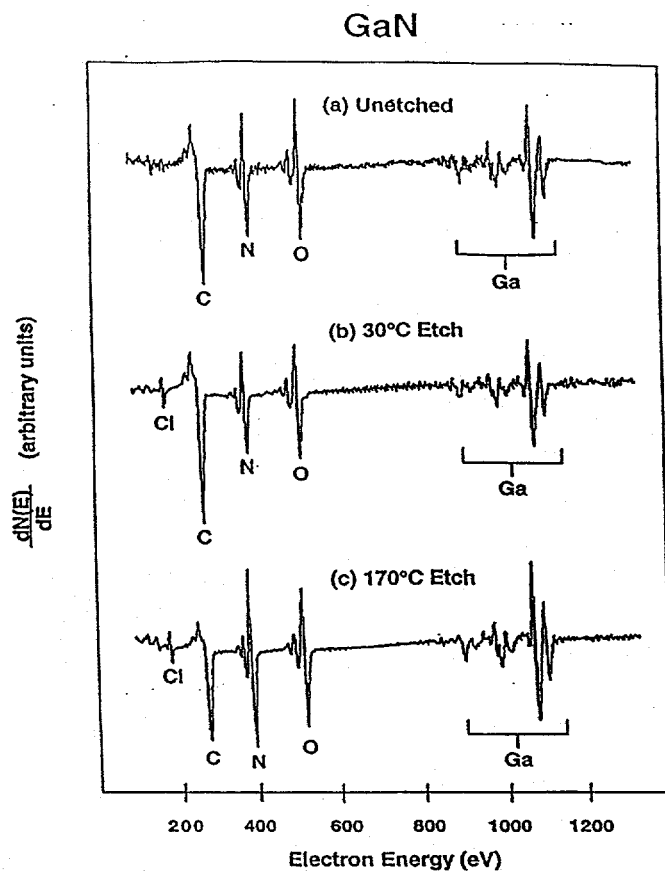
GaN

Figure 2. AES surface scans of GaN (a) before exposure to the plasma, (b) at 30 °C, and (c) at 170 °C in an ECR generated $Cl_2/CH_4/H_2/Ar$ plasma chemistry.

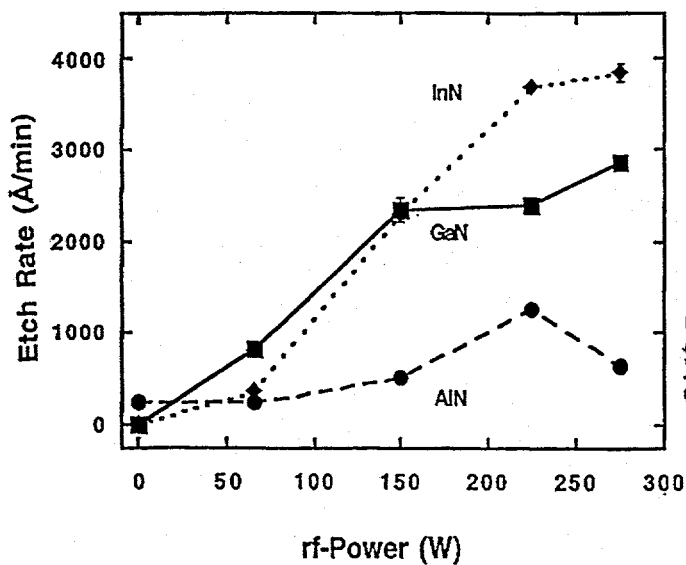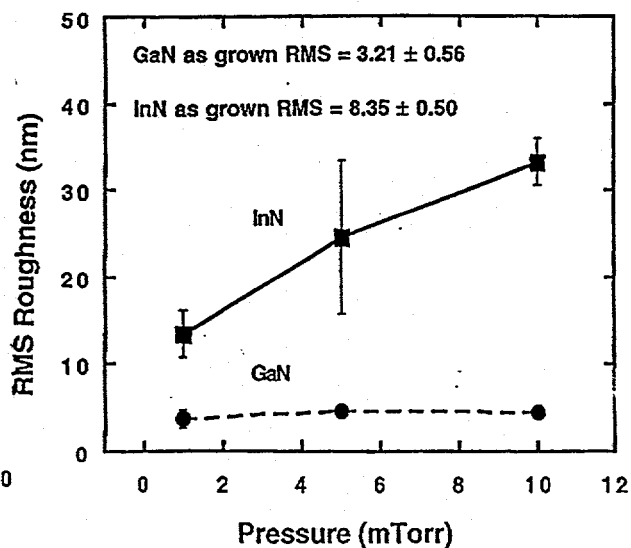Figure 3. Etch rates of GaN, InN and AlN as a function of rf-power for an ECR generated $Cl_2/CH_4/H_2/Ar$ plasma.

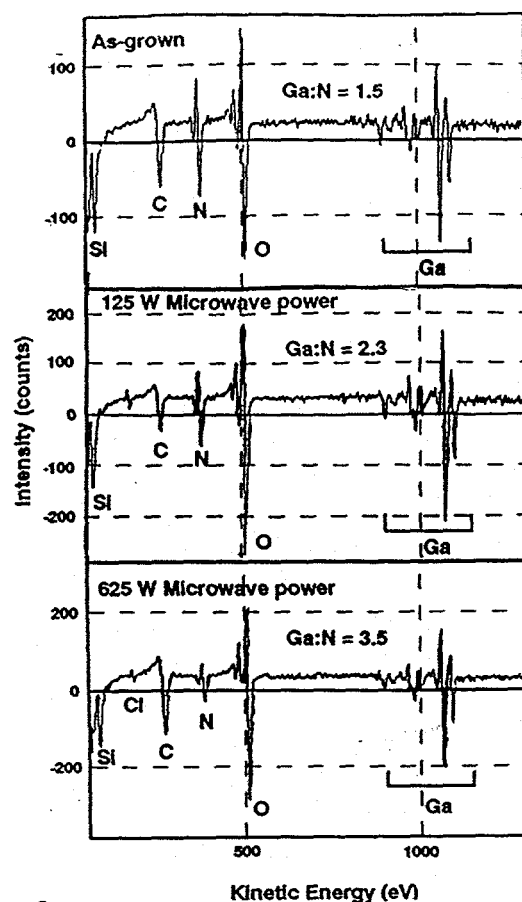Figure 4. RMS roughness for GaN and InN as a function of pressure in an ECR generated $Cl_2/CH_4/H_2/Ar$ plasma.

As-grown

100

Ga:N = 1.5

0

-100

C   N

SI   O   Ga

Intensity (counts)

125 W Microwave power

200

100   Ga:N = 2.3

0

-100   C   N

SI

-200

O   Ga

625 W Microwave power

200

Ga:N = 3.5

0

Cl

N

-200   SI   C

O   Ga

500   1000

Kinetic Energy (eV)

Figure 5. AES surface scans of GaN (a) before exposure to the plasma, (b) at 125 W microwave power, and (c) at 625 W microwave power in an ECR generated $Cl_2/CH_4/H_2/Ar$ plasma.

observed for both GaN and InN as a function of rf-power, microwave power, and pressure can be due to either a stoichiometric effect or a physical effect such as micro masking due to deposition. Some residual atomic Cl is observed for samples exposed to the plasma.

Summary

In summary, ECR etching of III-V nitrides has been examined for $Cl_2/CH_4/H_2/Ar$ and $Cl_2/H_2/Ar$ plasmas. Etch rates greater than 2250 Å·min^{-1} have been observed at 170 °C for both GaN and InN and suggest these are excellent plasma chemistries for non-selective etching of InGaN alloys. A competitive reaction mechanism to remove Ga or In has been suggested between Cl_2 and CH_4. The GaN and InN etch rates are greater with the addition of CH_4 to the plasma chemistry. This may be attributed to the formation of the group-III methyl etch product or kinetically favorable gas phase reactions.

Acknowledgments

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