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## ECR, ICP, AND RIE PLASMA ETCHING OF GaN

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The group III-nitrides continue to generate interest due to their wide band gaps and high dielectric constants. These materials have made significant impact on the compound semiconductor community as blue and ultraviolet light emitting diodes (LEDs). Realization of more advanced devices; including lasers and high temperature electronics, requires dry etch processes which are well controlled, smooth, highly anisotropic and have etch rates exceeding 0.5  $\mu\text{m}/\text{min}$ . In this paper, we compare electron cyclotron resonance (ECR), inductively coupled plasma (ICP), and reactive ion etch (RIE) etch results for GaN. These are the first ICP etch results reported for GaN. We also report ECR etch rates for GaN as a function of growth technique.

### INTRODUCTION

Interest in the wide band-gap group-III nitrides continues to increase as growth and process technologies improve and device demonstrations of blue, green, and ultraviolet emitters and detectors, and high temperature electronics are reported.[1-4] Realization of more advanced devices; including lasers, requires dry etch processes which are well controlled, smooth, highly anisotropic and have etch rates exceeding 0.5  $\mu\text{m}/\text{min}$ . Laser facet fabrication is especially dependent upon dry etching since the majority of epitaxially grown group-III nitrides is on sapphire substrates which inhibits cleaving the sample with reasonable yield.

GaN etching has been reported in reactive ion etch (RIE) systems with etch rates approaching 600  $\text{\AA}/\text{min}$  at dc-biases greater than -400 V.[5] The high rates and anisotropic profiles achieved with RIE are attributed to the acceleration of energetic ions from the plasma to the wafer. However, this energetic ion-bombardment of the surface can damage the sample and degrade both electrical and optical device performance. Attempts to minimize such damage by reducing the ion energy or increasing the chemical activity in the plasma often results in a loss of etch rate or anisotropy which significantly limits critical dimensions and reduces the utility of the process for device applications requiring vertical etch profiles. It is therefore necessary to develop plasma etch processes which couple

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anisotropy for critical dimension and sidewall profile control and high etch rates with low-damage for optimum device performance.

A great deal of interest has been generated in low-damage etch processes based on high-density electron cyclotron resonance (ECR) plasmas and inductively coupled plasmas (ICP). Due to the magnetic confinement of electrons in the microwave source, high-density ECR plasmas are formed at low pressures with low plasma potentials and ion energies. Therefore, less damage than that produced by RIE plasmas has been observed during ECR etching of III-V materials. ECR etching of GaN has been performed using  $\text{Cl}_2/\text{H}_2$ - and  $\text{Cl}_2/\text{H}_2/\text{CH}_4$ -based plasmas with etch rates ranging from a few hundred  $\text{\AA}/\text{min}$  to several thousand  $\text{\AA}/\text{min}$ .<sup>[6-9]</sup> High-density ICP plasmas are formed in a dielectric vessel encircled by an inductive coil into which rf power is applied. A strong magnetic field is induced in the center of the chamber which generates a high density plasma due to the circular region of the electric field that exists concentric to the coil. At low pressures,  $\leq 10$  mTorr, the plasma diffuses from the generation region and drifts to the substrate at relatively low ion energy. Thus, ICP etching is expected to produce less damage than RIE etching while maintaining high etch rates due to the high plasma density. For both ECR and ICP etch systems, anisotropic profiles can be obtained by superimposing an rf-bias on the sample to independently control ion energy. In this paper, we report the first GaN etch results obtained in an ICP and compare the etch rates to those obtained in ECR and RIE generated plasmas. We also report ECR etch rates for GaN grown by metal organic molecular beam epitaxy (MO-MBE), radio-frequency MBE (rf-MBE), and metal organic chemical vapor deposition (MOCVD).

## EXPERIMENTAL

The GaN films etched in this study were grown by MO-MBE, rf-MBE, or MOCVD. The MO-MBE GaN films were grown at 925°C on either GaAs or  $\text{Al}_2\text{O}_3$  substrates in an Intevac Gen II system described previously.<sup>[10]</sup> The group-III source was triethylgallium and the atomic nitrogen was formed in an ECR Wavemat source operating at 200 W forward power. The rf-MBE GaN film was grown in a commercial MBE system equipped with a conventional Ga effusion cell and a rf plasma source to supply atomic nitrogen during growth. The epitaxial layers were grown on a  $n^+$  GaAs substrate. After deposition of a 5000  $\text{\AA}$  Sn-doped GaAs buffer layer, growth was interrupted while the substrate temperature was stabilized at 620°C. The GaN epilayer was comprised primarily of the cubic phase. The MOCVD GaN film was approximately 1.8  $\mu\text{m}$  thick and was grown on a c-plane sapphire substrate in a multiwafer rotating disk reactor at 1040°C with a 20 nm GaN buffer layer grown at 530°C.<sup>[11]</sup>

The ECR plasma reactor used in this study was a load-locked Plasma-Therm SLR 770 etch system with a low profile Astex 4400 ECR source in which the upper magnet was operated at 165 A. Energetic ion bombardment was provided by superimposing an rf-bias (13.56 MHz) on the sample. 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 was run at 25 A. Plasma uniformity was further enhanced by a series of external permanent rare-earth magnets located between the microwave cavity and the sample. Unless otherwise mentioned, ECR etch parameters used in this study were: 10 sccm of  $\text{Cl}_2$ , 15 sccm of  $\text{H}_2$ , 10 sccm of Ar, 3

sccm of  $\text{CH}_4$ , 30°C electrode temperature, 1 mTorr total pressure, 1000 W of applied microwave power, and 1 to 450 W rf-power with corresponding dc-biases of -10 to -380  $\pm$  25 V.

For the RIE mode, the plasma was generated using a 13.56 MHz rf-power supply in the same chamber configuration mentioned above. Standard RIE etch parameters used in this study were identical to the ECR parameters with the exception of rf-power which ranged from 50 to 450 W with corresponding dc-biases of -270 to -950  $\pm$  50 V. In order to study ICP, the ECR source and chamber were removed from the SLR 770 etch system and replaced with a Plasma-Therm ICP source. The reactor was a cylindrical coil configuration with a dielectric vessel encircled by an inductive coil into which the rf power (2 MHz) was applied. A strong magnetic field was induced in the center of the chamber which generated a high density plasma due to the circular region of the electric field that exists concentric to the coil. Identical to the ECR, energetic ion bombardment was provided by superimposing an rf-bias (13.56 MHz) on the sample. Etch gases were introduced through an annular region at the top of the chamber. Etch conditions were the same used in the ECR with the exceptions of 500 W ICP power and rf-powers ranging from 1 to 450 W with corresponding dc-biases of -10 to -425  $\pm$  25 V.

All samples were mounted using vacuum grease on an anodized Al carrier that was clamped to the cathode and cooled with He gas. Samples were patterned using AZ 4330 photoresist. Etch rates were calculated from the depth of etched features measured with a Dektak stylus profilometer after the photoresist was removed with an acetone spray. Each sample was approximately 1  $\text{cm}^2$  and depth measurements were taken at a minimum of three positions. Standard deviation of the etch depth across the sample was nominally less than  $\pm$  10% with run-to-run variation less than  $\pm$  10%.

## GaN PLASMA ETCHING

Etch rates of MO-MBE grown GaN etched by ECR, ICP, and RIE are shown in Figure 1 as a function of rf-power. Under the plasma conditions used in this study, the lowest rf-power required to generate a stable RIE plasma was 50 W. Both ECR and ICP generated plasmas were stable at 1 W rf-power. Under all three etch techniques, the GaN etch rate increased as the rf-power or ion energy increased. This trend has been observed previously [5-9] and can be attributed to enhanced sputter desorption of the etch products. The GaN etch rate increased by almost a factor of 6 as the rf-power was increased from 50 to 450 W for all three etch techniques. The ICP etch rates for GaN were 10 to 50% faster than those etched in the ECR. Since the dc-bias was fairly similar for a given rf-power, higher etch rates in the ICP may be attributed to higher neutral densities which increased the chemical component of the etch mechanism. The ECR and ICP GaN etch rates were approximately 5 to 10 times faster than those obtained in the RIE mode due to plasma densities which were 3 to 4 orders of magnitude greater in the ECR and ICP. At constant pressure, the dc-bias was much higher in the RIE since the ion densities were so much lower thereby resulting in less collisions and higher ion energies.

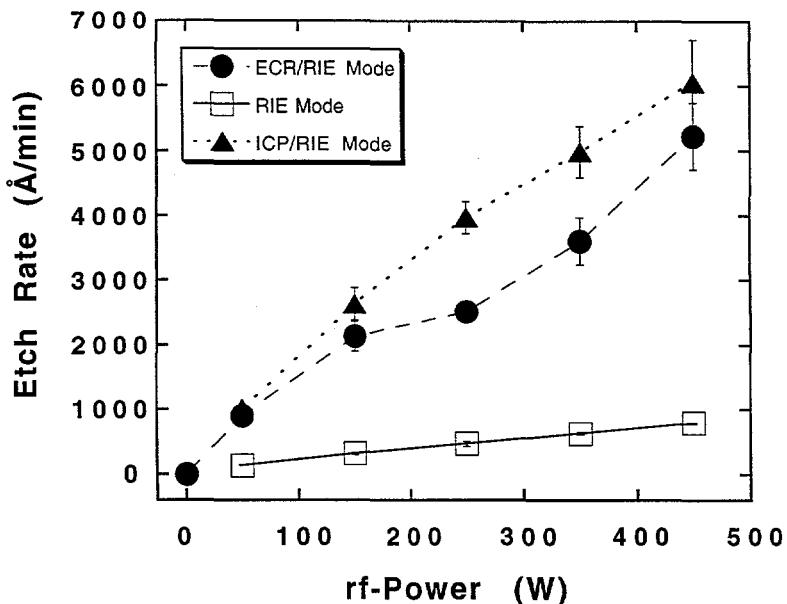


Figure 1. GaN (grown by MO-MBE) etch rates as a function of rf-power as etched in ECR, ICP, and RIE generated plasmas.

### ECR ETCH RATE DEPENDENCE ON GROWTH TECHNIQUE

GaN ECR etch rates were studied as a function of growth technique for MO-MBE, rf-MBE, and MOCVD GaN films. In Figure 3, GaN ECR etch rates are shown as a function of rf-power for samples grown by these three different techniques. The ECR plasma conditions were; 2 mTorr pressure, 22.5 sccm Cl<sub>2</sub>, 2.5 sccm H<sub>2</sub>, 5 sccm Ar, 30°C electrode temperature, 1000 W microwave power, and rf-powers ranging from 1 to 450 W with a corresponding dc-bias range of -25 to -275 ± 25 V. GaN samples were etched simultaneously. As the rf-power was increased the GaN etch rates increased due to higher ion energies, independent of growth technique. With 1 W rf-power, the dc-bias was approximately -25 V and the GaN samples did not etch during 1 minute of exposure to the plasma. However, with 150 W of applied rf-power (~ -110 V dc-bias) the GaN etch rates ranged from 3800 to 4975 Å/min. This suggested that either the etch products were not desorbed efficiently at low ion energy or that a thin surface oxide was present which was not effectively sputtered away during the 1 minute exposure. Etch rates approaching 9000 Å/min were obtained for the MO-MBE and rf-MBE GaN samples at 450 W rf-power (~ -275 V dc-bias). At rf-powers above 1 W, we observed a trend where the MO-MBE GaN etched faster than the rf-MBE GaN which was faster than the MOCVD GaN. Faster etch rates correlated with higher root-mean-square (rms) roughness for the as-grown GaN samples. Using atomic force microscopy (AFM), the rms-roughness was measured for the as-grown GaN samples and was 19.38 ± 0.44 nm for MO-MBE, 3.12 ± 0.84 nm for rf-MBE, and 1.76 ± 0.29 nm for MOCVD.

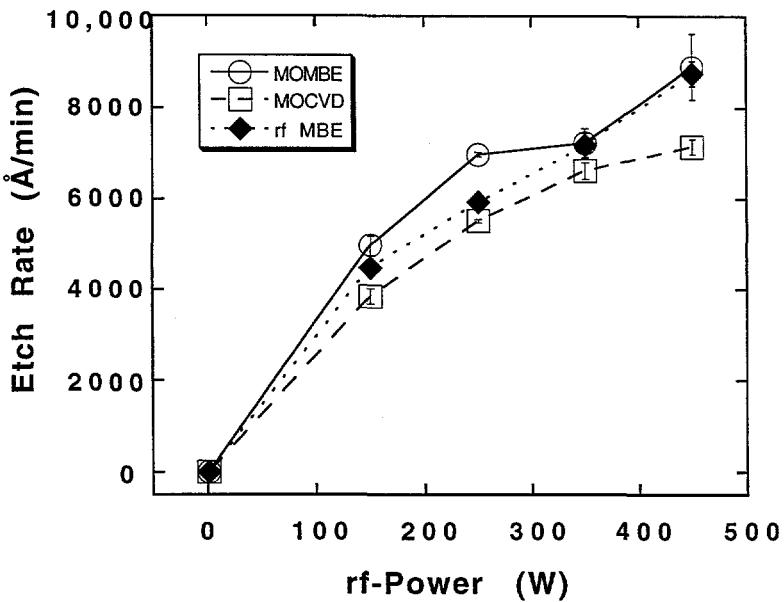


Figure 3. GaN ECR etch rates as a function of rf-power for MO-MBE, rf-MBE, and MOCVD grown samples.

### ICP ETCHING OF GaN

These data are the first reported for high density etching of GaN in an ICP system. Etch rate data was obtained using MOCVD grown GaN etched under the following ICP conditions; 1 mTorr pressure, 22.5 sccm  $\text{Cl}_2$ , 2.5 sccm  $\text{H}_2$ , 5 sccm Ar, 500 W ICP power, and 150 W rf-power with a corresponding dc-bias of  $-200 \pm 25$  V. In Figure 4, GaN etch rates are shown as a function of pressure. During these runs the rf-power was held constant at 150 W which resulted in an increase in dc-bias as the pressure was increased. Higher dc-biases were attributed to increased collisional recombination which decreased the plasma density at higher pressures. Etch rates increased for GaN as the pressure was increased from 1 to 5 mTorr suggesting a reactant limited regime at the lower pressures. As the pressure was increased to 10 mTorr, the GaN etch rates decreased due either to lower plasma density or redeposition on the etch surface.

In Figure 5, GaN etch rates are shown as a function of % $\text{Cl}_2$  flow in a  $\text{Cl}_2/\text{H}_2$  ICP- and ECR generated plasma. GaN samples etched in the ICP were grown by MOCVD and those etched in the ECR were grown by MO-MBE. The total  $\text{Cl}_2/\text{H}_2$  flow was held constant at 25 sccm with an additional 5 sccm of Ar to stabilize the plasma, 1 mTorr total pressure, 500 W ICP power, 850 W ECR power, and 150 W rf-power, with a corresponding dc-bias of  $-195 \pm 10$  V. The GaN etch rates increased by approximately 80% in the ICP as the % $\text{Cl}_2$  increased from 40 to 90 due to higher concentrations of reactive Cl. This was similar to samples etched in the ECR etch system where the GaN etch rates increased by approximately 75%. [12] GaN etch rates were greater in the ICP

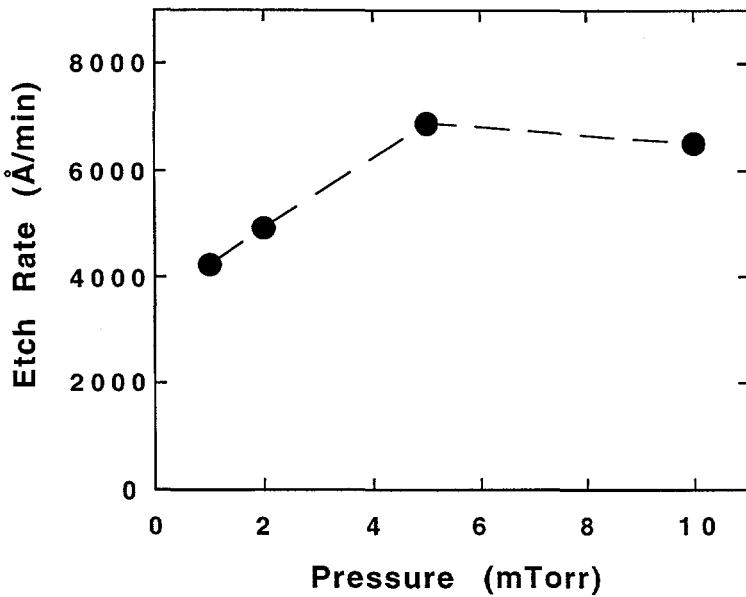


Figure 4. GaN ICP etch rates as a function of pressure for MOCVD grown samples.

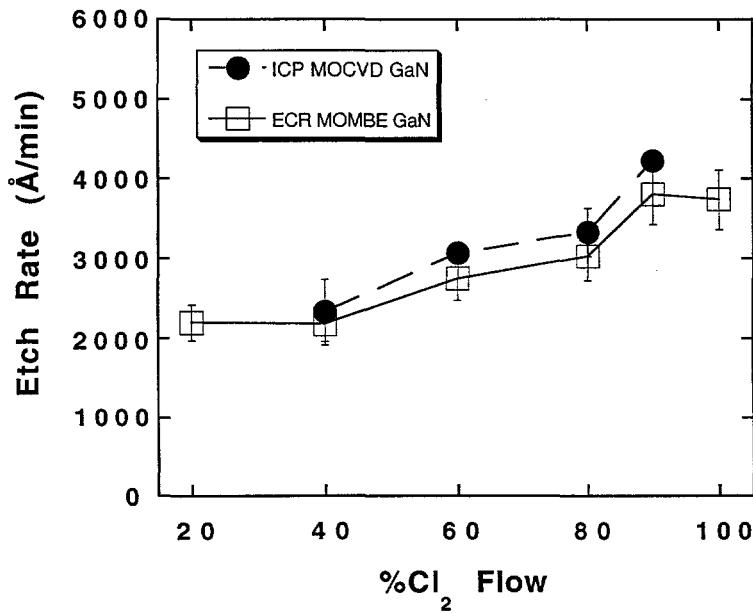


Figure 5. GaN ICP and ECR etch rates as a function of  $\%Cl_2$  flow in a  $Cl_2/H_2/Ar$  plasma. Samples etched in the ICP were grown by MOCVD whereas samples etched in the ECR were grown by MO-MBE.

despite using the MOCVD GaN which etched slower than MO-MBE GaN under the ECR etch conditions discussed above (see Figure 3).

In Figure 6, GaN etch rates are shown as a function of ICP power. During these runs the rf-power was held constant at 150 W which resulted in a decrease in dc-bias as the ICP power was increased. Lower dc-biases were attributed to increased plasma density and higher collisional frequencies at higher ICP powers. Etch rates increased for GaN as the ICP power was increased from 200 to 500 W suggesting a reactant limited regime. As the ICP power was increased further the GaN etch rates decreased due either to lower ion energies or desorption of the reactive species at the surface prior to reaction.

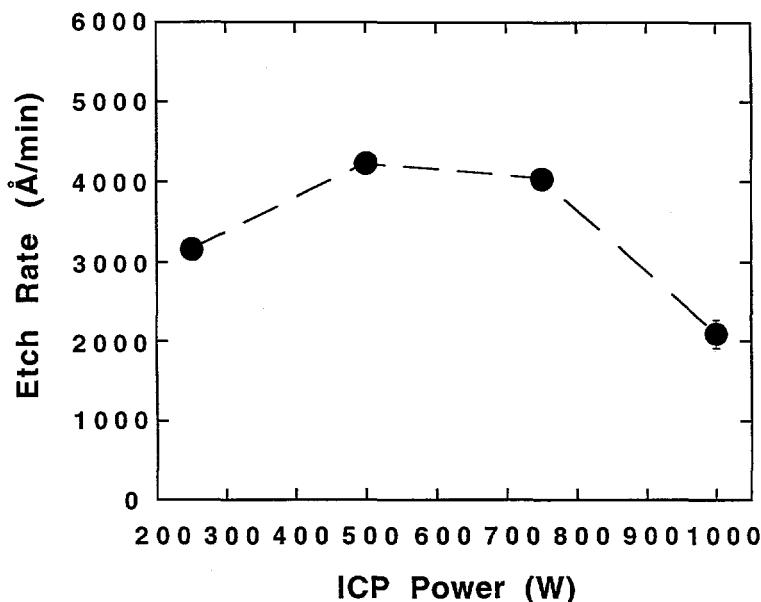


Figure 6. GaN ICP etch rates as a function of ICP power for MOCVD grown samples.

Figure 7 shows a SEM micrograph of MOCVD grown GaN etched in a  $\text{Cl}_2/\text{H}_2/\text{Ar}$  ICP-generated plasma. The GaN was overetched by approximately 15%. The plasma conditions were; 5 mTorr pressure, 500 W ICP power, 22.5 sccm  $\text{Cl}_2$ , 2.5 sccm  $\text{H}_2$ , 5 sccm Ar, 25°C electrode temperature, and 150 W rf-power with a corresponding dc-bias of  $-280 \pm 10$  V. Under these conditions the GaN etch rate was 6880 Å/min with highly anisotropic, smooth sidewalls. The vertical striations observed in the sidewall were due to striations in the photoresist mask which were transferred into the GaN feature during the etch. The sapphire substrate was exposed during the overetch period and showed significant pitting possibly due to defects in the substrate. With optimization of the masking process, these etch parameters may yield profiles and sidewall smoothness which enable etched laser facets.

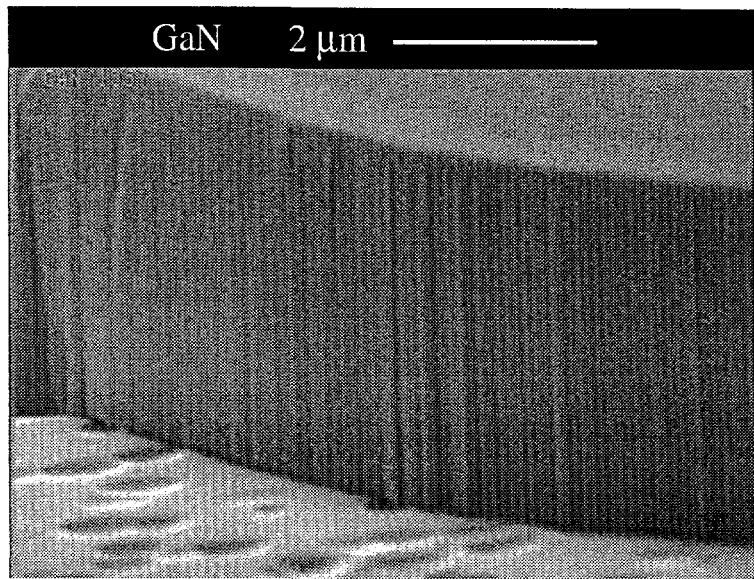


Figure 7. SEM micrograph of MOCVD GaN etched in an ICP-generated  $\text{Cl}_2/\text{H}_2/\text{Ar}$  plasma.

## CONCLUSIONS

In summary, the first etching of GaN are reported in a ICP etch system. GaN etch rates are reported as a function of pressure, plasma chemistry, ICP power, and rf-power. Etch rates of  $6875 \text{ \AA/min}$  were reported for MOCVD GaN in an ICP-generated  $\text{Cl}_2/\text{H}_2/\text{Ar}$  plasma at a dc-bias of  $-200 \pm 25 \text{ V}$ . ICP GaN etch rate data were compared to data obtained in ECR and RIE generated plasmas. The ICP etch rates were 10 to 50% faster than those etched in the ECR whereas GaN etch rates obtained in the RIE mode were approximately 5 to 10 times slower. This was attributed to slightly higher concentrations of reactive neutrals in the ICP as compared to the ECR and plasma densities which were 3 to 4 orders of magnitude greater in the ICP and ECR as compared to the RIE. GaN etch rates were also reported as a function of growth technique in the ECR. GaN grown by MO-MBE etched faster than the rf-MBE material which etched faster than the MOCVD material. This trend in etch rate correlates with rms-roughness of the as-grown films where the roughest films etched at the fastest rates. GaN etch rates approaching  $9000 \text{ \AA/min}$  were reported for MO-MBE and rf-MBE GaN samples etched in a  $\text{Cl}_2/\text{H}_2/\text{Ar}$  ECR-generated plasma at a dc-bias of  $-290 \pm 25 \text{ V}$ . High density plasmas are the etch technique of choice to provide anisotropic, smooth, high rate etching of GaN.

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## REFERENCES

- [1] S. Nakamura, M. Senoh, and T. Mukai, *Appl. Phys. Lett.* **62**, 2390 (1993).
- [2] M. A. Khan, J. N. Kuznia, A. R. Bhattacharai, and D. T. Olson, *Appl. Phys. Lett.* **62**, 1248 (1993).
- [3] S. C. Binari, L. B. Rowland, W. Kruppa, G. Kelner, K. Doverspike, and D. K. Gaskill, *Electron. Lett.* **30**, 1248 (1994).
- [4] J. C. Zolper, R. J. Shul, A. G. Baca, R. G. Wilson, S. J. Pearton, and R. A. Stall, *Appl. Phys. Lett.* **68**, 2273 (1996).
- [5] I. Adesida, A. Mahajan, E. Andideh, M. A. Khan, D. T. Olson, and J. N. Kuznia, *Appl. Phys. Lett.* **63**, 2777 (1993).
- [6] R. J. Shul, S. P. Kilcoyne, M. Hagerott Crawford, J. E. Parmeter, C. B. Vartuli, C. R. Abernathy, and S. J. Pearton, *Appl. Phys. Lett.* **66**, 1761 (1995).
- [7] R. J. Shul, A. J. Howard, S. J. Pearton, C. R. Abernathy, C. B. Vartuli, P. A. Barnes, and M. J. Bozack, *J. Vac. Sci. Technol. B* **13**, 2016 (1995).
- [8] S. J. Pearton, C. R. Abernathy, F. Ren, J. R. Lothian, P. W. Wisk, A. Katz, and C. Constantine, *Semicond. Sci. Technol.* **8**, 310 (1993).
- [9] S. J. Pearton, C. R. Abernathy, and F. Ren, *Appl. Phys. Lett.* **64**, 2294 (1994).
- [10] C. R. Abernathy, *J. Vac. Sci. Technol. A* **11**, 869 (1993).
- [11] C. Yuan, T. Salagaj, A. Gurary, P. Zawadzki, C. S. Chern, W. Kroll, R. A. Stall, Y. Li, M. Schurmann, C.-Y. Hwang, W. E. Mayo, Y. Lu, S. J. Pearton, S. Krishnankutty, and R. M. Kolbas, *J. Electrochem. Soc.* **142**, L163 (1995).
- [12] R. J. Shul, C. I. H. Ashby, D. J. Rieger, A. J. Howard, S. J. Pearton, C. R. Abernathy, C. B. Vartuli, P. A. Barnes, and P. Davis, *MRS Proceedings Fall Meeting*, Boston MA, 11/27-12/1/96, accepted.

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