DRY ETCHING OF III-V NITRIDES

SAND95-2699C
CONF-95/155--6

MRS invited
Fall

S. J. Pearton⁽¹⁾, R. J. Shul⁽²⁾, G. F. McLane⁽³⁾ and C. Constantine⁽⁴⁾

⁽¹⁾University of Florida, Gainesville, FL 32611 USA

⁽²⁾Sandia National Laboratories, Albuquerque NM 87185 USA

⁽³⁾Army Research Laboratory, Ft. Monmouth NJ 07703 USA

⁽⁴⁾Plasma Therm IP, St. Petersburg FL 33716 USA

ABSTRACT

The chemical inertness and high bond strengths of the III-V nitrides lead to slower plasma etching rates than for more conventional III-V semiconductors under the same conditions. High ion density conditions ($>3 \times 10^{11} \text{ cm}^{-3}$) such as those obtained in ECR or magnetron reactors produce etch rates up to an order of magnitude higher than for RIE, where the ion densities are in the 10^9 cm^{-3} range. We have developed smooth anisotropic dry etches for GaN, InN, AlN and their alloys based on $\text{Cl}_2/\text{CH}_4/\text{H}_2/\text{Ar}$, BCl_3/Ar , Cl_2/H_2 , Cl_2/SF_6 , HBr/H_2 and HI/H_2 plasma chemistries achieving etch rates up to $\sim 4,000 \text{ \AA}/\text{min}$ at moderate dc bias voltages ($\leq 150 \text{ V}$). Ion-induced damage in the nitrides appears to be less apparent than in other III-V's. One of the key remaining issues is the achievement of high selectivities for removal of one layer from another.*

INTRODUCTION

Applications for the wide bandgap nitrides include emitters in the blue/green/UV sections of the spectrum, solar-blind UV detectors and transistors capable of operation up to $\sim 500^\circ \text{C}$.⁽¹⁾ Much of the recent progress in these technologies has occurred on the materials side,⁽²⁻⁵⁾ with improvements in epitaxial growth quality, higher n- and particularly p-type doping levels and lower impurity concentrations. A significant road-block to realization of a continuous wave, electrically-pumped diode laser is the fact that most GaN and related alloys are grown on c- Al_2O_3 substrates with hexagonal symmetry. Therefore, cleavage to form laser facets is not feasible, at least with any practical yield. There is interest in dry etched laser facets for the nitrides and this will require achievement of smooth, highly anisotropic sidewalls in GaN-based epitaxial layers. A particularly relevant feature of forming laser mirrors or mesas by dry etching is that the sidewall usually has vertical striations that result from transfer of roughness on the mask edge into the semiconductors. The other requirement is that the GaN etch rates be reasonably fast (at least more than a few thousand angstroms per minute) since the total etch depth is going to be $\geq 4 \mu\text{m}$.

Table 1 shows a compilation of published dry etch rates for GaN.⁽⁶⁻¹⁶⁾ The conclusions from this data are fairly clear, namely

(i) etch rates under high ion density conditions (Electron Cyclotron Resonance, ECR, or magnetron-enhanced reactive ion etching, MIE) are much higher than for conventional RIE.

(ii) Halogen-based plasma chemistries produce much higher rates than for CH_4/H_2 , regardless of the etching technique.

(iii) the highest etch rates are $\leq 4,000 \text{ \AA}/\text{min}$, which is slower by a factor of 3-5 than conventional III-V's like GaAs under the same conditions.

*This work was performed at Sandia National Laboratories and was supported by the U.S. Department of Energy under contract DE-AC04-94-OR21400.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

In this paper we contrast some of the results obtained with Cl_2/H_2 , HBr/H_2 and HI/H_2 ECR etching of the binary nitrides in terms of rates, surface morphology and quality of the resultant sidewall. Under optimized conditions, the quality of this sidewall again appears to be determined by the initial mask material.

EXPERIMENTAL

The nitride layers were grown on Al_2O_3 or GaAs substrates by Metal Organic Molecular beam Epitaxy.⁽¹⁷⁻¹⁹⁾ The materials are defective single-crystal with a high density of threading dislocations and stacking faults ($\sim 10^{10} \text{ cm}^{-2}$). They were patterned with SiN_x masks and etched in several SLR 770 Plasma-Therm systems with rf biased, He-backside cooled sample chucks and ECR plasma sources.

RESULTS AND DISCUSSION

In general etch rates increased with rf power (or ion energy) or microwave power (ion current) and decreased with increasing pressure in $\text{Cl}_2/\text{CH}_4/\text{H}_2/\text{Ar}$ plasma chemistries, while there was little dependence on temperature. In Figure 1, we observe a general increase in etch rate as the microwave power and therefore the ion density is increased. This trend agrees with decreasing etch rates which were observed at higher pressures and lower ion densities. The etch rate for GaN and AlN increases moderately (less than a factor of 2) as the microwave power is increased from 125 to 850W, whereas the InN etch rate increases monotonically from 1040 to 3670 Å/min. Following exposure to the plasma, within experimental error, there is no change in the stoichiometry of the GaN surface for either 30 or 170°C etching and some residual atomic Cl is present. Similar results were observed for the InN and AlN samples.

Table I. Plasma chemistries for dry etching of GaN

Plasma	Technique	GaN etch rate (Å/min)	dc bias	Ref.
Cl_2/H_2	ECR	1,100	-150	10, 11
Cl_2/SF_6	ECR	900	-150	11
$\text{CH}_4/\text{H}_2/\text{Ar}$	ECR	400	-250	10
$\text{Cl}_2/\text{CH}_4/\text{H}_2/\text{Ar}$	ECR	3,100	-125	12
$\text{Cl}_2/\text{H}_2/\text{Ar}$	ECR	2,200	-100	13
CCl_2F_2	ECR	400	-250	14
BCl_3	RIE	500	-230	15
BCl_3	MIE	3,500	-75	16
$\text{SiCl}_4(\text{Ar}, \text{SiF}_4)$	RIE	500	-400	17
$\text{HBr}(\text{H}_2/\text{Ar})$	RIE	600	-400	18
HI/H_2	ECR	1,100	-150	19
HBr/H_2	ECR	900	-150	19
Ar	ion milling	250	-400	20
Cl_2/Ar	CAIBE	2,000	-600	13

RET2AM

Figure 1. Etch rates of GaN, InN and AlN as a function of microwave power for an ECR generated $\text{Cl}_2/\text{H}_2/\text{CH}_4/\text{Ar}$ plasma.

SEM micrographs of mesas formed in GaN by ECR etching in a $10\text{HI}/10\text{H}_2$, -150V , 1000W (microwave) discharge are shown in Figure 2. The SiN_x mask has been removed. The etched field has similar morphology to that of the initial (masked) area on top of the mesa. The anisotropy is reasonably good ($\sim 75^\circ$ sidewall angle). The striations present originate from similar roughness on the edge of the SiN_x mask, which in turn is transferred from the original photoresist that was used to pattern the SiN_x . This illustrates one of the key problems in trying to form an etched laser facet. The striations lead to scattering and loss of light either propagating down a laser stripe or incident on a facet.

Figure 2. SEM micrographs of feature etched into GaN with HI/H_2 .

The fastest etch rates were obtained with $\text{Cl}_2/\text{CH}_4/\text{H}_2/\text{Ar}$ ECR discharges. Figure 3 shows both GaN etch rate and root mean square (RMS) surface roughness measured by AFM, as a function of rf power in $10\text{Cl}_2/3\text{CH}_4/15\text{H}_2/10\text{Ar}$ discharges at a pressure of 1mTorr and a microwave power of 850W. Note that the etch rate increases in a linear fashion, suggesting that the sputter-assisted desorption of the etch products is the limiting step. The GaN surface roughness remains fairly similar to that of the as-grown material until ~150W, and worsens rapidly thereafter. However it is still possible to achieve a rate of $\sim 2,500\text{\AA}/\text{min}$ with excellent morphology. The onset of surface roughening corresponds to an increasing Ga-to-N ratio measured by Auger Electron Spectroscopy as N is preferentially lost by sputtering at high ion energies. The $\text{Cl}_2/\text{CH}_4/\text{H}_2/\text{Ar}$ plasma chemistry produces etch rates of $\geq 1\mu\text{m}/\text{min}$ for InP, GaAs and other more common III-V materials for these same conditions, emphasizing the difficulty in achieving very high rates for the nitrides.

Figure 3. GaN surface roughness and etch rate as a function of rf power in ECR $\text{Cl}_2/\text{CH}_4/\text{H}_2/\text{Ar}$ discharges.

Figure 4 (top) shows SEM micrographs of features produced in nitride structures with $10\text{HBr}/10\text{H}_2$, 1000W (microwave) discharges. The structure is an $\text{AlN}/\text{GaN}/\text{AlN}$ multilayer, which clearly demonstrates the differential undercut between the two materials in HBr/H_2 discharges. By contrast, use of a HI/H_2 plasma chemistry under the same conditions produces relatively uniform mesas (Figure 4, bottom). Note that the etched surface morphology even after removing $\sim 3.5\mu\text{m}$ is still good, and there is little differential etching between the foot of the mesa and areas out on the field. This is a benefit of the low process pressures employed under ECR conditions, which minimize such effects.

The sidewall roughness is also considerably worse under high dc bias conditions (Figure 5, left) due to mask erosion, whereas it is much smoother at dc biases $\leq 125\text{V}$ (right of figure)

Figure 4. SEM micrographs of features etched into AlN/GaN/AlN structure using HBr/H₂ or HI/H₂ (bottom).

CONCLUSIONS AND SUMMARY

The same basic plasma chemistries that are used for conventional III-V materials also work for GaN, AlN and InN. The resulting etch rates are typically 3-4 times slower than for GaAs, InP and so on. High ion densities conditions such as those found in ECR or MIE systems produce significantly faster rates than reactive ion etching. Sidewall corrugations on dry etched photonic device structures are usually present, and will require careful control of the masking material quality and its integrity during the etching processes.

Figure 5. SEM of laser structure sidewall using (left) high dc bias or (right) low dc bias.

ACKNOWLEDGMENTS

The authors at UF is partially supported by a DOD University Research Initiative administered through AFOSR (Project 3484RS). The work at SNL is supported by DOE under contract no. DE-AC04-94AL85000. The work at UF is performed in the Microfabritech facility.

REFERENCES

1. see for example, Properties of Group III Nitrides, ed. J. H. Edgar, INSPEC Datareview (IEEE, London UK, 1994).
2. I. Akasaki, H. Amano, M. Kito and K. Hiramatsu, J. Lumin. **48/49** 666 (1991).
3. T. Matsuoka, J. Cryst. Growth **124** 433 (1992).
4. C. R. Abernathy, S. J. Pearton, F. Ren, P. Wisk, J. Vac. Sci. Technol. B **11** 179 (1993).
5. S. Nakamura, T. Mukai and M. Senoh, Jap. J. Appl. Phys. **32** L169 (1993).
6. S. J. Pearton, C. R. Abernathy and F. Ren, Appl. Phys. Lett. **64** 2294 (1994).
7. S. J. Pearton, C. R. Abernathy and F. Ren, Appl. Phys. Lett. **64** 3643 (1994).
8. 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).
9. R. J. Shul, S. P. Kilcoyne, M. H. Crawford, J. E. Parmeter, C. B. Vartuli, C. R. Abernathy and S. J. Pearton, Appl. Phys. Lett. **66** 1761 (1995).
10. S. J. Pearton, C. R. Abernathy, F. Ren, J. R. Lothian, P. Wisk, A. Katz and C. Constantine, Semicond. Sci. Technol. **8** 310 (1993).
11. M. E. Lin, Z. F. Fan, Z. Ma, L. H. Allen and H. Morkoc, Appl. Phys. Lett. **64** 887 (1994).
12. G. F. McLane, L. Casas, S. J. Pearton and C. R. Abernathy, Appl. Phys. Lett. **66** 3328 (1995).
13. I. Adesida, A. Mahajan, E. Andideh, M. A. Khan, D. T. Olsen and J. N. Kuznia, Appl. Phys. Lett. **63** 2777 (1993).
14. A. T. Ping, I. Adesida, M. A. Khan and J. N. Kuznia, Electron. Lett. **30** 1895 (1994).
15. S. J. Pearton, C. R. Abernathy and C. B. Vartuli, Electron. Lett. **30** 1985 (1994).
16. S. J. Pearton, C. R. Abernathy, F. Ren and J. R. Lothian, J. Appl. Phys. **76** 1210 (1994).
17. C. R. Abernathy, J. Vac. Sci. Technol. A **11** 869 (1993).
18. C. R. Abernathy, J. D. MacKenzie, S. J. Pearton, S. Bharatan and K. S. Jones, J. Vac. Sci. Technol. A **13** 2104 (1995).
19. C. R. Abernathy, J. D. MacKenzie, S. J. Pearton and W. S. Hobson, Appl. Phys. Lett. **66** 1969 (1995).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.