ELSEVIER

Materials Chemistry and Physics 45 (1996) 80–83

MATERIALS
CHEMISTRY AND
PHYSICS

Materials Science Communication

Reactive ion etching of GaN with BCl_3/SF_6 plasmas

M.S. Feng [a,*], J.D. Guo [b], Y.M. Lu [a], E.Y. Chang [a]

[a] *Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30049, Taiwan, ROC*
[b] *Department of Electronic Engineering, Institute of Electronic Engineering, National Chiao Tung University, Hsinchu 30049, ROC*

Received 26 July 1995; accepted 11 September 1995

Abstract

Reactive ion etching (RIE) with BCl_3/SF_6 plasmas of high quality GaN films grown by low pressure metallorganic chemical vapor deposition (LP-MOCVD) is reported. A high etch rate of 2100 Å min^{-1} was achieved with BCl_3/SF_6 plasmas at gas pressure 40 mtorr, total gas flow rate 40 sccm, and radio-frequency (RF) power 300 W. The parameters affecting the etch rates such as BCl_3/SF_6 flow ratio, total gas pressure, RF power and self-bias voltage have been studied. Results indicate that under high RF power (300 W) the radical concentration is an etch rate-limiting factor at lower BCl_3/SF_6 pressure (lower than 40 mtorr), while self-bias voltage (ion bombardment) is a rate-limiting factor at higher pressure (more than 40 mtorr). Under lower RF power (150 W), self-bias voltage becomes the dominant factor of etch rate. Scanning electron microscopy (SEM) shows that the etched profile is highly anisotropic, and the etched area has some columnar residues due to Al compound contamination from the Al cathode during RIE.

Keywords: Reactive ion etching; Gallium nitride films; Plasmas

---

1. Introduction

Gallium nitride (GaN) is a compound semiconductor with a wide direct band gap (3.4 eV) and chemical stability. That makes it attractive for the applications of UV/blue light emitting diodes and high power temperature devices. However, because of the lack of a suitable substrate with a structural and thermal match to GaN, it is quite difficult to grow a high quality GaN film. Recently, significant improvements have been made due to the understanding of heteroepitaxial growth on highly mismatched substrates. High quality GaN epitaxial GaN films can be grown on sapphire substrates by metallorganic chemical vapor deposition (MOCVD) using a thin AlN or GaN layer deposited at low temperatures as the buffer layer. GaN based electronic and photonic devices including visible light emitting diodes [1–5], metal semiconductor field effect transistors [6], high electron mobility transistors [7], UV photoconductive detectors [8] and UV photovoltaic vectors [9] have been demonstrated. However, the etching technique for GaN electronics is relatively immature. A reliable and effective etching method is needed for device fabrication. However, GaN is fairly chemically inert. The most widely used chemical solutions can not react with GaN at room temperature [10–12]; even in a hot alkali solution [10] GaN is etched at a very low rate. The plasma based etching in chlorine-related and/or fluorine-related compounds has been shown as a viable approach for GaN etching. Pearton et al. [13] have succeeded in the dry etching of GaN with a rate 700 Å min^{-1} in electron cyclotron resonance (ECR) Cl_2/H_2 discharges. Lin et al. [14] and Adesida et al. [15] reported on the reactive ion etching (RIE) of GaN films using $SiCl_4/BCl_3$ and $SiCl_4/SiF_4$ plasmas with etch rates 17.5 Å s^{-1} and 500 Å min^{-1}, respectively.

In this report, the RIE etching process of high quality GaN films using BCl_3/SiF_6 discharges is presented. An etching rate as high as 2100 Å min^{-1} has been achieved.

2. Experimental

The GaN films are grown on sapphire substrates by low pressure metallorganic vapor deposition (LP-MOCVD). A horizontal type MOCVD reactor with water cooling is used for the epitaxial growth at low

---

* Corresponding author.

0254-0584/96/$15.00
SSDI 0254-0584(95)01703-3

pressure. The chamber (reactor) size is 2 cm high and 2.5 cm wide. Triethylgallium (TEGa) of purity >99.9999% and ammonia (NH_3) of purity >99.995% are used as the Ga and N sources, and hydrogen (H_2) as carrier gas. The TEGa bubble is operated at 10 °C and 200 torr. The carrier gas H_2 is purified with a Pt purifier. The gas mixture is fed to a slanted substrate by epifold at a velocity of 96 cm s^{-1}. Optical grade polished (0001)-orientation (C-face) sapphires are used as substrates. Substrate preparation consists of degreasing in successive rinses of trichloroethane, acetone, and methyl alcohol. Then the substrates are etched in a hot 3:1 H_2SO_4:H_2PO_3 solution (160 °C) for 10 min and placed on a graphite susceptor in the chamber. Before film growth, the substrates are heated to 1100 °C for 10 min in a pure H_2 ambient and for 10 min in a H_2/NH_3 ambient in order to remove the surface damaged layer and negative oxide. A thin GaN buffer layer (500 Å) is deposited at 525 °C just before the epitaxial GaN growth at 1000 °C. The flow rates of H_2, NH_3, and TEGa of the main flow are 1000 sccm, 1500 sccm, and 8.3 μmol min^{-1}, respectively. The growth rate is about 7500 Å h^{-1} at 1000 °C. The surfaces of the films are very smooth. Various thicknesses of the GaN layer are prepared ranging from 0.7 to 5 μm. The epitaxial GaN films are n-type (carrier concentration about 2×10^{17} cm^{-3}) with mobility 360 cm^2 V^{-1} per s.

The reactive ion etching process was carried out in a Plasma Therm 70 series RIE system. The RF-driven (13.56 MHz) cathode was made of aluminum. Both electrodes were water cooled to maintain a nominal temperature of 30 °C. The RIE chamber was equipped with a turbomolecular pump and a mechanical pump. The base pressure of the chamber was below 3×10^{-5} torr. The gas pressure was controlled by an auto pressure controller system (APC).

To examine the etched profile, the GaN samples were patterned with lift-off Ni–Cr masks. The etch depths were evaluated using a Dektak profilometer. Surface morphology and etching profiles were inspected by scanning electron microscopy (SEM). An energy dispersion X-ray spectrometer (EDS) was used for the chemical composition analysis of the residue on the etched surface.

3. Results and discussion

Fig. 1 shows the etch rate of (0001) GaN as a function of BCl_3/SF_6 gas composition at total gas pressure 40 mtorr, total gas flow rate of 40 sccm with a radio-frequency (RF) power of 300 W (power density 0.48 W cm^{-2}). The etch rate is poor in BCl_3 or SF_6 plasmas alone, but it is increased tremendously by using BCl_3/SF_6 mixtures. When the BCl_3/SF_6 gas flow ratio is equal to 1 (BCl_3 and SF_6 are 20 sccm), the etch rate is 2000 Å min^{-1}. The highest etch rate ever reported, 2100 Å min^{-1}, was obtained in the study when the gas flow rates of BCl_3 and SF_6 were 15 sccm and 25 sccm, respectively. The gas pressure was 40 mtorr and the RF power was 300 W. The enhancement of GaN etching by using the BCl_3/SF_6 mixture could be explained by the formation of the volatile products gallium chloride ($GaCl_x$) and nitrogen fluoride (NF_3). The removal of volatile $GaCl_x$ is much faster than that of involatile GaF_3. NF_3 has a much lower formation energy than N_2. However, Adesida et al. [15] reported that no chemical etching of GaN was driven from the addition of SiF_4 into $SiCl_4$ plasmas, and Pearton et al. [12,16] reported that CCl_2F_2/Ar discharges yield similar etching characteristics for GaN, compared to BCl_3/Ar. Therefore, the formation of the volatile product may not be the only reason for the high etch rate. Lin et al. [14] observed that the cathode self-bias voltage of $SiCl_4$ is lower than that of BCl_3 under the same

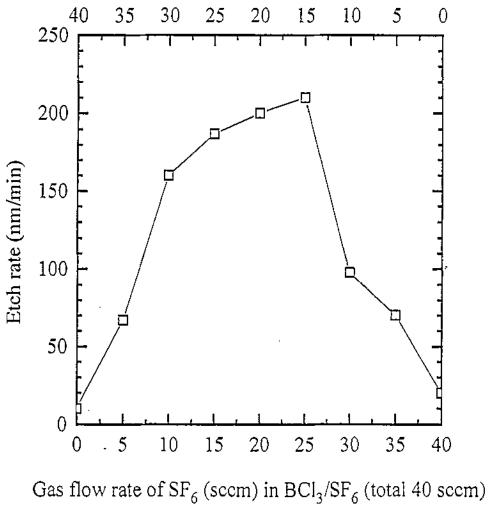

Fig. 1. The dependence of GaN etch rates on BCl_3/SF_6 gas composition at a fixed RF power 300 W and chamber pressure 40 mtorr.

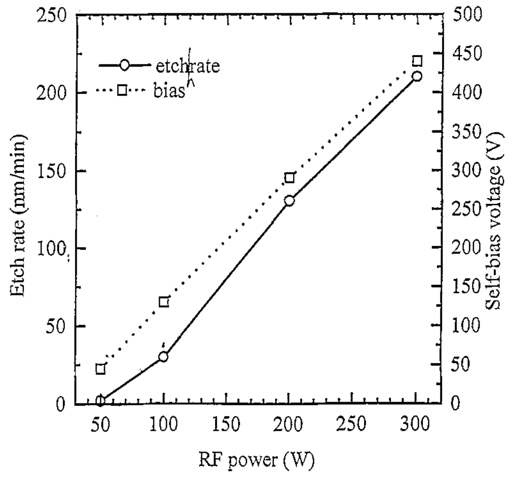

Fig. 2. The etch rates and the d.c. self-bias voltage as a function of RF power in 20 sccm BCL_3/20 sccm SF_6 discharges at chamber pressure 40 mtorr.

conditions for $SiCl_4$ and BCl_3 plasmas. The higher self-bias voltage built by BCl_3 plasma may be responsible for the enhanced etch rate in BCl_3/SF_6 discharges.

The etch rates and self-bias voltages as a function of RF power under the condition of 20 sccm BCl_3/20 sccm SF_6 discharges at 40 mtorr are shown in Fig. 2. It is observed that the etch rates increase with the increase of RF power from 50 to 300 W. The cathode self-bias voltages are also proportional to the RF power. This indicates that ion bombardment is an etch rate-limiting factor. We should also mention that the etch rate is 320 Å min^{-1} under the condition of 20 BCl_3/20 SF_6 mixture, 40 mtorr, and low RF power (100 W), which is much higher than that in the BCl_3 discharge alone, even at high RF power 400 W (105 Å min^{-1}). This confirms that the addition of SF_6 is essential for the enhancement of the etch rate. As mentioned above, in the BCl_3/SF_6 discharges, fluorine should be effective in removing nitrogen from GaN.

Fig. 3(a) shows the results of etch rates and d.c. self-bias voltages plotted as a function of BCl_3/SF_6 gas pressure at gas flow rate 10 sccm BCl_3/30 sccm SF_6, and RF power 300 W. The etch rate increases slightly in the pressure range of 8–40 mtorr. From gas pressure 40–100 mtorr, the etch rates decrease. The self-bias voltages decrease nearly linearly as the chamber pressure increases. At a lower pressure condition, the chemical radical concentration is low and there are not enough chemical radicals to react with GaN. Therefore the etch rates increase as the chamber pressure increases though the self-bias voltage decreases with increasing chamber pressure. While the chamber pressure is above 40 mtorr, the reactive chemical radical concentration is high enough and the etching rate is limited by the ion-bombardment effect. The results indicate that the etch rate-limiting factor is the reactive radical concentration in the low pressure condition (< 40 mtorr) and the self-bias voltage (ion bombardment) in the high pressure condition (> 40 mtorr), at high RF power (300 W). However, at lower RF power (150 W), the etch rates are

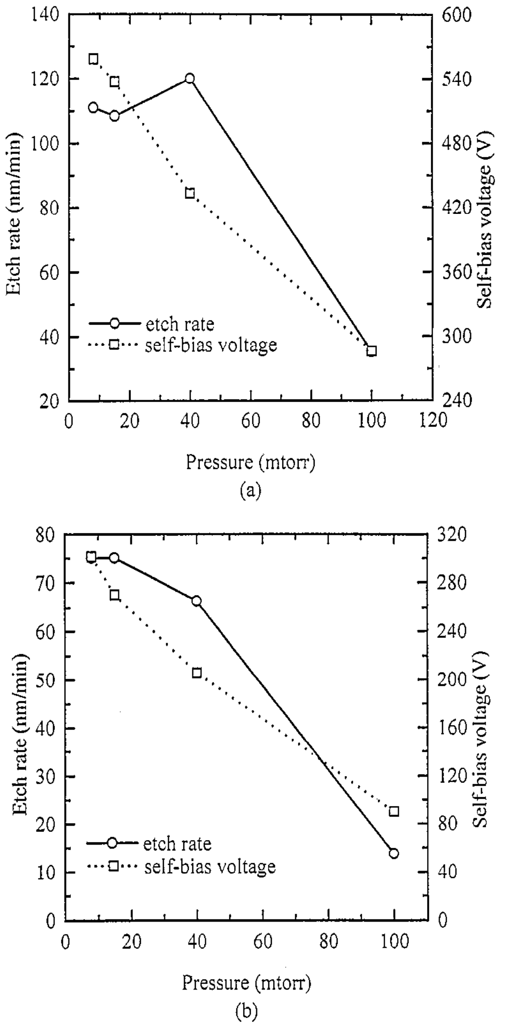

Fig. 3. The etch rates as a function of chamber pressure: (a) 10 sccm BCl_3/20 sccm SF_6 discharges at 300 W and (b) 20 sccm BCl_3/20 sccm SF_6 discharges at 150 W. The total gas flow rate was 40 sccm in both cases.

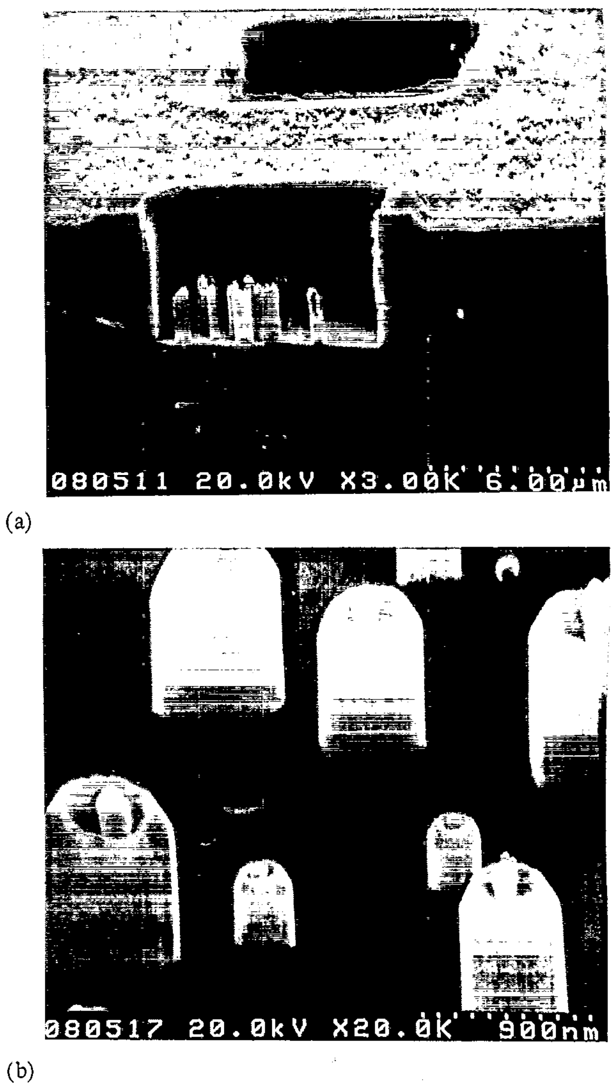

Fig. 4. The surface profile and surface morphology of the etched GaN: (a) etched profile of GaN etched at RF power 300 W, 40 mtorr, 20 sccm BCl_3/20 sccm SF_6 for 25 min and (b) 'candle like' residues on the etched area.

almost proportional to the self-bias voltage over the whole pressure range (10–100 mtorr) as shown in Fig. 3(b). Therefore, ion bombardment is the dominant factor in the etch rate at the lower RF power (150 W).

Fig. 4(a) and (b) shows the SEM micrographs of a GaN sample etched at RF power 300 W, 40 mtorr and 20 sccm BCl_3/20 sccm SF_6 discharges. The anisotropic etched profile can be seen from Fig. 4(a). Despite the sharp edge of the etched profile, lots of column residues exist at the etched surface (see Fig. 4(b)). These residues are probably caused by a micromasking effect. The results of quantitative EDS analysis show that there is aluminum oxide and/or aluminum fluoride at the top of these residues. Similar columnar residues of the SiC etched profile in fluorine-based plasmas have been found by Steckl and Yih [17]. They also proposed a formation mechanism by a micromasking effect. Originally, the aluminum particles were sputtered from the aluminum cathode and deposited on the GaN surface forming an unwanted micromask. Then the column residues formed gradually due to the micromasking effect. The column residues could be eliminated by the isolation of the Al cathode by graphite.

4. Summary

In summary, we have found that the BCl_3/SF_6 discharges produced by an RF generator provided reasonable etch rates and anisotropic profiles for GaN. Etch rates over 2000 Å min^{-1} have been achieved by using a BCl_3/SF_6 mixture (composition 15/25 to 20/20), total gas pressure 40 mtorr and RF power 300 W. This is the highest etch rate ever reported for GaN. The high etch rate and anisotropic etched profile make reactive ion etching in BCl_3/SF_6 discharges practical for GaN device fabrication. The column residues caused by an Al micromasking effect should be eliminated. Further investigation of these residues is still underway.

Acknowledgements

This work was supported by the National Sciences Council NSC 82-0417-E009-348 and Opto-Electronics & Systems Laboratories of ITRI C 83020. We wish to thank C.Y. Chang of the Nano Devices Laboratory for his encouragement in the III–V nitride effort.

References

[1] S. Nakamura, T. Mukai and M. Senoh, *Appl. Phys. Lett.*, *64* (1994) 28.
[2] H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, *Jpn. J. Appl. Phys.*, *28* (1989) L2112.
[3] S. Nakamura, M. Senoh and T. Mukai, *Jpn. J. Appl. Phys.*, *30* (1991) L1998.
[4] M. Asif Khan, J.N. Kuznia, J.M. Van Hove, N. Pan and J. Carter, *Appl. Phys. Lett.*, *60* (1992) 3027.
[5] S. Nakamura, T. Mukai and M. Senoh, *Appl. Phys. Lett.*, *62* (1993) 10.
[6] M. Asif Khan, J.N. Kuznia, A.R. Bhattarai and D.T. Olson, *Appl. Phys. Lett.*, *62* (1993) 1786.
[7] M. Asif Khan, A.R. Bhattarai, J.N. Kuznia and D.T. Olson, *Appl. Phys. Lett.*, *63* (1993) 1214.
[8] M. Asif Khan, J.N. Kuznia, D.T. Olson, J.M. Van Hove, M. Blasingame and L.F. Reitz, *Appl. Phys. Lett.*, *60* (1992) 2917.
[9] M. Asif Khan, J.N. Kuznia, D.T. Olson, J.M. Van Hove, M. Blasingame and L.F. Reitz, *Appl. Phys. Lett.*, *63* (1993) 1.
[10] J.I. Pankore, *J. Electrochem. Soc.*, *119* (1972) 1110.
[11] T.L. Chu, *J. Electrochem. Soc.*, *118* (1971) 1200.
[12] S.J. Pearton, C.R. Abernathy, F. Ren, J.R. Lothian, P.W. Wisk and A. Katz, *J. Vac. Sci. Technol. A*, *11* (1993) 1772.
[13] S.T. Pearton and C.R. Abernathy, *Appl. Phys. Lett.*, *64* (1994) 2294.
[14] M.E. Lin, *Appl. Phys. Lett.*, *64* (1994) 887.
[15] I. Adesida, A. Mahajan and E. Andideh, *Appl. Phys. Lett.*, *63* (1993) 2777.
[16] S.T. Pearton, C.R. Abernathy, F. Ren, J.R. Lothian, P.W. Wisk, A. Katz and C. Constantine, *Semicond. Sci. Technol.*, *8* (1993) 310.
[17] A.J. Steckl and P.H. Yih, *Appl. Phys. Lett.*, *60* (1992) 1966.