Reactive ion etching of GaN using BCl_3

M. E. Lin, Z. F. Fan, Z. Ma, L. H. Allen, and H. Morkoç
Materials Research Laboratory and Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, 104 South Goodwin Avenue, Urbana, Illinois 61801

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Reactive ion etching with $SiCl_4$ and BCl_3 of high quality GaN films grown by plasma enhanced molecular beam epitaxy is reported. Factors such as gas chemistry, flow rate, and microwave power affecting the etching rate are discussed. The etch rate has been found to be larger with BCl_3 than with $SiCl_4$ plasma. An etch rate of 8.5 Å/s was obtained with the BCl_3 plasma for a plasma power of 200 W, pressure of 10 mTorr, and flow rate of 40 sccm. Auger electron spectroscopy (AES) was used to investigate the surface of GaN films after etching. Oxygen contamination has been detected from the AES profiles of etched GaN samples.

III-V nitride materials have recently gained considerable recognition. Wide band gaps combined with extraordinary chemical stability at elevated temperatures possessed by III-V nitrides made them attractive for high temperature and high power applications as well as blue light emitters.[1] In order to harness these attractive accolades for device fabrication, procedures such as etching must be developed.

Up to now, there has been no reliable wet-chemical etch for high quality GaN. GaN has been found to dissolve in hot alkali solutions at a very slow rate.[2] Inherent stability of these wide band-gap nitrides precludes simple and pliable wet chemical processing, leaving plasma processing as the only viable approach. Moustakas,[3] and Adesida[4] reported, at informal meetings, on their preliminary investigations of reactive ion etching (RIE) of GaN films using CCl_2F_2 and CF_3Br/Ar (3:1), and $SiCl_4$ chemistry, respectively. The latter also took advantage of ion assisted etching for side wall profile as well as other purported benefits associated with that technique.

In this letter we report on the RIE etching of high quality GaN samples using BCl_3 chemistry. As part of this investigation, factors affecting the etch rate are detailed.

GaN films were grown on (0001) sapphire substrates which were cleaned by a hydrogen plasma treatment prior to growth.[5] The samples were then transferred into a Perkin Elmer 430 molecular beam epitaxy (MBE) system equipped with an electron cyclotron resonance (ECR) source to commence nitride growth. Films investigated were grown to a thickness of 1 μm. The details of the growth conditions have been reported elsewhere.[6] The undoped nitride films have a typical electron concentration in the range of 10^{17} cm^{-3} and were etched in a Plasma-Therm 700 Series RIE system after growth. Two different chemistries, BCl_3 and $SiCl_4$, were used to etch the nitride films, with more parametric attention given to BCl_3. Among the parameters investigated were flow rate, pressure, and plasma power. The plasma etched surfaces along with the control surface were analyzed for chemical composition using a Perkin-Elmer Scanning AES Multiprobe with an incident electron energy of 5 keV.

Figure 1 shows the effect of one of the process parameters, plasma power, on the etch rate of GaN in BCl_3 and $SiCl_4$ plasma. The plasma flow rate and the pressure used to generate the data of Fig. 1, were 15 sccm and 50 mTorr, respectively. Under the same plasma conditions, the etch rate with BCl_3 is larger than that with $SiCl_4$. The etch rate increases with increasing plasma power reaching 8 and 5.5 Å/s for BCl_3 and $SiCl_4$ plasmas at a power of 200 W. Moreover, as shown in Fig. 2 (solid squares), the etch rate decreases with increasing pressure for a flow rate and plasma power of 15 sccm and 150 W, respectively. The etch rate is about 17.5 Å/s with the BCl_3 chemistry for a pressure of 10 mTorr before bottoming out at about 4–4.5 Å/s for pressures over 40 mTorr.

We also noted that the cathode self-bias voltage increases from 42 to 231 V with the decrease of pressure from 100 to 10 mTorr. The increase in the self-bias voltage as the pressure decreases may be responsible for the enhanced etch rate. We should also mention that as the self-bias voltage increases the more likely that damage via ion bombardment will also increase. Furthermore, under the same conditions (20 sccm, 150 W, and 50 mTorr) for BCl_3 and $SiCl_4$ plasmas, the cathode self-bias voltage of $SiCl_4$ (105 V) is lower than that for BCl_3 (170 V). This can explain the larger etch rates obtained with the BCl_3 plasma with the caveat of increased plasma damage. Alternatively put, the $SiCl_4$ plasma may be a more efficient etchant than BCl_3 for the same extrinsic process conditions and voltage. Also shown in Fig. 2 (open circles) is the relationship between the BCl_3 flow rate and the etch rate at a pressure and plasma power of 50 mTorr and 150 W, respectively. As expected, the etch rate increases lin-

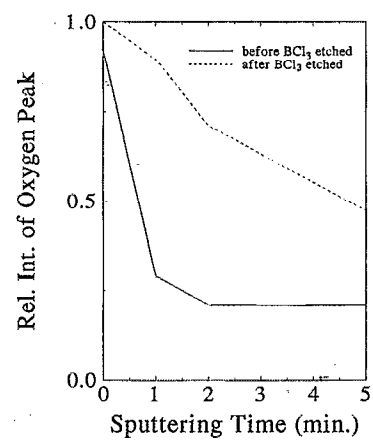

FIG. 1. GaN etch rate vs plasma power in BCl_3 and $SiCl_4$ plasmas (pressure=50 mTorr, and flow rate=15 sccm).

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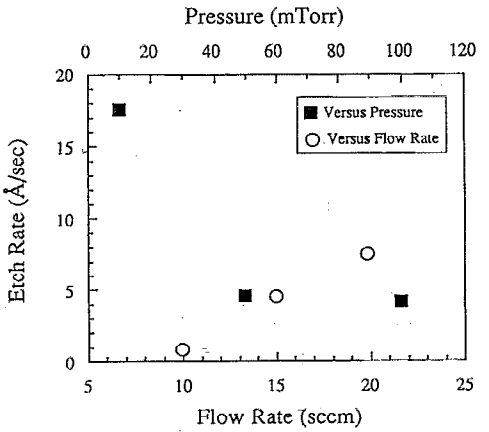

FIG. 2. GaN etch rate vs pressure in BCl_3 plasma (plasma power=150 W, and flow rate=15 sccm), solid squares. Also shown in open circles is the dependence of the etch rate on flow rate (plasma power=150 W, and pressure=50 mTorr).

early with increasing flow rate in the range of 0–20 mTorr. This linear relationship indicates that the etching process is determined solely by the availability of the reactive chlorine species. In this case the most plausible pathway for which etching is most likely to occur is through the dissociation of GaN by chlorine and formation of volatile $GaCl_3$.

The results reported here compare well with those of Ref. 3 wherein CCl_2F_2 and CF_3Br plasma processes were employed to etch GaN. When CCl_2F_2 chemistry was used an etch rate of 3 Å/s was obtained at 10 mTorr of pressure and 600 V. With the CF_3Br/Ar (3:1) chemistry much higher etching rates, about 828 Å/min, were obtained at 10 mTorr of pressure and 600 V. The side walls were found to be not vertical, instead forming a 60° angle with respect to the *R* plane of the basal plane sapphire substrates employed.

Changes in composition near the surface following exposure to air, is generally considered to be a good indirect indicator of the surface damage caused by the RIE process. As the amount of damage increases in the film the more reactive the GaN films will become. In this case the damaged

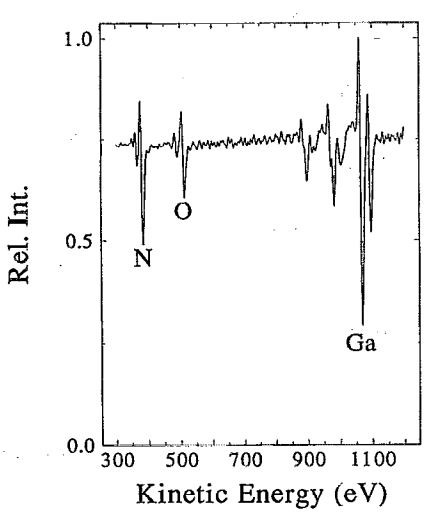

FIG. 3. Auger electron spectrum recorded after two minutes Ar^+ sputtering for GaN surface after plasma etching with BCl_3.

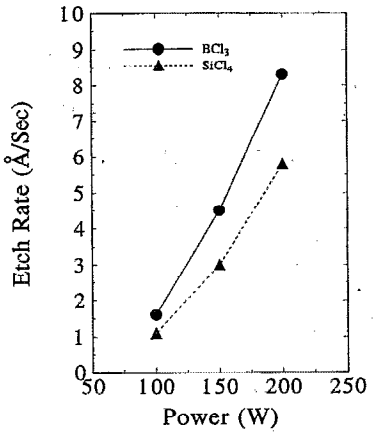

FIG. 4. Auger oxygen profile of BCl_3 etched nitride surface before and after etch. BCl_3 plasma was operated at 50 mTorr and 150 W.

surface layer of GaN readily reacts with oxygen. Shown in Fig. 3 is the first derivative AES electron count versus energy of an BCl_3 RIE GaN layer. The spectrum was recorded after a 2 min sputtering. Figure 4 shows the oxygen profiles of GaN films before and after the BCl_3 etch. Before the plasma treatment, oxygen is detected only at the surface. However, in samples which have undergone RIE treatment in BCl_3, an appreciable amount of oxygen (≈1 % at.) is present in the top 100 Å of the film. It is deduced that oxygen reacts with the damaged layer via O_2 diffusion from the surface, thus qualitatively indicating that damage has occurred via ion bombardment at the surface.

In conclusion, the absence of wet chemical etches makes imperative the development of dry etching processes such as RIE for GaN and its allied films. We have achieved etching of high quality GaN films in BCl_3 and $SiCl_4$ plasmas, the former leading to etch rate as high as 17.5 Å/s for, in order, 15 sccm, 150 W, and 10 mTorr, flow rate, plasma power, and pressure, respectively. For the same set of plasma conditions, BCl_3 was observed to have a larger etch rate than $SiCl_4$ due to inherently larger self-bias voltages developed with BCl_3 plasma. The etch rate with BCl_3 was observed to be linearly dependent on the flow rate. Increased chamber pressures led to smaller etch rates due to smaller self-bias voltages developed. The surface damage was limited to the top few hundred angstroms as determined from the AES electron spectrum of oxygen profile.

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