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New plasma chemistries for etching GaN and InN: BI_3 and BBr_3

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Smooth, anisotropic etching of InN and GaN is obtained in BI_3- or BBr_3-based Inductively Coupled Plasmas. Etch selectivities of 100:1 were achieved for InN over both GaN and AlN in the BI_3 mixtures, while for BBr_3 discharges values of 100:1 for InN over AlN and 25:1 for InN over GaN were measured. The etched surface morphologies of InN and GaN with both mixtures are similar or better than those of control samples.

1 Introduction

The predominant plasma chemistries for dry etching of III-nitrides are based on Cl_2 [a] [2] [3] [4] [5] [6] [7] [8]. These have worked well for fabrication of laser and light-emitting diodes where the etching is non-selective [9] [10]. As attention turns to application of nitride materials in high power, high temperature electronics, there is increasing need for plasma chemistries that will remove In-based nitrides from underlying AlGaN alloy layers with high selectivity. It is expected that InN or InGaN contact layers will be necessary to produce acceptable contact resistance in transistor or thyristor devices. Besides Cl_2-based mixtures, there have been some reports of Br_2(in the form of HBr) [11] [12] and I_2(in the form of HI) [12] plasma etching of nitrides. In particular it has long been recognized that InI_x etch products have higher volatility than the corresponding $InCl_x$ species, making iodine an attractive etchant for InGaN alloys.

In this paper we describe use of two new dry etch chemistries for nitrides, namely BI_3 and BBr_3. Both are found to provide high etch selectivity for InN over both GaN and AlN. Vartuli et al. [13] previously reported selectivities of ~6 for InN over GaN in CH_4/H_2 Electron Cyclotron Resonance(ECR) plasmas, whereas Cl_2/Ar, ICl/Ar and IBr/Ar chemistries all showed values less than unity. Subsequently, Shul et al. [14] [15] investigated selective Inductively Coupled Plasma(ICP) etching of group III-nitrides in BCl_3 and Cl_2 mixtures with addition of Ar, N_2, SF_6 and H_2, and found selectivities as high as 8 for GaN/AlN and 6.5 for GaN/InN under optimum conditions. Our new results for BI_3 and BBr_3 mean that there are now available chemistries that will allow the full range of desired etching properties, i.e. non-selective, selective for In-based nitrides over GaN and AlN, and selective for GaN over AlN and In-based materials. We also find that BI_3 and BBr_3 produce smooth surface morphologies and anisotropic etched sidewalls.

2 Experimental

The epitaxial films were grown on c-plane α-Al_2O_3 by either Metal Organic Chemical Vapor Deposition(GaN) at 1040°C, or by Metal Organic Molecular Beam Epitaxy [16] (InN and AlN) at 600°C and 800°C, respectively. The layers were 1.2-3.0μm thick and were nominally undoped($n \sim 6x10^{16}cm^{-3}$ for GaN, $n \sim 10^{20}cm^{-3}$ for InN and resistive, $> 10^8\Omega\cdot cm$, for AlN).

BI_3 is a white crystalline solid with a melting point of ~40°C, while BBr_3 is a red liquid with a boiling point of 91.2°C. Approximately 50g of each was placed in a quartz container within a stainless steel vacuum vessel heated to ~45°C to increase the vapor pressure of the reactants. The resultant flow rates were in the range of 5-10 standard cubic centimeters per minute(sccm). Etching was performed in a Plasma Therm 790 system in which the samples are thermally bonded to a Si carrier wafer mechanically clamped to an rf-biased(13.56MHz, 450W), He backside cooled chuck. The 3 turn coil ICP source operates at 2MHz and powers up to 1500W. The process pressure was held constant at 5mTorr. Typically Ar was added to the gas flow to facilitate plasma ignition and enhance the physical component of the etching.

Etch rates were obtained from stylus profilometry measurements of the features, while scanning electron microscopy(SEM) and atomic force microscopy(AFM) were used to examine surface morphology.

3 Results and Discussion

Discharges were readily sustained with both BI_3 and BBr_3. Pure BI_3 plasmas were blue-white, and optical emission spectra revealed many strong transitions in the range 380-440nm(Figure 1, top), which are related to atomic iodine. Similarly, pure BBr_3 discharges were slightly darker in appearance, but also showed many atomic transitions dominated by lines at 484nm, 658nm and 826nm(Figure 1, bottom).

Figure 2 shows etch rates(top), etch yields(center) and selectivities for InN over both GaN and AlN(bottom) as a function of BI_3 percentage in BI_3/Ar discharges with fixed source power(750W) and rf chuck power(150W). Note that dc chuck self-bias decreases as BI_3 content increases, indicating that the ion density in the plasma is increasing under these conditions, and that BI_3 is therefore more easily ionized than Ar. The InN etch rate is monotonically dependent on BI_3 content, indicating the presence of a strong chemical component to its etching. By contrast AlN and GaN show insignificant rates until ~50% BI_3 where values of ~500Å·min^{-1} for AlN and ~1700Å·min^{-1} for GaN are obtained. Further increasing the BI_3 content in discharges actually leads to a reduction in etch rate for those two materials. There are at least two possible explanations for this result. First, the corresponding fall-off in chuck self-bias and hence ion energy under these conditions may more than compensate for the increased active iodine available. Second, since GaI_x and AlI_x etch products are not that volatile, a selvedge or reaction layer may form involving these species that quenches further etching. A precedent for the latter mechanism is reactive ion etching of InP in Cl_2 plasmas, where etching does not proceed unless elevated sample temperatures or high dc biases are used to facilitate removal of the $InCl_3$ etch product [17]. Due to the behavior of GaN and AlN etch rates with BI_3 percentage, the InN selectivity to both materials initially increases but also goes through a minimum. Note however that selectivities of > 100 can be achieved for both InN/AlN and InN/GaN.

Similar data is shown in Figure 3 for BBr_3/Ar discharges with fixed source power(750W) and rf chuck power(350W). We needed higher rf powers to initiate etching with BBr_3 than with BI_3. Another difference is that now dc self-bias increases with BBr_3 content, indicating that it is less readily ionized than Ar. The etch rate of InN again increases with boron halide content, while GaN shows significant rates(~1800Å·min^{-1}) only for pure BBr_3 discharges. By contrast, AlN shows very low etch rates over the whole range of conditions investigated. Maximum selectivities of ~100:1 for InN/AlN and ~7.5:1 for InN/GaN are obtained.

One feature of the etching with these two new chemicals was the good surface morphologies obtained. Figure 4 shows examples of AFM scans(10x10μm^2) of GaN before and after BI_3/Ar etching with different BI_3 percentages, while Figure 5 shows similar data for BBr_3/Ar etched samples. While there are clearly differences in the resulting surfaces, with pits or hillocks evident in some cases, the most important result is that all of the etched surfaces have lower root-mean-square(RMS) roughness than the control value. Figure 6 shows the dependence of RMS values for both chemistries as a function of discharge composition. This type of surface smoothing has been reported previously for GaN [18], and ascribed to the angular dependence of ion milling rates producing faster removal of sharp features. We were able to obtain AFM data over a much narrower range of conditions for InN because of the much higher etch rates and consequent difficulty in etching to a pre-determinant depth for AFM measurements, but the surfaces were also quite good for this material.

In high density plasma sources, ion density is basically controlled by the power applied to the source, while ion energy is mostly dependent on applied rf chuck power. If the latter is fixed, then increasing the source power will reduce the chuck self-bias. Figure 7 shows that source power had a significant effect only on InN etch rate for $4BI_3/6Ar$ discharges at fixed rf power(150W). Etch yields are quite low, even for InN, and under the best conditions about 9 incident ions on average are required to remove one In and one N atom. The etch selectivity for InN/AlN and InN/GaN increases with source power and reaches ~100 at 750W.

Basically similar trends were observed for $4BBr_3/6Ar$ discharges as a function of source power, as shown in Figure 8. InN etch rates and etch yields are lower than with BI_3/Ar, and therefore selectivities of ~30 for InN/AlN and ~40 for InN/GaN were obtained. There is a minimum in the InN/GaN data around 750W source power, which may result from a competition between increased etch rate of GaN due to higher flux, and desorption of the active bromine by ion-assistance at still higher fluxes.

As mentioned above, incident ion energy in high density plasmas can be controlled by the rf chuck power. The resultant dc self-bias is the potential through which ions are accelerated as they cross the plasma sheath. Ion energy is then the sum of plasma potential (typically 20-30eV), plus the dc chuck bias. Figure 9 shows the dependence of etch rate, etch yield and InN/AlN and InN/GaN selectivity on rf chuck power for $4BI_3/6Ar$ discharges at fixed source power(750W). While GaN and AlN etch rates increase only at the highest chuck powers investigated, the InN etch rate increases rapidly to 250W, indicating a strong ion-assisted component to the etching, and then decreases at higher powers. This behavior produces corresponding maxima in both etch yield and selectivity. This type of behavior is quite common to high density plasma etching of III-V materials, where the etching is predominantly ion-assisted desorption of somewhat volatile products, with insignificant rates under ion-free conditions [19]. In this scenario, at very high ion energies, the active etching species(iodine neutrals in this case) can be removed by sputtering before they have a chance to complete the reaction with substrate atoms.

Similar data is shown in Figure 10 for BBr_3/Ar mixtures, as a function of rf chuck power. For this chemistry the InN etch rate saturates and we did not observe a reduction, although this might be expected to occur if higher powers could be applied(our power supply is limited to 450W). GaN does show an etch rate maximum at ~350W, producing a minimum in the resultant InN/GaN selectivity. Note again that the InN etch yields for BI_3/Ar are much higher than for BBr_3/Ar.

AFM scans for InN before and after etching in BI_3/Ar discharges as a function of applied rf chuck power at fixed plasma composition and source power are shown in Figure 11. Note that the RMS surface roughness remain roughly constant and similar to that of the control value. Similar data is shown in Figure 12 for samples etched in BBr_3/Ar at different rf chuck powers. In this case, there is consistent smoothing of the surface occurring, as shown in the data in Figure 13. The fact that the smoothing effect decreases at higher powers is probably not unexpected, given that very high ion energies should eventually produce preferential sputtering of the higher N atoms.

Finally, we found the etched features to have vertical sidewalls which is expected given the ion-assisted nature of the etch mechanism. Figure 14 shows a few examples of SEM micrographs taken from GaN samples etched in either BI_3/Ar or BBr_3/Ar, using a SiN_x mask. The striations on the feature sidewalls originate from roughness on the initial photoresist mask used to pattern the SiN_x, and then this is replicated into the GaN.

4 Summary and Conclusions

Two new plasma chemistries have been examined for etching III-nitrides. BI_3 produces etch rates for InN as high as 7,500 $Å \cdot min^{-1}$ under ICP conditions, whereas the maximum rate with BBr_3 is ~5,500 $Å \cdot min^{-1}$. The rate for AlN are low under all conditions, while GaN rates up to 1700-1800 $Å \cdot min^{-1}$ can be obtained in both mixtures. Under optimum conditions etch selectivities of ~100 for InN over AlN and GaN were achieved in BI_3 chemistries, while in BBr_3 maximum values of ~100 for InN/AlN and ~25 for InN/GaN were obtained. These are the highest values reported for high density conditions, and result from the good volatility of InI_x etch products. The etched surface morphologies of GaN and InN were also very good, having similar or even lower RMS roughness than control samples. Both of these plasma chemistries appear useful for selective etch processes in nitride electronic device fabrication.

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REFERENCES

[a] See, for example, ref. [1]and references therein.

[1] H. P. Gillis, D. A. Choutov, K. P. Martin, *J. Miner. Met. Mater. Soc.* ***48***, 50 (1996).

[2] "Etching of III-nitrides",S.J. Pearton and R.J. Shul, in GaN, Vol I, ed. J.I. Pankove and T.D. Moustakas, (Academic Press, San Diego, 1998)

[3] "High density ECR etching of group III-nitrides", R.J. Shul, in GaN and Related Materials, ed. S.J. Pearton,(Gordon and Breach, NY 1997)

[4] I. Adesida, A. Mahajan, E. Andideh , M. Asif Khan, D. T. Olsen, J. N. Kuznia , *Appl. Phys. Lett.* ***63***, 2777-2779 (1993).

[5] L. Zhang, J. Ramer, J. Brown, K. Zheng, L. F. Lester, S. D. Hersee , *Appl. Phys. Lett.* ***68***, 367-369 (1996).

[6] CB Vartuli, JD MacKenzie, JW Lee, CR Abernathy, SJ Pearton, RJ Shul, *J. Appl. Phys.* ***80***, 3705-3709 (1996).

[7] RJ Shul, GB McClellan, SA Casalnuovo, DJ Rieger, SJ Pearton, C Constantine, C Barratt, RF Karlicek, C Tran, M Schurman, *Appl. Phys. Lett.* ***69***, 1119-1121 (1996).

[8] S. J. Pearton, C. R. Abernathy , F. Ren , *Appl. Phys. Lett.* ***64***, 2294-2296 (1994).

[9] Shuji Nakamura, Takashi Mukai, Masayuki Senoh , *Appl. Phys. Lett.* ***64*** , 1687-1689 (1994).

[10] S Nakamura, M Senoh, S Nagahama, N Iwasa, T Yamada, T Matsushita, H Kiyoku, Y Sugimoto, *Jpn. J. Appl. Phys.* ***35*** , L74-L76 (1996).

[11] AT Ping, I Adesida, MA Khan, et al., *Electron. Lett.* ***30*** , 1895-1897 (1994).

[12] SJ Pearton, CR Abernathy, CB Vartuli, *Electron. Lett.* ***30*** , 1985-1986 (1994).

[13] C. B. Vartuli, S. J. Pearton, J. D. MacKenzie, C. R. Abernathy, R. J. Shul, *J. Electrochem. Soc.* ***143*** , L246 (1996).

[14] R. J. Shul, C. G. Willison, M. M. Bridges, J. Han, J. W. Lee, S. J. Pearton, C. R. Abernathy, J. D. MacKenzie, S. M. Donovan, L. Zhang, L. F. Lester, unpublished.

[15] R. J. Shul, C. G. Willison, M. M. Bridges, J. Han, J. W. Lee, S. J. Pearton, C. R. Abernathy, J. D. MacKenzie, S. M. Donovan, *Mater. Res. Soc. Symp. Proc.* ***478*** , 208 (1998).

[16] C. R. Abernathy, *Mat. Sci. Eng. Rep.* ***14*** , 203 (1996).

[17] J. W. Lee, J. Hong, S. J. Pearton, *Appl. Phys. Lett.* ***68*** , 847 (1996).

[18] CB Vartuli, SJ Pearton, JW Lee, J Hong, JD MacKenzie, CR Abernathy, RJ Shul, *Appl. Phys. Lett.* ***69*** , 1426-1428 (1996).

[19] S. J. Pearton, *Int. J. Mod. Phys. B* ***8*** , 1761 (1994).

FIGURES

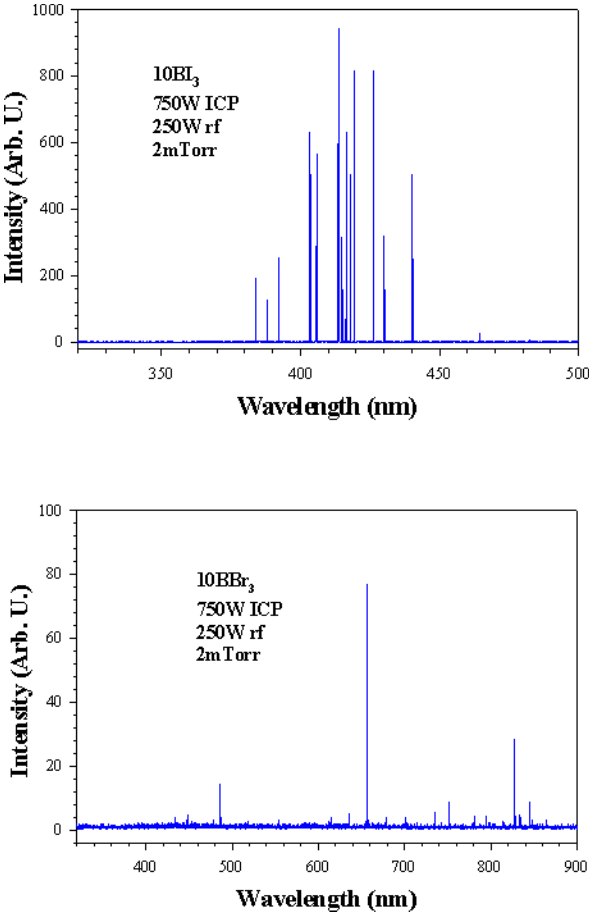


Figure 1. Optical emission spectra from pure BI_3(top) or BBr_3(bottom) discharges under ICP conditions.

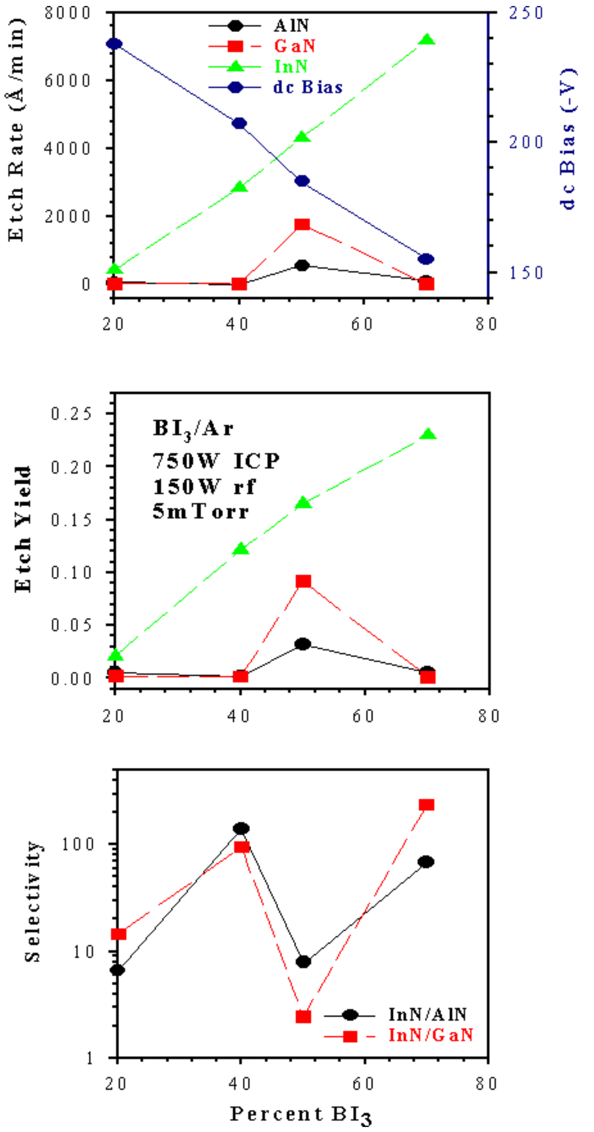


Figure 2. Nitride etch rates(top) and yields(center) and etch selectivities for InN/AlN and InN/GaN(bottom) in BI_3/Ar discharges(750W source power, 150W rf chuck power, 5mTorr) as a function of BI_3 content.

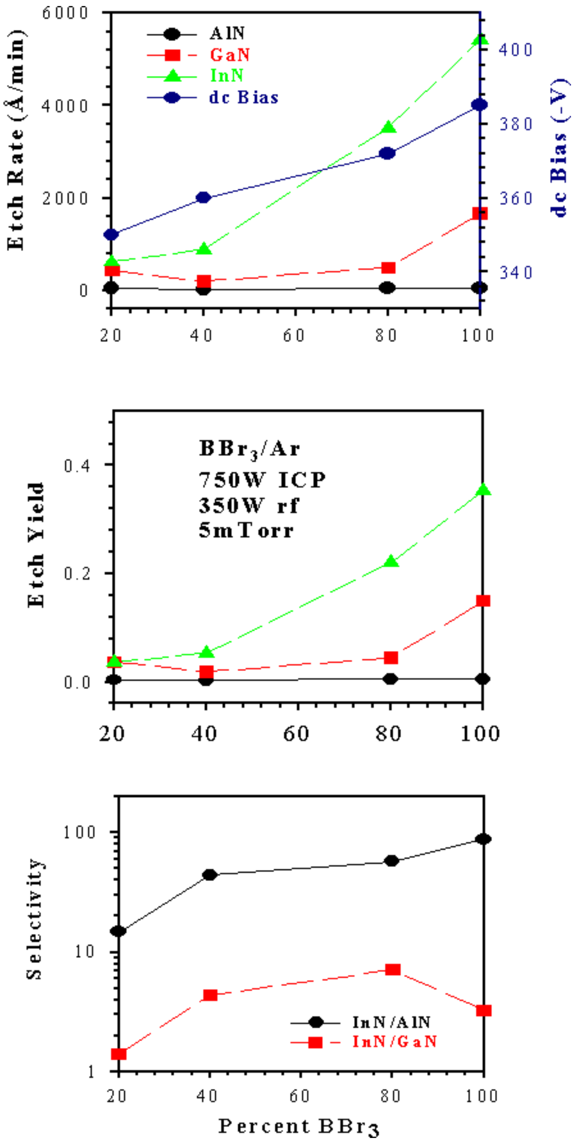


Figure 3. Nitride etch rates(top) and yields(center) and etch selectivities for InN/AlN and InN/GaN(bottom) in BBr_3/Ar discharges(750W source power, 350W rf chuck power, 5mTorr) as a function of BBr_3 content.

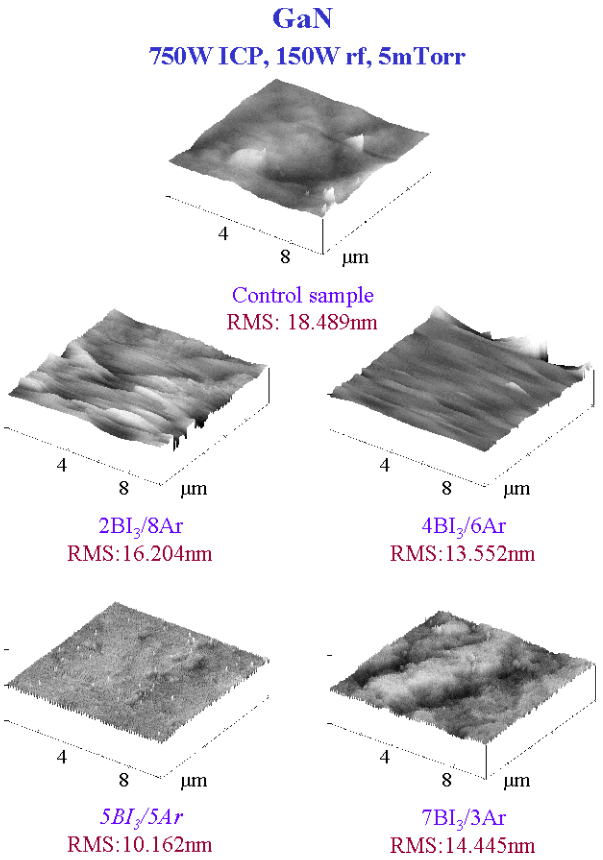


Figure 4. AFM scans of GaN surfaces before and after etching in 750W source power, 150W rf chuck power BI_3/Ar discharges as a function of BI_3 content.

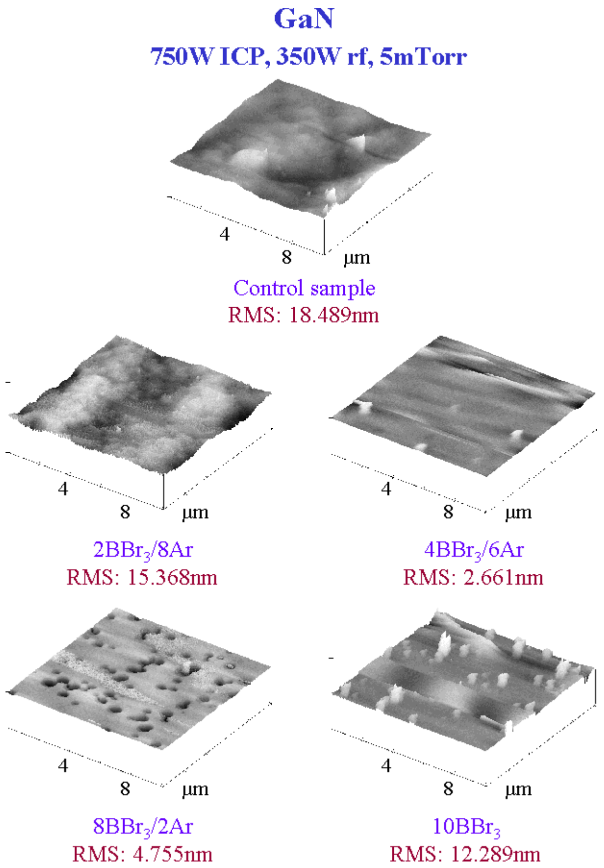


Figure 5. AFM scans of GaN surfaces before and after etching in 750W source power, 350W rf chuck power BBr_3/Ar discharges as a function of BBr_3 content.

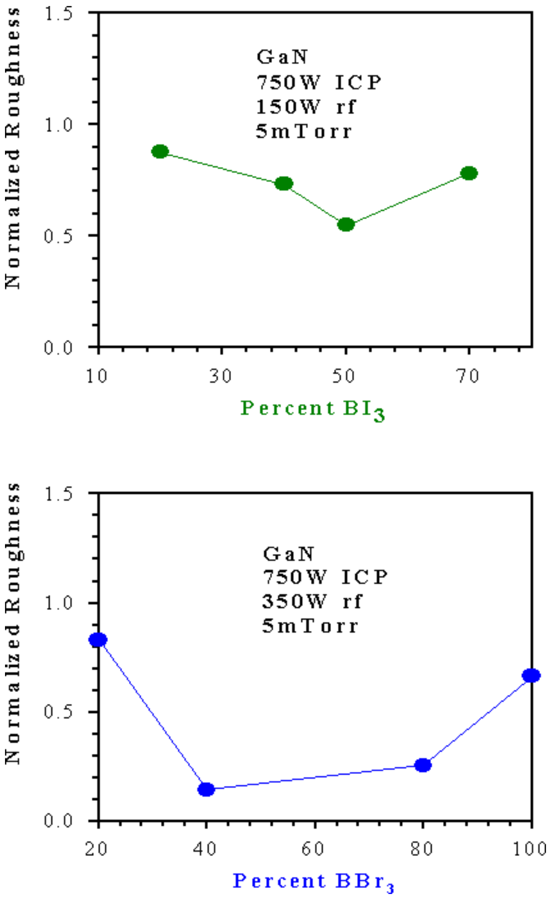


Figure 6. Dependence of GaN normalized etched surface roughness on boron halide percentage in BI_3/Ar or BBr_3/Ar discharges.

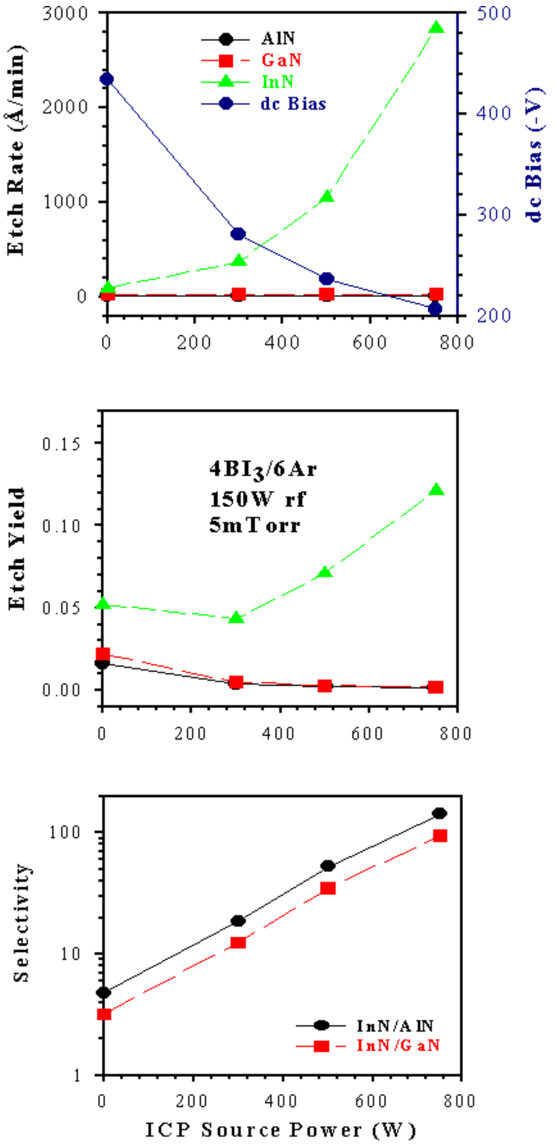


Figure 7. Nitride etch rates(top) and yields(center) and etch selectivities for InN/AlN and InN/GaN(bottom) in $4BI_3/6Ar$ discharges(150W rf chuck power, 5mTorr) as a function of ICP source power.

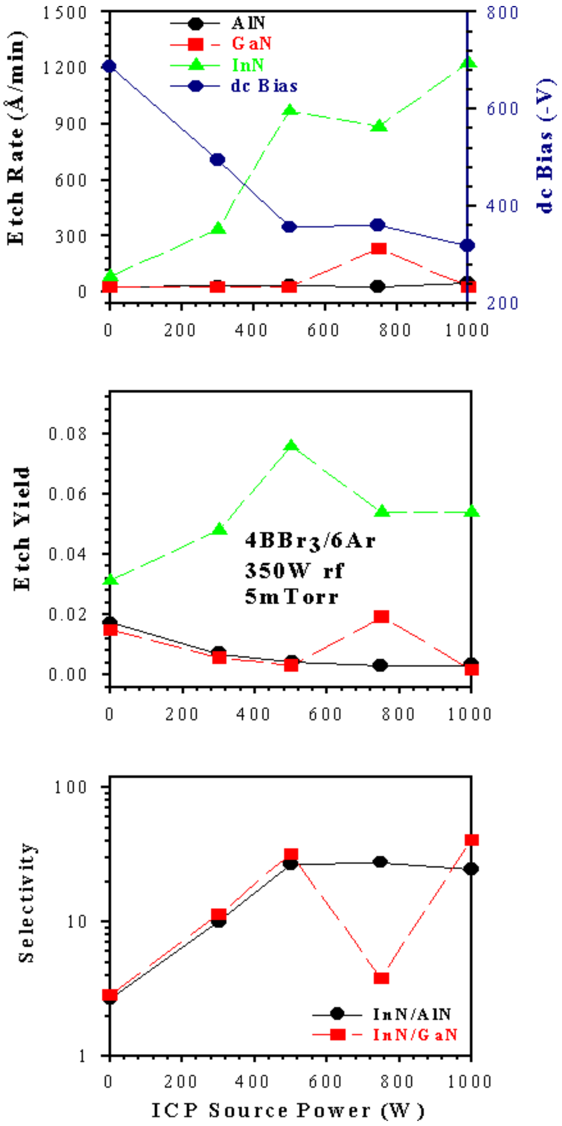


Figure 8. Nitride etch rates(top) and yields(center) and etch selectivities for InN/AlN and InN/GaN(bottom) in 4BBr$_3$/6Ar discharges(350W rf chuck power, 5mTorr) as a function of ICP source power.

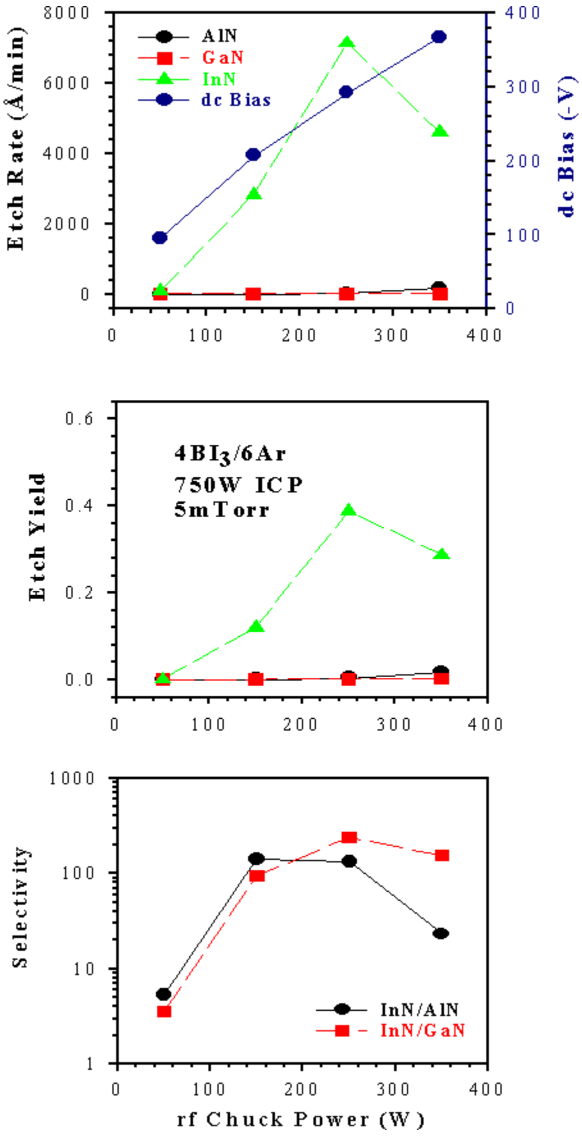


Figure 9. Nitride etch rates(top) and yields(center) and etch selectivities for InN/AlN and InN/GaN(bottom) in 4BI$_3$/6Ar discharges(750W source power, 5mTorr) as a function of rf chuck power.

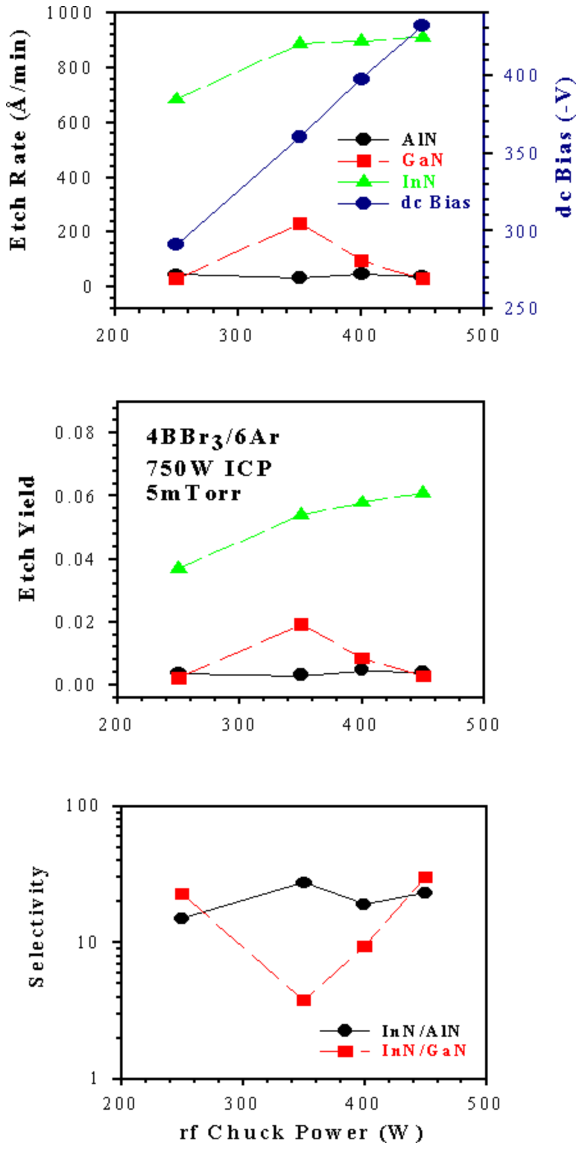


Figure 10. Nitride etch rates(top) and yields(center) and etch selectivities for InN/AlN and InN/GaN(bottom) in $4BBr_3/6Ar$ discharges(750W source, 5mTorr) as a function of rf chuck power.

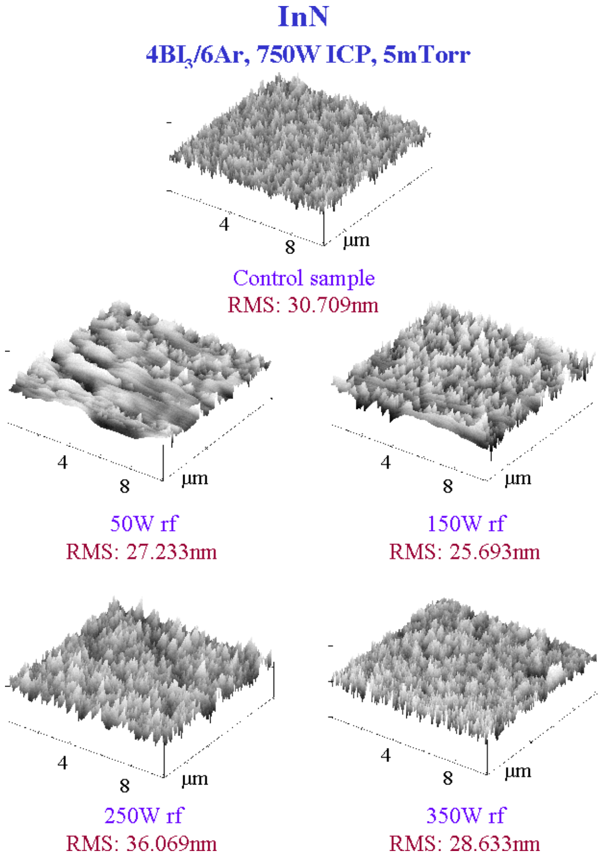


Figure 11. AFM scans of InN surfaces before and after etching in 750W source power, $4BI_3/6Ar$ discharges as a function of rf chuck power.

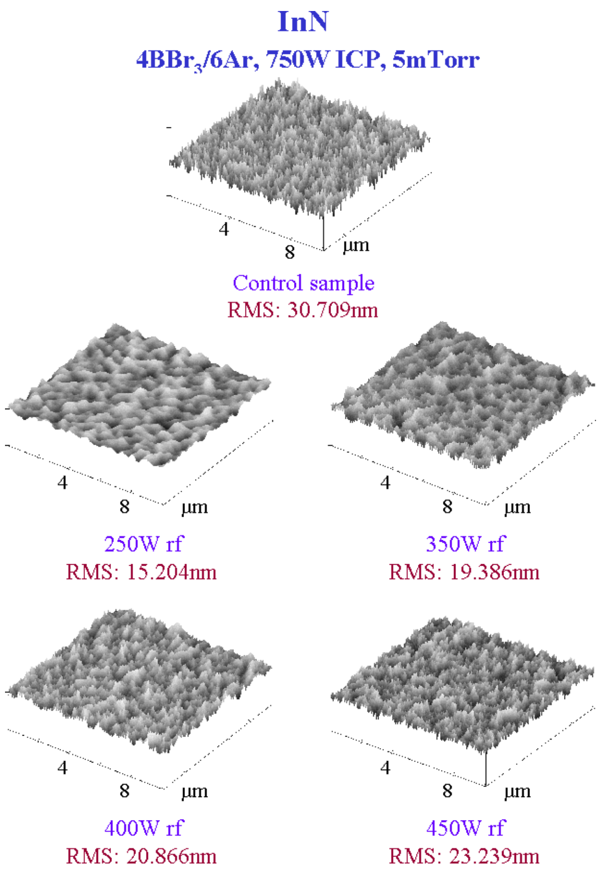


Figure 12. AFM scans of InN surfaces before and after etching in 750W source power, $4BBr_3/6Ar$ discharges as a function of rf chuck power.

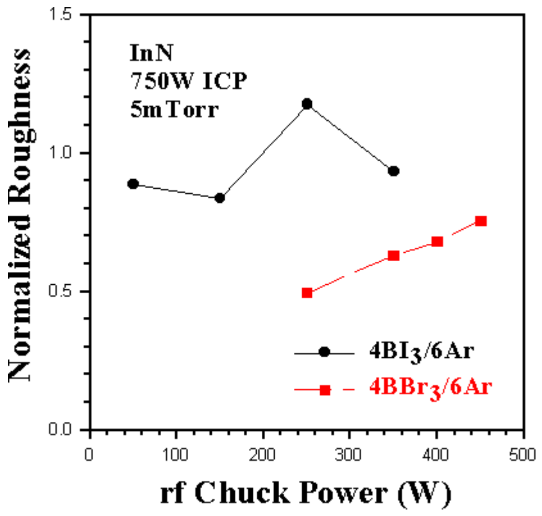
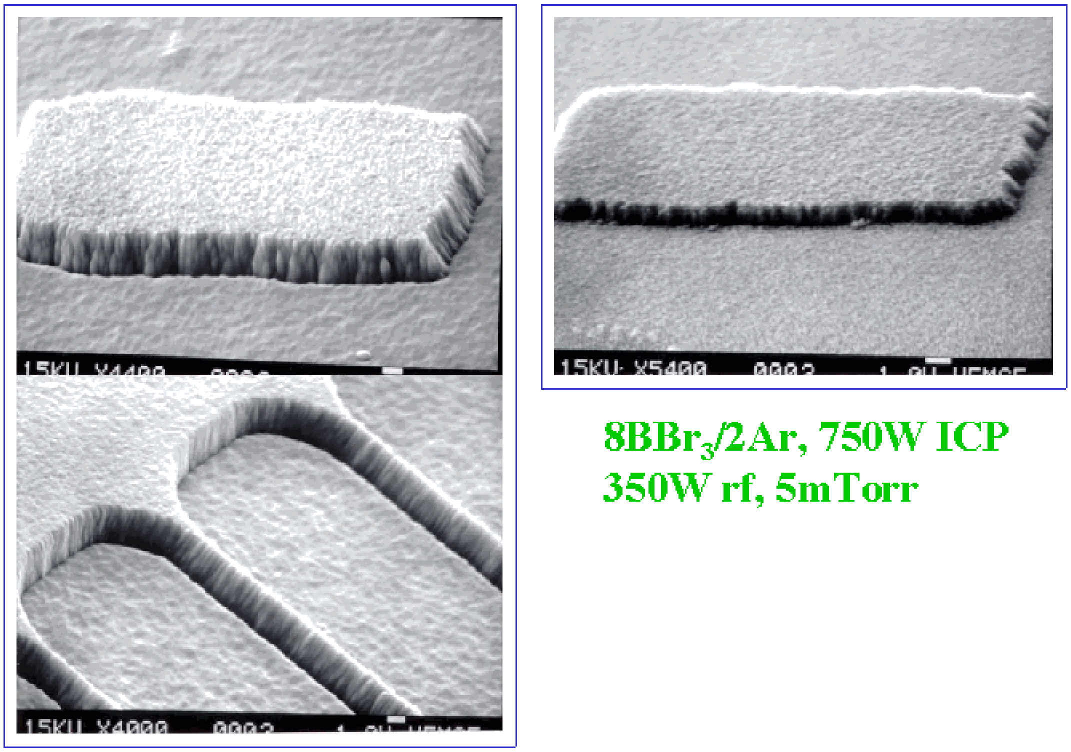


Figure 13. Dependence of InN normalized etched surface roughness on rf chuck power in $4BI_3/6Ar$ discharges(750W source power, 5mTorr).

GaN/SiN_x



$8BBr_3/2Ar$, 750W ICP
350W rf, 5mTorr

$5BI_3/5Ar$, 750W ICP
150W rf, 5mTorr

Figure 14. SEM micrographs of features etched into GaN using either BI_3/Ar or BBr_3/Ar discharges. The SiN_x masks are still in place.