SAND98-2514J

III-NITRIDE DRY ETCHING - COMPARISON OF INDUCTIVELY COUPLED PLASMA CHEMISTRIES

H. Cho[(1)], Y-.B. Hahn[(1)*], D.C. Hays[(1)], C.R. Abernathy[(1)], S.M. Donovan[(1)], J.D. MacKenzie[(1)], S.J. Pearton[(1)], J. Han[(2)] and R.J. Shul[(2)]

[(1)] Department of Materials Science and Engineering

University of Florida, Gainesville FL 32611

[(2)] Sandia National Laboratories, Albuquerque, NM 87185

ABSTRACT

A systematic study of the etch characteristics of GaN, AlN and InN has been performed with boron halides- (BI_3 and BBr_3) and interhalogen- (ICl and IBr) based Inductively Coupled Plasmas. Maximum etch selectivities of ~ 100:1 were achieved for InN over both GaN and AlN in the BI_3 mixtures due to the relatively high volatility of the InI_x etch products and the lower bond strength of InN. Maximum selectivities of ~ 14 for InN over GaN and >25 for InN over AlN were obtained with ICl and IBr chemistries. The etched surface morphologies of GaN in these four mixtures are similar or better than those of the control sample.

* Present address: Department of Chemical Engineering and Technology, Chonbuk National University, Chonju 561-756, Korea

INTRODUCTION

The absence of convenient wet etch processes for group III-nitrides has led to a strong development effort on dry etching[1-3]. The most common use of dry etching to this point have been creation of mesas in light-emitting diodes to expose the n-side of the junction[4], or to form a ridge waveguide in laser diodes[5]. In these applications, the main focus has been on obtaining the relatively large etch depths (2-4μm) typical of ridge or facet heights. Less attention has been paid to obtaining high selectivity between the different nitride materials. There is a strong interest in the development of GaN-based high power/high temperature electronics for power switching and transmission applications[6-10]. For devices of this type, the etch depth is shallower than in photonic devices, but smooth morphologies and high selectivities for InN over the other nitrides are required. This is due to the fact that layers based on InN will probably be used to obtain low ohmic contact resistance. In field effect transistor structures, a rectifying contact may be deposited on the etched surface, so that preservation of material quality is a critical issue.

Past work on Inductively Coupled Plasma (ICP) etching of GaN, AlN, InN, InAlN and InGaN at low dc biases ($\leq$ -100V) has employed Cl_2, CH_4/H_2, Cl_2/Ar, Cl_2/N_2 and Cl_2/H_2 plasma chemistries[11,12]. The etch rates were in the range of 500-1500Å/min with maximum etch selectivities of ~ 6 at higher ICP source powers (850W) for InN over the other nitrides. In addition to Cl_2-based mixtures, alternative chemistries have included Br_2 (in the form of HBr)[13,14], I_2 (in the form of HI)[14], IBr[15] and ICl[16] mixtures. InI_x etch products have higher volatility than the corresponding $InCl_x$ species, making iodine an attractive etchant for InGaN alloys. The interhalogen compounds are weakly bonded, and therefore should easily break apart under plasma excitation to form reactive iodine, bromine and chlorine.

In this paper we report a comparison study on ICP etching of GaN, AlN and InN with boron halides- (BI_3 and BBr_3) and interhalogen- (ICl and IBr) based plasma chemistries. BI_3 and BBr_3 mixtures were found to be very promising chemistries that allow the full range of desired etching properties, i.e. non-selective, selective for InN over GaN and AlN, while ICl and IBr produced controllable etch rates (500-1500Å·min^{-1}), relatively high selectivities (up to 30) and smooth surfaces.

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[(17)] (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, BBr_3, ICl and IBr were 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 typically 15 standard cubic centimeters per minutes (sccm). The samples were patterned with Apiezon wax for etch rate measurements. Etching was performed in a Plasma Therm 790 system in which the samples are thermally bonded to a Si carrier wafer mechanically clamped to a 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.

RESULTS AND DISCUSSION

(a) BI_3- and BBr_3-based chemistries

Figure 1 shows etch rates for the binary nitrides (top) and selectivities for InN over both GaN and AlN (bottom) as a function of boron halide percentage by flow in the gas load. The dc chuck self-bias decreases as BI_3 content increases, suggesting that the ion density in the plasma is increasing. The InN etch rate is proportional to BI_3 content, indicating the presence of a strong chemical component to its etching. In comparison, AlN and GaN show very low rates until ~ 50% BI_3 (~ 500Å·min^{-1} for AlN and ~ 1700Å·min^{-1} for GaN). An increase in the BI_3 content in the discharges actually produces a fall-off in etch rate for both AlN and GaN. We expect there are several possible mechanisms explaining this data. First, the decrease in chuck self-bias and hence ion energy under these conditions may more than compensate for the higher active iodine neutral flux. Second, the formation of the less volatile GaI_x and AlI_x etch products may create a selvedge layer which suppresses the etch rate. This mechanism occurs in the Cl_2 reactive ion etching of InP. In this system, etching does not occur unless elevated sample temperatures or high dc biases are used to facilitate removal of the $InCl_3$ etch product[18]. InN etch 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.

Data for BBr_3/Ar discharges is also shown in Figure 1 for fixed source power (750W) and rf chuck power (350W). Higher rf powers were required to initiate etching with BBr_3

compared to BI_3, and dc self-bias increased with BBr_3 content. The etch rate of InN is again a strong function of boron halide content, while GaN shows significant rates (~ 1800Å·min^{-1}) only for pure BBr_3 discharges. 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.

Figure 2 (top) shows that source power had a significant effect only on InN etch rate for both $4BI_3/6Ar$ and $4BBr_3/6Ar$ discharges at fixed rf power (150W). The etch rate of InN continues to increase with source power, which controls ion flux and dissociation of the discharge, whereas GaN and AlN rates are low for both plasma chemistries. The InN etch rates are approximately a factor of two faster in BI_3/Ar compared to BBr_3/Ar even for lower rf chuck powers. This is expected from a consideration of the relative stabilities of the respective In etch products (InI_3 melting point 210°C; $InBr_3$ sublimes at < 600°C). The resultant selectivities are shown at the bottom of Figure 2 - once again a value of ~ 100:1 for InN over GaN is achieved with BI_3, whereas BBr_3 produces somewhat lower values.

The dependence of etch rate (top), InN/AlN and InN/GaN selectivity (bottom) on rf chuck power for both plasma chemistries at fixed source power (750W) is shown in Figure 3. While GaN and AlN etch rates (top left) increase only at the highest chuck powers investigated for $4BI_3/6Ar$ discharges, the InN etch rate increases rapidly to 250W. This is consistent with a strong ion-assisted component for the latter under these conditions. The subsequent decrease in etch rate at higher power produces corresponding maxima (≥ 100) in etch selectivity for chuck powers in the range of 150-250W. 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 for BBr_3/Ar mixtures is also shown in Figure 3. For this chemistry the InN etch rate saturates and we did not observe any reduction in etch rate, 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. The etch selectivity of InN over the other two nitrides for BI_3/Ar are again much higher than for BBr_3/Ar.

Smooth etched surface morphologies were obtained for GaN with these two plasma chemistries. Figure 4 shows GaN root-mean-square (RMS) roughness dependence on discharge composition for both chemistries. The most important result is that all of the etched surfaces have lower RMS roughness values than the control value. This type of surface smoothing has been reported previously for GaN[(19)], 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. We also found the etched features to have vertical sidewalls, which is expected given the ion-assisted nature of the etch mechanism.

(b) ICl- and IBr-based chemistries

The effect of plasma composition on etch rates (top) and selectivities (bottom) of GaN, AlN and InN in ICl/Ar and IBr/Ar discharges at 750W source power, 250W rf chuck power and 5mTorr is shown in Figure 5. The etch rates of InN and AlN are relatively independent of plasma composition for both chemistries over a broad composition range, indicating the etch mechanism is dominated by physical sputtering. The dc bias voltages increased with increasing interhalogen concentrations. The decrease in ion flux also implies an increase in concentrations of neutral species such as Cl, Br and I[20]. The etch rate of GaN steadily increased with increasing ICl concentration. By contrast the etch rate of GaN saturated beyond 66.7% IBr. These results indicate that etching of GaN in both chemistries is more attributed to chemical etching by increased concentrations of reactive neutrals than by ion-assisted sputtering. The effect of plasma composition showed an overall trend of decrease in selectivities for InN over both AlN and GaN as the concentrations of ICl and IBr increase.

The ICP source power dependence of the etch rates (top) and selectivities (bottom) is shown in Figure 6 for ICl/Ar and IBr/Ar discharges at fixed plasma composition, chuck power (250W) and process pressure (5mTorr). InN again showed higher etch rates than AlN and GaN. The increase in etch rate with increasing the source power is due to the higher concentration of reactive species in the plasma, suggesting a reactant-limited regime, and to higher ion flux to the substrate surface. The relatively constant etch rate with further increase of the ICP power is attributed to the competition between ion-assisted etch reaction and ion-assisted desorption of the reactive species at the substrate surface prior to etch reactions. The selectivity of InN over AlN showed maximum values depending ICP source power while that of InN over GaN increased overall as the source power increased.

The effect of rf chuck power on the etch rates (top) and selectivities (bottom) of InN over AlN and over GaN is shown in Figure 7. Etch rates for all materials increased as the rf power or the ion-bombarding energy increased. The increase in etch rate with the chuck power can be attributed to enhanced sputter desorption of etch products as well as physical sputtering of the

InN surface. It is also interesting to see that the magnitude of etch rate is in the order of bond energies, InN (7.72 eV) < GaN (8.92 eV) < AlN (11.52 eV)[21]. Maximum values of selectivity ~ 30 for InN/AlN and ~ 14 for InN/GaN were obtained.

The plasma composition dependence of GaN normalized roughness is shown in Figure 8. As with BI_3 and BBr_3 results, the etched surfaces are smoother than the as-grown samples, for the same reason.

SUMMARY AND CONCLUSIONS

The effects of plasma composition, source power and rf chuck power on the III-nitrides etch rate and selectivity were examined in BI_3-, BBr_3-, ICl- and IBr-based Inductively Coupled Plasmas. 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. In the ICl and IBr mixtures the etch rates of InN and AlN are relatively independent of plasma composition, while GaN showed increased etch rates with etch gas concentrations. Etch rates for all materials in the ICl- and IBr-based discharges increased with increasing the rf chuck power, indicating that higher bombarding energies are more efficient in enhancing sputter desorption of etch products. The maximum selectivities obtained in ICl and IBr mixtures were ~ 30 for InN/AlN and ~ 14 for InN/GaN, respectively. All four of these plasma chemistries appear useful for selective etch processes in nitride electronic device fabrication.

ACKNOWLEDGEMENTS

The work at UF is partially supported by a DARPA/EPRI grant MDA-972-98-1-0006 (E.R. Brown/J. Melcher). Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin company, for the US Department of Energy under contract DEAC-94AL-85000. One of the authors (H.C.) acknowledges partial support from the Korea Science and Engineering Foundation (KOSEF). YBH gratefully acknowledges the support of the Korea Research Foundation for Faculty Research Abroad.

References

1. S.J. Pearton and R.J. Shul, in GaN Vol 1., ed. J.I. Pankove and T.D. Moustakas (Academic Press, San Diego, 1998).
2. H.P. Gillis, D.A. Choutov and K.P. Martin, J. Materials 48 50 (1996).
3. I. Adesida, A. Mahajan, E. Andideh, M.A. Khan, D.T. Olsen and J.N. Kuznia, Appl. Phys. Lett. 63 2777 (1993).
4. S. Nakamura, T. Mukai and M. Senoh, Appl. Phys. Lett. 64 1687 (1994).
5. S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H Kiyoku and Y. Sugimoto, Jap. J. Appl. Phys. 35 L74 (1996).
6. O. Aktas, Z. Fan, S.N. Mohammad, A. Botcharev, and H. Morkoc, Appl. Phys. Lett. 69 25 (1996).
7. M.A. Khan, J.N. Kuznia, M.S. Shur, C. Eppens, J. Burm, and W. Schaff, Appl. Phys. Lett. 66 1083 (1995).
8. Y.F. Wu, B.P. Keller, S. Keller, D. Kapolnek, S.D. Den Baars, and U.K. Mishra, IEEE Electron. Dev. Lett. 17 455 (1996).
9. M.A. Khan, Q. Chen, M.S. Shur, B.T. McDermott, J.A. Higgins, J. Burm, W. Schaff, and L.F. Eastman, Electron. Lett. 32 357 (1996).
10. Y.T. Wu, S. Keller, P. Kozodoy, B.P. Keller, P. Parikh, D. Kapolnek, S.P. Denbaars, and U.K. Mishra, IEEE Electron. Dev. Lett. 18 290 (1997).
11. R.J. Shul, G.B. McClellan, S.A. Casalnuova, D.J. Rieger, S.J. Pearton, C. Constantine, C. Barrat, R.F. Karlicek, Jr., C. Tran, and M. Schurman, Appl. Phys. Lett. 69 1119 (1996).

12. R.J. Shul, R.D. Briggs, S.J. Pearton, C.B. Vartuli, C.R. Abernathy, J.W. Lee, C. Constantine, and C. Barratt, Mat. Res. Soc. Symp. Proc. 449 969 (1997).

13. A.T. Ping, I. Adesida, M.A. Khan and J.N. Kuznia, Electron. Lett. 30 1895 (1994).

14. S.J. Pearton, C.R. Abernathy and C.B. Vartuli, Electron. Lett. 30 1985 (1994).

15. C.B. Vartuli, S.J. Pearton, J.W. Lee, J.D. Mackenzie, C.R. Abernathy, and R.J. Shul, J. Vac. Sci. Technol. B 15 98 (1997).

16. J.W. Lee, J. Hong, E.S. Lambers, and S.J. Pearton, J. Vac. Sci. Technol. B 15 652 (1997).

17. C.R. Abernathy, Mat. Sci. Eng. Rep. 14 203 (1996).

18. J.W. Lee, J. Hong and S.J. Pearton, Appl. Phys. Lett. 68 847 (1996).

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

20. M.A. Lieberman and A.J. Lichtenberg, Principles of Plasma Discharges and Materials Processing (John Wiely & Sons Inc., N.Y. 1994).

21. CRC Handbook of Chemistry and Physics, 70th Ed., eds. R.C. Weast, D.R. Lide, M.J. Astle, and W.H. Beyer (CRC Press Inc., Boca Raron, FL, 1989).

Figure Captions

Figure 1. Nitride etch rates (top) and etch selectivities for InN/AlN and InN/GaN (bottom) in BI_3/Ar or BBr_3/Ar discharges (750W source power, 5mTorr) as a function of Boron halide content.

Figure 2. Nitride etch rates (top) and etch selectivities for InN/AlN and InN/GaN (bottom) in BI_3/Ar or BBr_3/Ar discharges as a function of source power.

Figure 3. Nitride etch rates (top) and etch selectivities for InN/AlN and InN/GaN (bottom) in BI_3/Ar or BBr_3/Ar discharges as a function of rf chuck power.

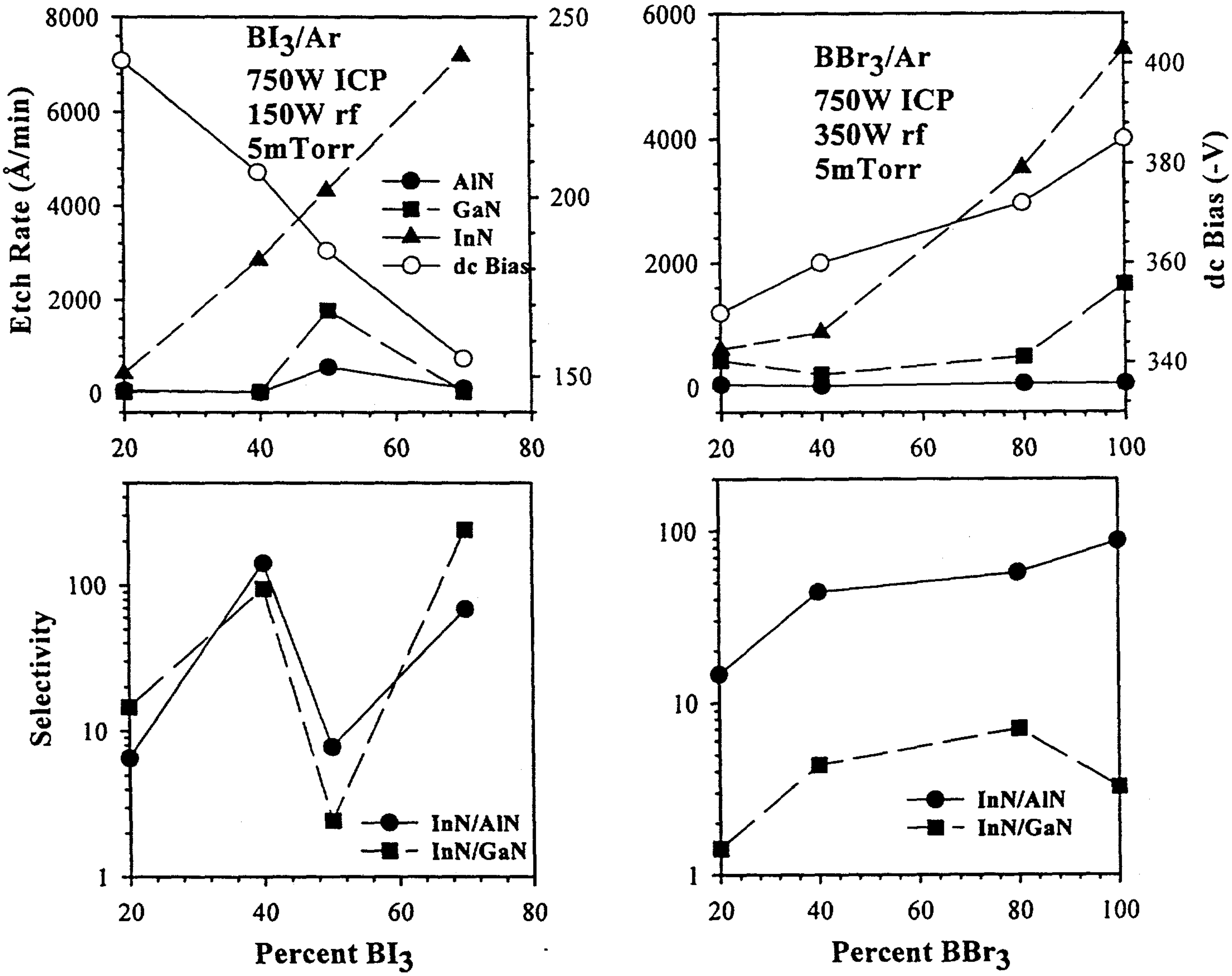
Figure 4. Dependence of GaN normalized etched surface roughness on boron halide percentage in BI_3/Ar or BBr_3/Ar discharges.

Figure 5. Nitride etch rates (top) and etch selectivities for InN/AlN and InN/GaN (bottom) in ICl/Ar or IBr/Ar discharges (750W source power, 250W rf, 5mTorr) as a function of interhalogen content.

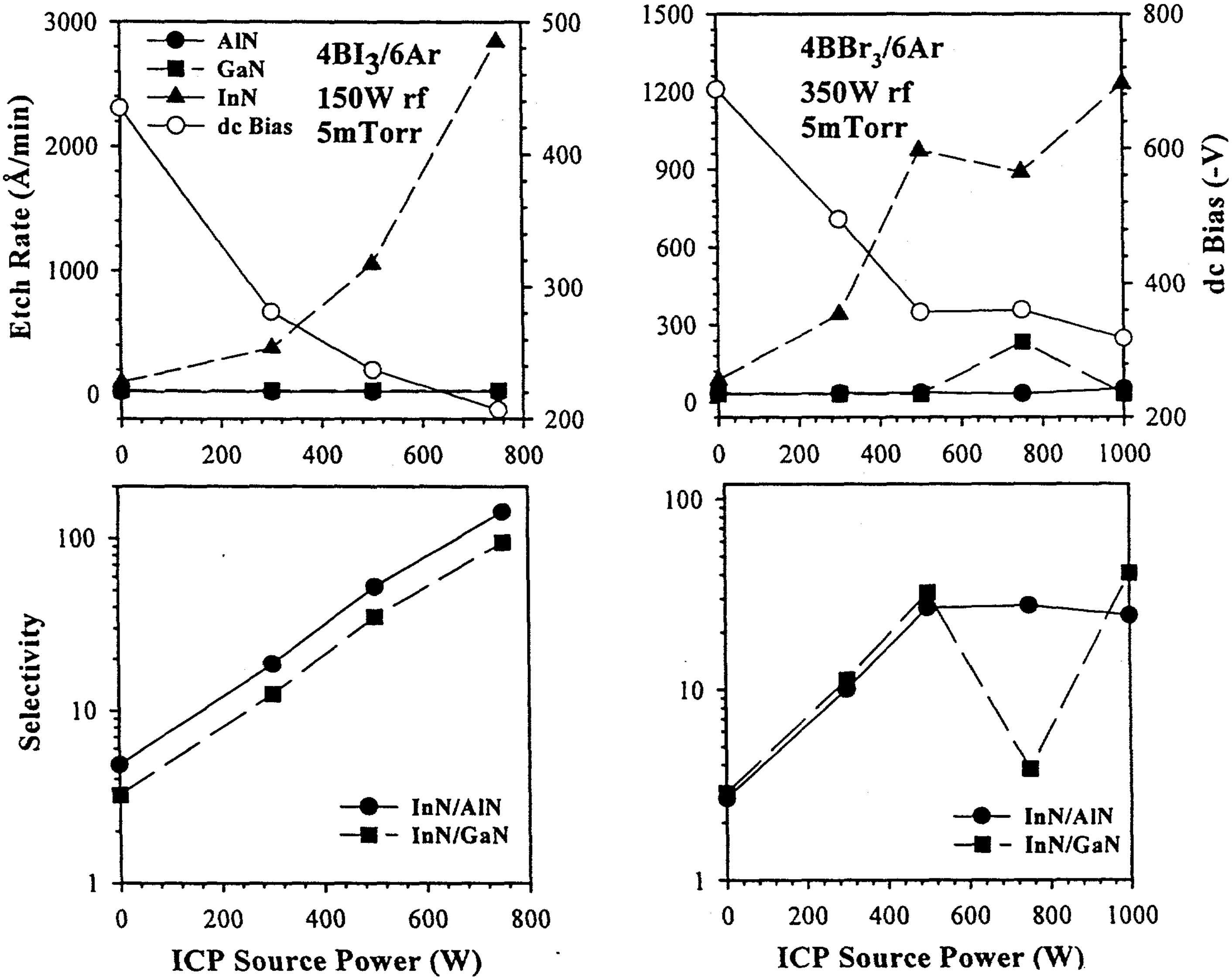
Figure 6. Nitride etch rates (top) and etch selectivities for InN/AlN and InN/GaN (bottom) in ICl/Ar or IBr/Ar discharges (250W rf, 5mTorr) as a function of source power.

Figure 7. Nitride etch rates (top) and etch selectivities for InN/AlN and InN/GaN (bottom) in ICl/Ar or IBr/Ar discharges (750W source power, 5mTorr) as a function of rf chuck power.

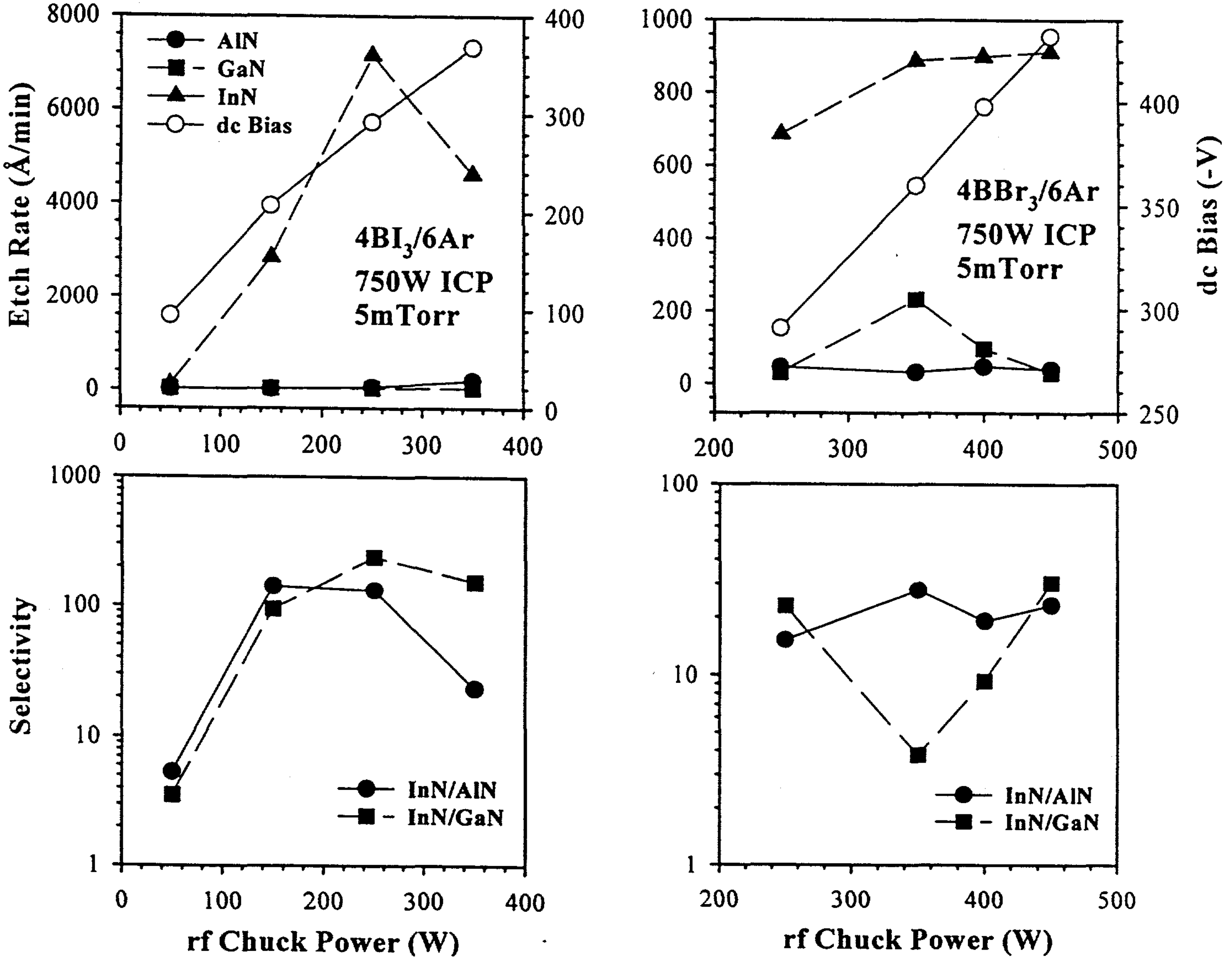
Figure 8. Dependence of GaN normalized etched surface roughness on interhalogen content in ICl/Ar or IBr/Ar discharges.



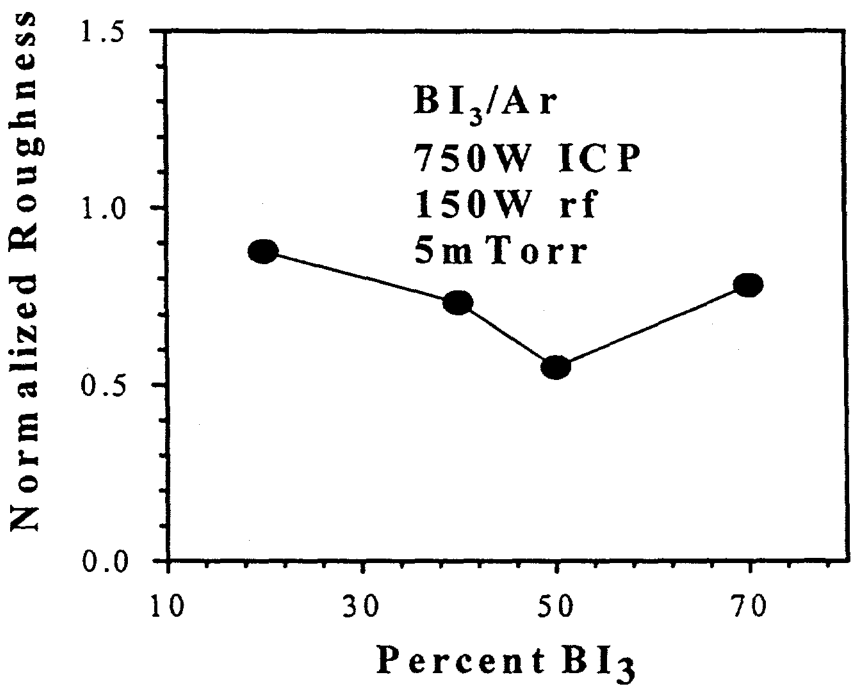
BI3/Ar
750W ICP
150W rf
5mTorr
AlN
GaN
InN
dc Bias
Etch Rate (Å/min)
BBr3/Ar
750W ICP
350W rf
5mTorr
dc Bias (-V)
Selectivity
InN/AlN
InN/GaN
Percent BI3
Percent BBr3



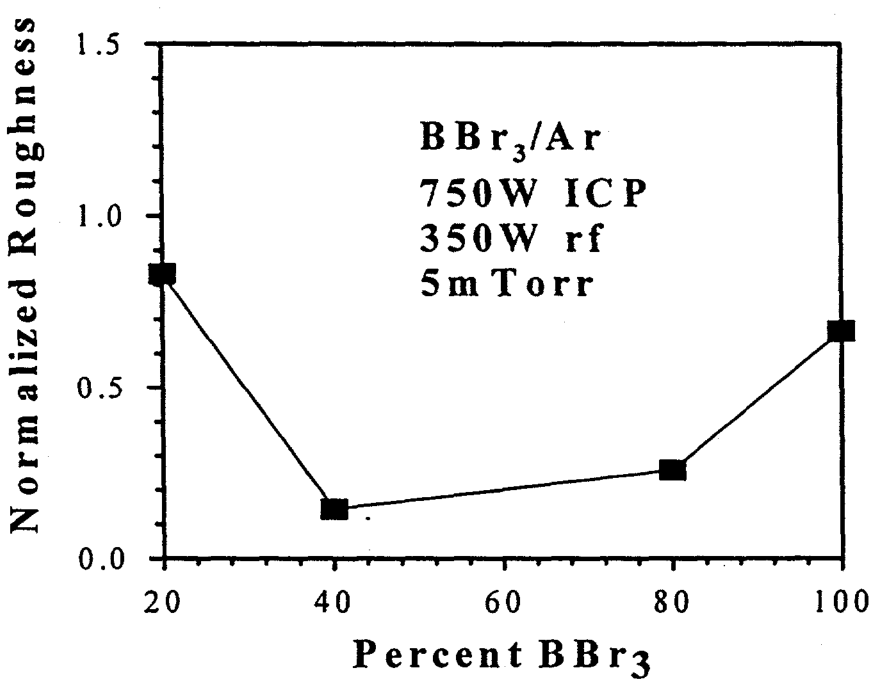
AlN
GaN
InN
dc Bias
4BI$_3$/6Ar
150W rf
5mTorr
4BBr$_3$/6Ar
350W rf
5mTorr
Etch Rate (Å/min)
dc Bias (-V)
Selectivity
InN/AlN
InN/GaN
ICP Source Power (W)
ICP Source Power (W)



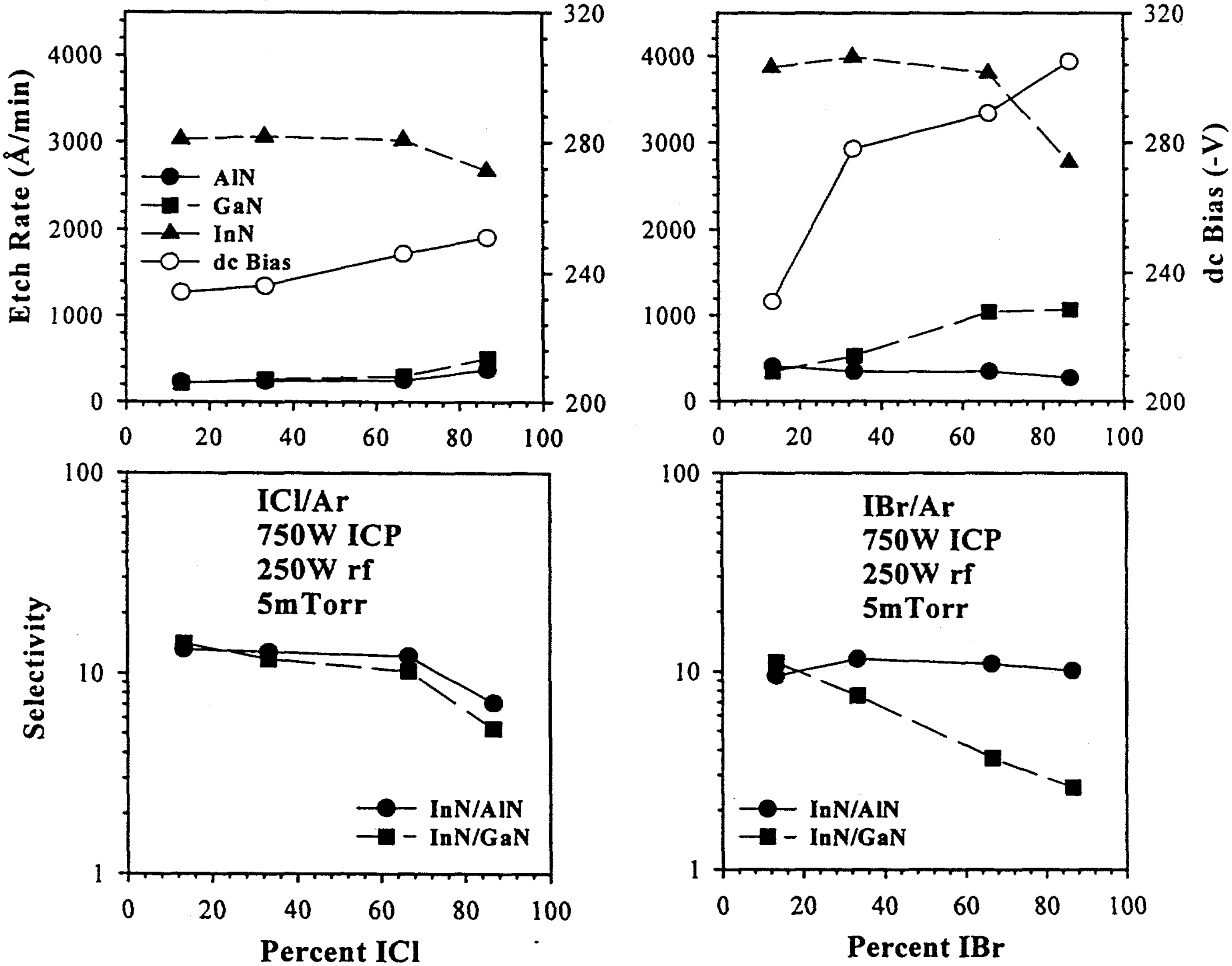
AlN
GaN
InN
dc Bias
4BI3/6Ar
750W ICP
5mTorr
Etch Rate (Å/min)
4BBr3/6Ar
750W ICP
5mTorr
dc Bias (-V)
Selectivity
InN/AlN
InN/GaN
rf Chuck Power (W)

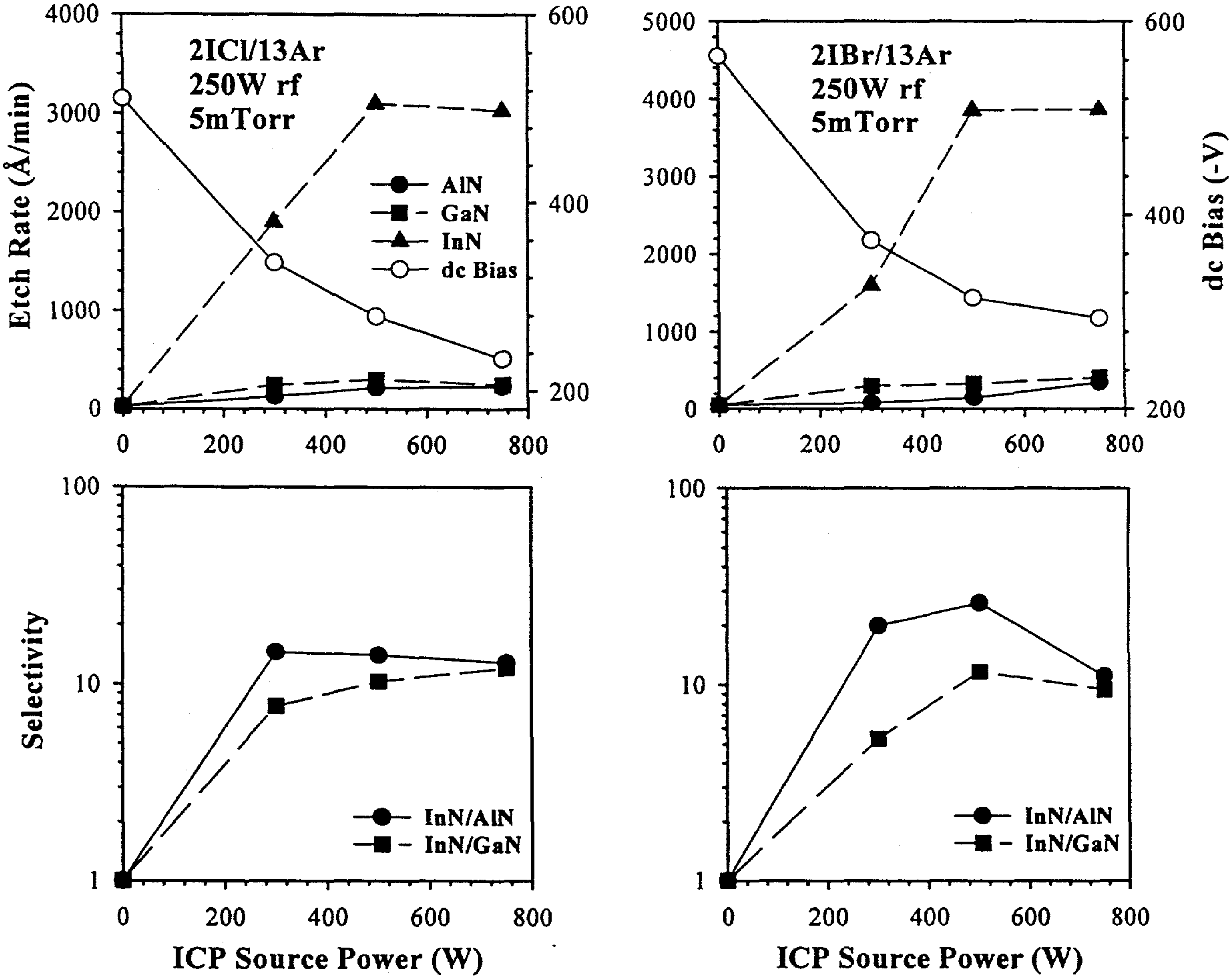


Normalized Roughness
1.5
1.0
0.5
0.0
10
30
50
70
Percent BI_3
BI_3/Ar
750W ICP
150W rf
5mTorr

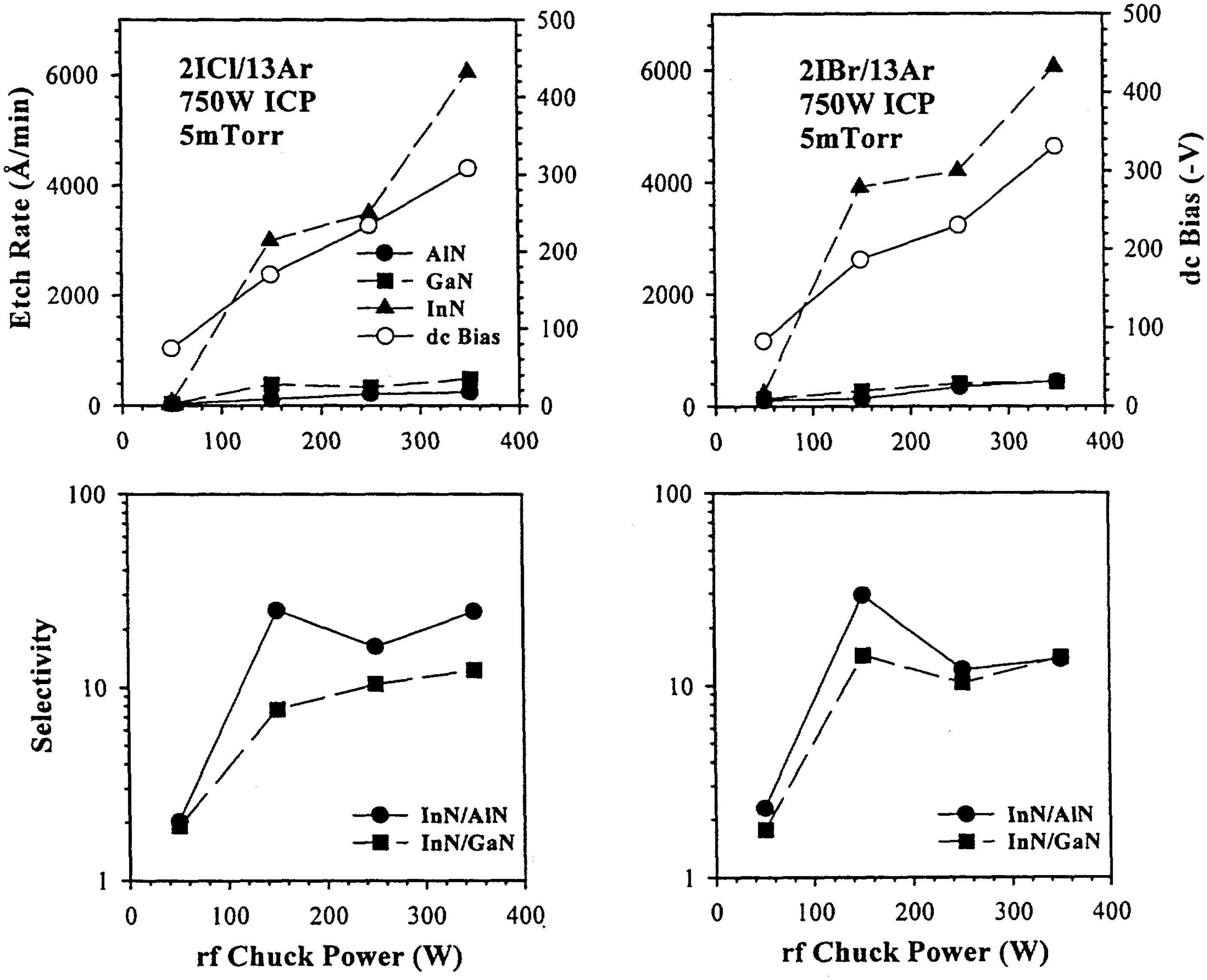


Normalized Roughness
1.5
1.0
0.5
0.0
20
40
60
80
100
Percent BBr_3
BBr_3/Ar
750W ICP
350W rf
5mTorr

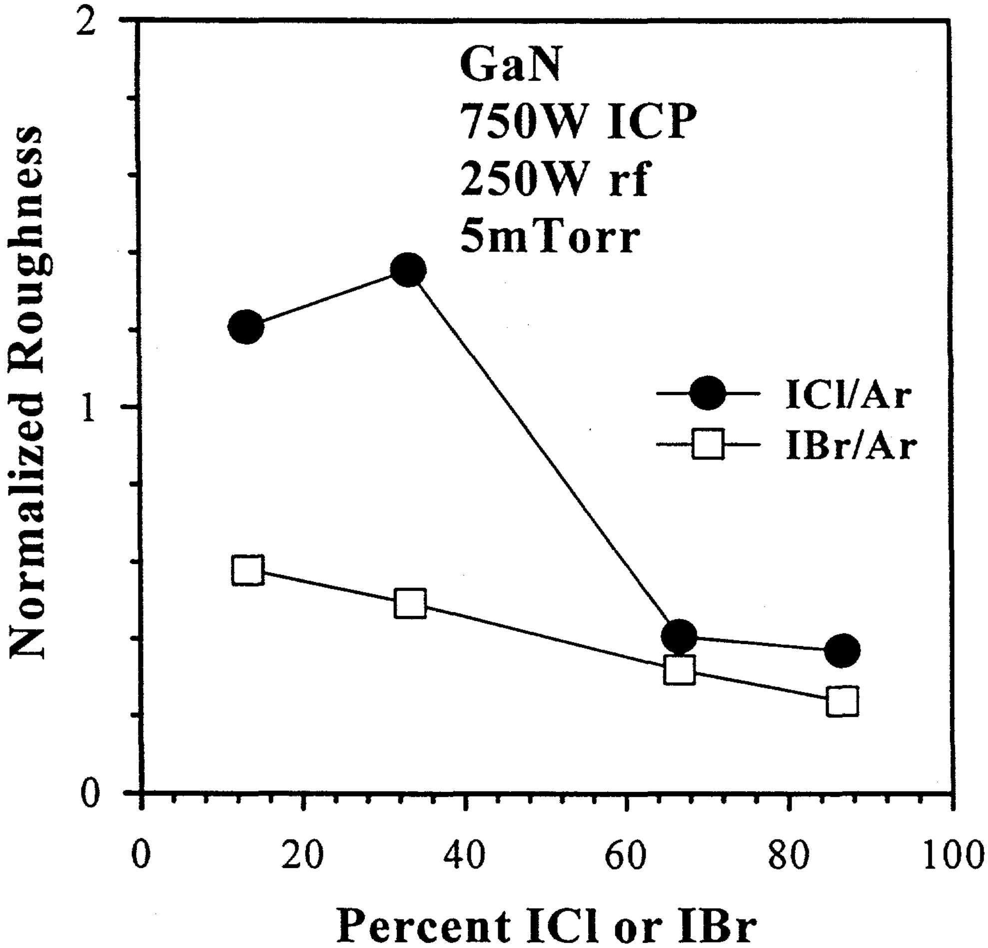

Etch Rate (Å/min)
dc Bias (-V)
AlN
GaN
InN
dc Bias
Selectivity
ICl/Ar
750W ICP
250W rf
5mTorr
IBr/Ar
750W ICP
250W rf
5mTorr
InN/AlN
InN/GaN
Percent ICl
Percent IBr



2ICl/13Ar
250W rf
5mTorr
AlN
GaN
InN
dc Bias
Etch Rate (Å/min)
2IBr/13Ar
250W rf
5mTorr
dc Bias (-V)
Selectivity
InN/AlN
InN/GaN
ICP Source Power (W)
ICP Source Power (W)



2ICl/13Ar
750W ICP
5mTorr
Etch Rate (Å/min)
AlN
GaN
InN
dc Bias
2IBr/13Ar
750W ICP
5mTorr
dc Bias (-V)
Selectivity
InN/AlN
InN/GaN
rf Chuck Power (W)



GaN
750W ICP
250W rf
5mTorr
ICl/Ar
IBr/Ar
Normalized Roughness
Percent ICl or IBr
0
1
2
0
20
40
60
80
100