

INDUCTIVELY COUPLED PLASMA ETCHING OF III-V SEMICONDUCTORS IN  
BCl<sub>3</sub>-BASED CHEMISTRIES : PART I : GaAs, GaN, GaP, GaSb AND AlGaAs

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ABSTRACT

BCl<sub>3</sub>, with addition of N<sub>2</sub>, Ar or H<sub>2</sub>, is found to provide smooth anisotropic pattern transfer in GaAs, GaN, GaP, GaSb and AlGaAs under Inductively Coupled Plasma conditions. Maxima in the etch rates for these materials are observed at 33% N<sub>2</sub> or 87% H<sub>2</sub> (by flow) addition to BCl<sub>3</sub>, whereas Ar addition does not show this behavior. Maximum etch rates are typically much higher for GaAs, GaP, GaSb and AlGaAs (~1.2 μm/min) than for GaN (~0.3 μm/min) due to the higher bond energies of the latter. The rates decrease at higher pressure, saturate with source power (ion flux) and tend to show maxima with chuck power (ion energy). The etched surfaces remain stoichiometric over a broad range of plasma conditions.

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## INTRODUCTION

There are a wide variety of electronic and photonic devices fabricated from compound semiconductors that require precise pattern transfer that maintains the stoichiometry of the binary or ternary material<sup>(1-7)</sup>. The GaAs/AlGaAs system is used for high electron mobility transistors (HEMTs), heterojunction bipolar transistors (HBTs), 0.98  $\mu\text{m}$  fiber pump lasers and red light-emitting diodes (LEDs), while GaP is important for high power LEDs<sup>(8)</sup>. GaN and related alloys are attracting tremendous interest for blue/green/UV laser diodes and LEDs and high temperature electronics<sup>(9)</sup>. In particular there are no simple wet etch solutions for GaN, placing emphasis on the development of dry etch processes<sup>(10)</sup>.

High density plasma conditions have been reported to provide fast etch rates for GaAs/AlGaAs, GaP and GaN using  $\text{Cl}_2$  (with additions of Ar or  $\text{N}_2$ ) or  $\text{BCl}_3$  (with additions of Ar or  $\text{N}_2$ ). Most of this work has focused on Electron Cyclotron Resonance (ECR) sources<sup>(11-17)</sup>, but a few reports have appeared dealing with Inductively Coupled Plasmas (ICP)<sup>(18-20)</sup>. There are compelling reasons to focus on the latter source, because of its superior uniformity and absence of expensive electromagnets that require active cooling<sup>(13)</sup>. In particular,  $\text{BCl}_3$ -based discharges are of primary interest because of the ability of  $\text{BCl}_3$  to remove the native oxides on compound semiconductors and hence to provide a wide process window.

In this paper we report on a parametric study of  $\text{BCl}_3/\text{N}_2$ ,  $\text{BCl}_3/\text{Ar}$  and  $\text{BCl}_3/\text{H}_2$  ICP etching of GaAs, AlGaAs, GaP, GaSb and GaN. The etch products for these materials, namely  $\text{GaCl}_x$ ,  $\text{AlCl}_x$ ,  $\text{AsCl}_x$ ,  $\text{PCl}_x$ ,  $\text{SbCl}_x$  and  $\text{NCl}_x$  or  $\text{N}_2$  (the nitrogen products are not yet established) are quite volatile, and thus high etch rates would be expected. In part II of this paper we report results of similar experiments on In-based compound semiconductors, where the  $\text{InCl}_x$  products are much less volatile than their  $\text{GaCl}_x$  counterparts. We find that  $\text{BCl}_3$ -based chemistries under ICP conditions are universal etchants for III-V semiconductors. This means that the  $\text{CH}_4/\text{H}_2$  chemistry, popular in the past under reactive ion etching conditions, is not necessary when high density reactors are employed. The main advantage of this situation is the absence of hydrogen passivation effects, which reduce the effective doping in the near-surface of device structures.

## EXPERIMENTAL

The following samples were employed in this study: semi-insulating undoped (100) GaAs and undoped (100) GaSb substrates grown by the Czochralski process; nominally undoped ( $p \sim 10^{16} \text{ cm}^{-3}$ )  $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$  grown by either Metal Organic Molecular Beam Epitaxy<sup>(21)</sup> or Metal Organic Chemical Vapor Deposition (MOCVD)<sup>(22)</sup> at 550 - 650°C on semi-insulating GaAs substrates; nominally undoped GaP substrates ( $n \sim 10^{15} \text{ cm}^{-3}$ ) grown by the Czochralski process and nominally undoped ( $n \sim 10^{17} \text{ cm}^{-3}$ ) GaN grown on  $\text{Al}_2\text{O}_3$  substrates by MOCVD at 1040°C. All samples were patterned with a Shipley 4330 photoresist.

Experiments were performed in a Plasma Therm 790 System which utilizes a He backside-cooled, rf (13.56MHz)-powered sample chuck and a 2 MHz, 1500 W ICP source<sup>(13, 18)</sup>. The total gas load was held constant at 15 standard cubic centimeters per minute (sccm). Electronic grade  $\text{BCl}_3$ ,  $\text{N}_2$ , Ar or  $\text{H}_2$  were injected directly into the ICP source. The process pressure was varied from 2 - 15 mTorr, the rf chuck power from 50 - 350 W (corresponding to dc biases of approximately -100 to -680 V) and the source power from 0 - 1000 W. Etch depths were measured by stylus profilometry of the features after removal of the photoresist, while etch anisotropy was examined by scanning electron microscopy (SEM). Surface morphology was quantified by atomic force microscopy (AFM) and near-surface stoichiometry was examined by Auger Electron Spectroscopy (AES).

## RESULTS AND DISCUSSION

Figure 1 (top) shows material etch rates as a function of discharge composition in  $\text{BCl}_3/\text{N}_2$  at fixed pressure (2 mTorr), source power (500 W) and dc self-bias (-250 V). The rates are a maximum at ~33%  $\text{N}_2$  addition. Ren et al.<sup>(7)</sup> and Shul et al.<sup>(1, 5)</sup> reported similar results for ECR or ICP  $\text{BCl}_3/\text{N}_2$  etching of InP, GaAs and GaP. In the former work, maximum emission intensities for atomic chlorine was found at 25%  $\text{N}_2$  addition, which provides an explanation for the etch rate behavior through the enhanced dissociation of  $\text{BCl}_3$  to provide reactive atomic chlorine neutrals. While the rates for GaAs, AlGaAs and GaP are relatively close, those for GaN are about a factor of 4 lower at higher  $\text{BCl}_3$  percentages. Since the products for GaN are equally as volatile as those of the other materials, this suggests the limiting step is product formation because of the higher bond energy of GaN (8.92 eV/atom compared to 6.52 eV/atom for GaAs)<sup>(23)</sup>. Note that the rates for GaAs, AlGaAs and GaP can be controlled over a very wide

range (a factor of approximately sixty) at fixed bias, pressure and source power by simply varying the  $\text{BCl}_3$  percentage in the discharge. Etch yields are shown at the bottom of Figure 1. The calculations for etch yield will be described elsewhere<sup>(24)</sup>, but in brief, we define the etch yield as the number of substrate atoms per incident ion at the energy employed in these experiments (which is about 274 eV, based on the dc self-bias of about 250 V, and the plasma potential of about 24 eV). The ion flux is determined from a semi-empirical calculation similar to that of Stewart et al.<sup>(25)</sup>

We can contrast the results with  $\text{BCl}_3/\text{N}_2$  to those obtained with  $\text{BCl}_3/\text{Ar}$  or  $\text{BCl}_3/\text{H}_2$  (Figure 2). In the latter case we see an initial rise in etch rate as  $\text{BCl}_3$  is added to  $\text{H}_2$  due to the presence of chlorine neutrals that form more volatile etch products for the group III elements compared to hydrogen, but beyond ~10%  $\text{BCl}_3$  there is a broad range of plasma conditions where the etch rates are low. Optical emission spectroscopy and mass spectroscopy of the discharges under these conditions shows there is virtually no atomic chlorine, due to recombination to form  $\text{HCl}$ . Thus, both active etchants (Cl and H) are reduced in concentration, leading to reduced etch rates. These rates tend to rise again for pure  $\text{BCl}_3$  plasmas due to the increase in available atomic chlorine. For  $\text{BCl}_3/\text{Ar}$  there is no parasitic scavenging of the active species; for GaAs, AlGaAs and GaP this leads to a general increase in rates as  $\text{BCl}_3$  is added and a reduced etch rate for pure  $\text{BCl}_3$  due to the reduced ion-assisted component of the etch mechanism. For GaN the etch rate decreases beyond relatively low  $\text{BCl}_3$  percentages for the same reason; the difference is due to the fact that GaN has a high bond energy and requires a strong ion-assisted etch component.

The effect of process pressure at fixed dc chuck bias is shown in Figure 3. The general trend is for a drastic fall-off in etch rates above 5 mTorr as chlorine neutrals recombine with  $\text{BCl}_x$  fragments. This was confirmed by optical emission spectroscopy, which showed the chlorine atom lines between 726 - 775 nm decreasing to undetectable levels. For  $\text{BCl}_3/\text{N}_2$  discharges the rates peak in the range 5 - 10 mTorr for materials other than GaN, where there is a good correlation with the atomic chlorine emission intensity maxima.

As ICP source power is increased, producing higher ion fluxes, there is a general tendency for etch rates to increase (Figure 4). The top two sections of this figure show results for two different  $\text{BCl}_3/\text{N}_2$  conditions, at fixed dc chuck bias. The etch rates either saturate or start to decrease at the highest source powers, which is commonly observed in ECR etching and is

usually ascribed to sputter desorption of the active species before they can react with the sample surface. At fixed rf chuck power (bottom of the figure), where dc chuck bias will decrease as source power increases (from -250 V at zero source power to -105 V at 1000 W), a similar trend is observed. This data is related to that shown in Figure 5, which displays etch rates as a function of either rf chuck power (which increases chuck bias) or chuck bias for fixed source power and several pressures. Since this bias controls the energy of ions impacting the sample surface<sup>(26)</sup>, there will be a general tendency for increased etch rates until the point at which reactants are desorbed by ion-assistance before they form etch products. Note that maximum etch rates exceeding 1  $\mu\text{m}/\text{min}$  for GaAs, AlGaAs, GaP and GaSb and 0.3  $\mu\text{m}/\text{min}$  for GaN are obtained in  $\text{BCl}_3/\text{N}_2$  at 2 mTorr and moderate source power and chuck bias. These are good conditions for production of through-wafer via holes in GaAs, GaP or GaSb substrates for power transistor applications.

As expected for low pressure operation with ion-assisted etch chemistries, the pattern transfer was smooth and anisotropic. Figure 6 show SEM micrographs of features etched into GaAs (top), AlGaAs (center) or GaN (bottom) using a  $10\text{BCl}_3/5\text{Ar}$  discharge. The photoresist mask has been removed in all cases, using acetone. No other post etch cleaning steps were performed. Note that the etch depth on the AlGaAs sample is much larger than for the other samples, and thus the surface appears rougher. Similarly good results were obtained with  $10\text{BCl}_3/5\text{N}_2$  discharges, as shown in Figure 7 for GaAs (top left), AlGaAs (bottom left) and GaN (top and bottom right). The addition of  $\text{N}_2$  to  $\text{BCl}_3$  chemistries typically enhances photoresist etch rates and can provide sidewall protection through redeposition, but for these Ga-based materials there does not appear to be significant undercut in any case.

AFM imaging of the etched surfaces also provided confirmation of the high quality of the pattern transfer. Figure 8 shows the root-mean-square (RMS) roughness for a fixed etch depth of one micron, measured over  $5 \times 5 \mu\text{m}^2$  regions of GaAs and AlGaAs surfaces etched at fixed source power (500 W), dc bias (-250 V) and pressure (2 mTorr) in either  $\text{BCl}_3/\text{N}_2$  or  $\text{BCl}_3/\text{Ar}$  discharges. As-grown samples typically show RMS values in the range 0.2 - 0.8 nm, and therefore the ICP etching process is not producing any significant surface roughening.

In III-V dry etching, a smooth surface essentially guarantees that it is also stoichiometric<sup>(2, 4)</sup>, i.e. there has been equi-rate removal of the group III and group V etch products. Figure 9 shows AES surface scans of GaAs after etching in  $5\text{BCl}_3/10\text{Ar}$  (top left),  $10\text{BCl}_3/5\text{Ar}$  (bottom left),

5BCl<sub>3</sub>/10N<sub>2</sub> (top right) or 10BCl<sub>3</sub>/5N<sub>2</sub> (bottom right). There is oxygen present from the native oxide that grows during transfer of the sample from the reactor to the AES system, and adventitious carbon from the atmospheric exposure. The residual chlorine is near the detection limit of AES ( $\leq 1\%$  at %). The etched surface are therefore chemically quite clean, and remain stoichiometric, as shown in the depth profiles of Figure 10. The Ga/As ratio remains constant even at the surface, indicating that both are being removed at the same rate during the etching process.

## SUMMARY AND CONCLUSIONS

Under conventional reactive ion etching conditions, BCl<sub>3</sub> has been found to be an attractive plasma chemistry for patterning GaAs and related compounds because of its ability to getter water vapor and readily remove the native oxides on these materials. The results from this current work on ICP etching using BCl<sub>3</sub>-based mixtures show that it is also an attractive choice under high density conditions. The addition of N<sub>2</sub> at around 33% by flow produces a strong enhancement in etch rates due to dissociation of the BCl<sub>3</sub> and consequently higher atomic chlorine density. Under these conditions the etch rates for GaAs, AlGaAs, GaSb and GaP are 4 - 8 times higher than with BCl<sub>3</sub>/Ar or BCl<sub>3</sub>/H<sub>2</sub> discharges of the same relative BCl<sub>3</sub> composition. The rates are found to generally decrease with pressure and to generally increase with both ion flux and ion energy. In the latter two cases the rates may saturate or even decrease at very high fluxes or energies due to reactant desorption. The pattern transfer is smooth and anisotropic over a broad range of plasma conditions.

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## Figure Captions

Figure 1. Etch rate (top) and etch yield (bottom) of Ga-based semiconductors as a function of  $\text{BCl}_3$  percentage in  $\text{BCl}_3/\text{N}_2$  ICP discharges at fixed source power (500 W), pressure (2 mTorr) and dc self-bias (-250 V).

Figure 2. Etch rates of Ga-based semiconductors as a function of  $\text{BCl}_3$  percentage in  $\text{BCl}_3/\text{Ar}$  or  $\text{BCl}_3/\text{H}_2$  ICP discharges at fixed source power (500 W), pressure (2 mTorr) and dc self-bias (-250 V).

Figure 3. Etch rates of Ga-based semiconductors as a function of pressure in  $10\text{BCl}_3/5\text{N}_2$  or  $10\text{BCl}_3/5\text{Ar}$  ICP discharges at fixed source power (500 W) and dc self-bias (-250 V).

Figure 4. Etch rates of Ga-based semiconductors as a function of ICP source power in  $\text{BCl}_3/\text{N}_2$  or  $\text{BCl}_3/\text{Ar}$  ICP discharges of different composition.

Figure 5. Etch rates of Ga-based semiconductors as a function of rf chuck power or dc chuck bias in  $\text{BCl}_3/\text{Ar}$  or  $\text{BCl}_3/\text{N}_2$  ICP discharges at fixed source power (500 W) and pressures of 2 - 5 mTorr.

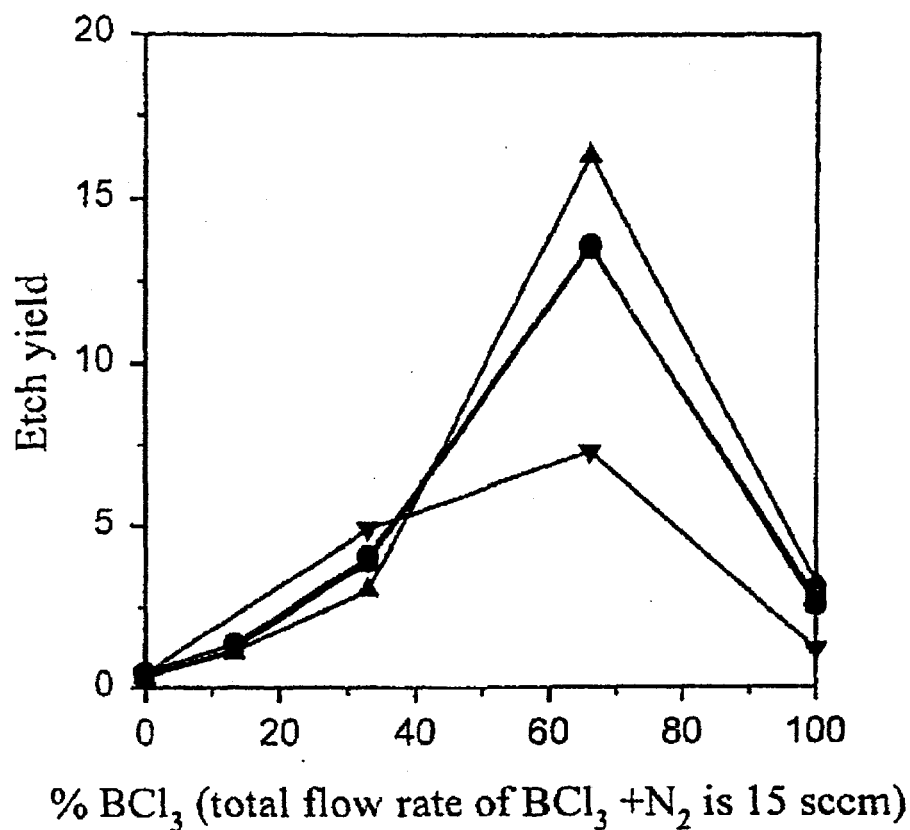
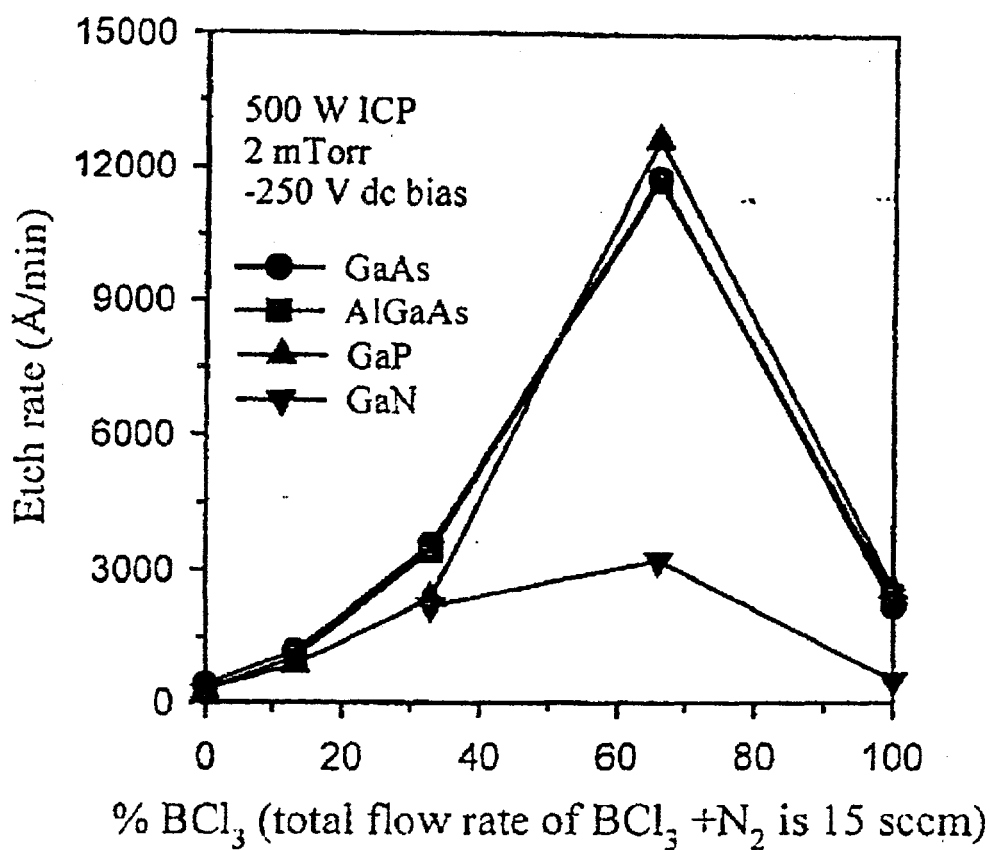
Figure 6. SEM micrographs of features etched into GaAs (top), AlGaAs (center) and GaN (bottom) with  $10\text{BCl}_3/5\text{Ar}$ , 2 mTorr, 500 W source power, 250 W rf chuck power discharges. The photoresist masks have been removed in all cases.

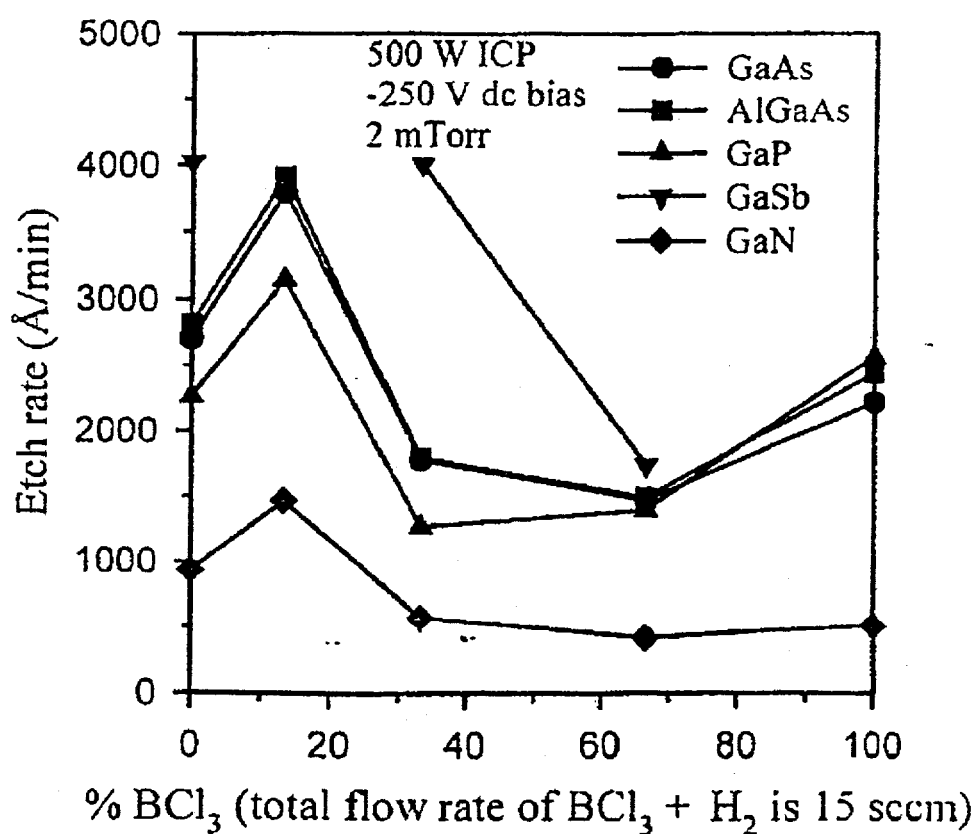
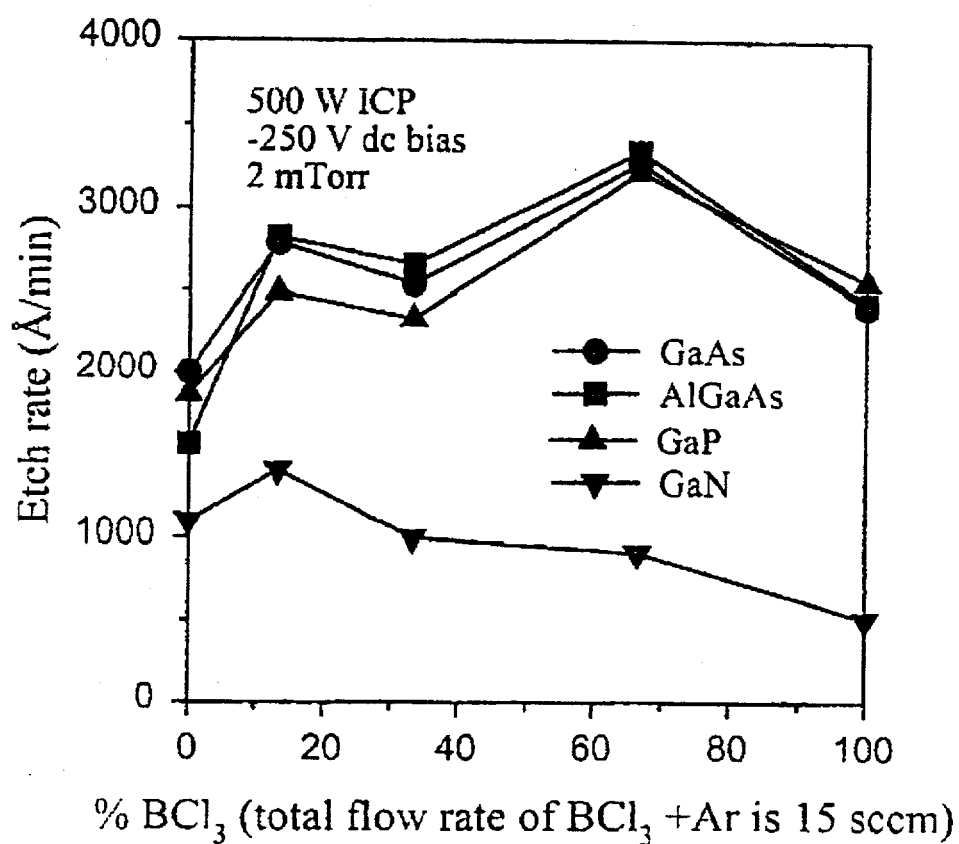
Figure 7. SEM micrographs of features etched into GaAs (top left), AlGaAs (bottom left) or GaN (top and bottom right) with  $10\text{BCl}_3/5\text{N}_2$ , 2 mTorr, 500 W source power, 250 W rf chuck power discharges. The photoresist masks have been removed in all cases.

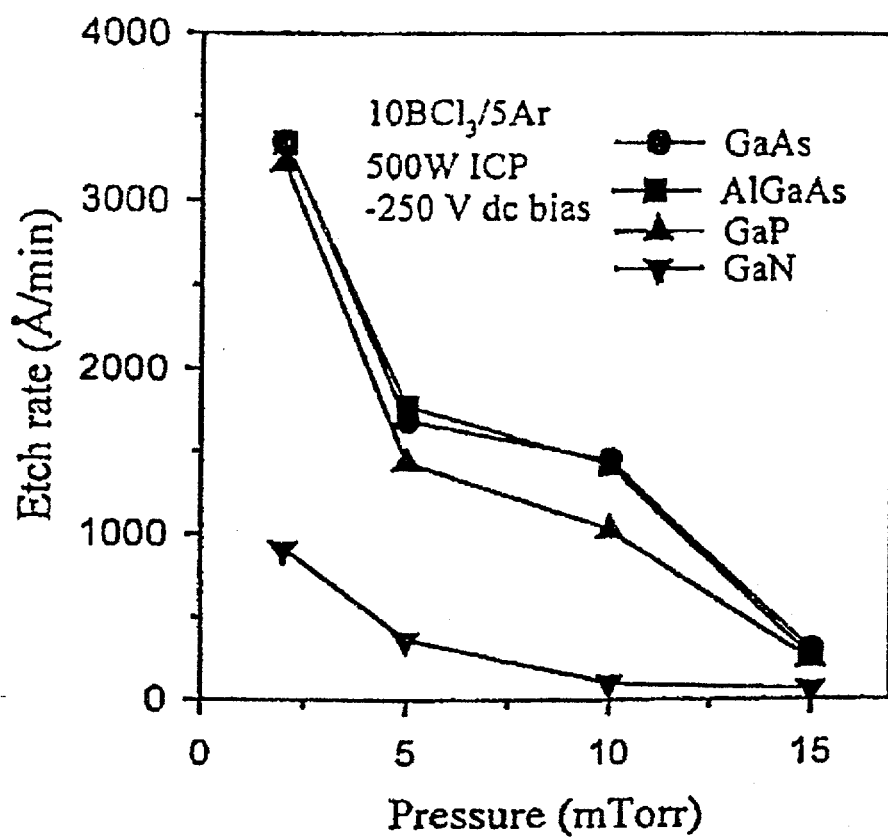
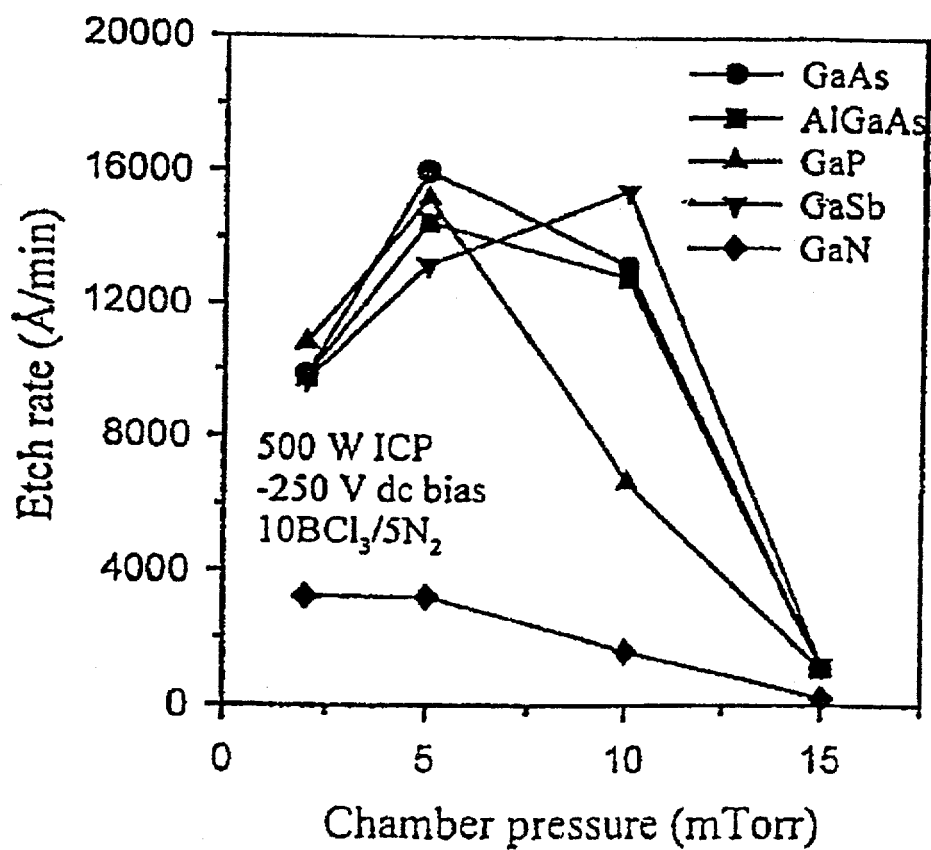
Figure 8. RMS roughness measured by AFM for GaAs and AlGaAs etched with  $\text{BCl}_3/\text{N}_2$  or  $\text{BCl}_3/\text{Ar}$  ICP discharges as a function of discharge composition at fixed source power (500 W), pressure (2 mTorr) and dc self-bias (-250 V).

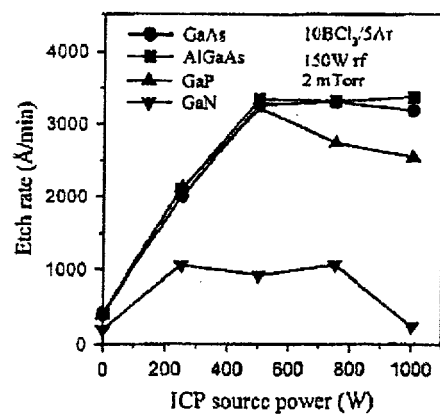
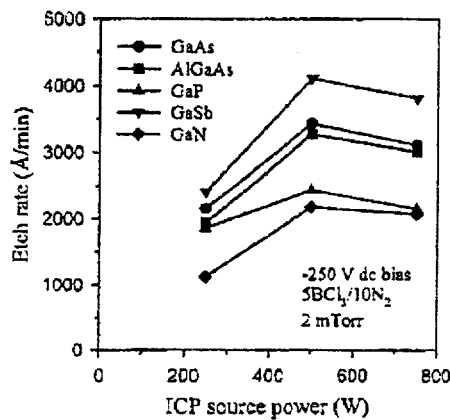
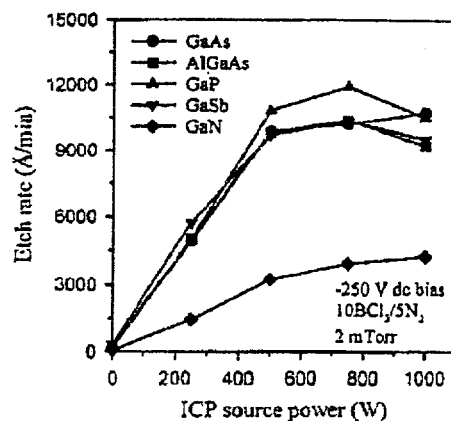
Figure 9. AES surface scans of GaAs etched in 2 mTorr, 500 W source power, -250 V dc bias discharges of  $5\text{BCl}_3/10\text{Ar}$  (top left),  $10\text{BCl}_3/5\text{Ar}$  (bottom left),  $5\text{BCl}_3/10\text{N}_2$  (top right) or  $10\text{BCl}_3/5\text{N}_2$  (bottom right).

Figure 10. AES depth profiles of GaAs etched in 2 mTorr, 500 W source power, -250 V dc bias discharges of  $10\text{BCl}_3/5\text{Ar}$  (top),  $5\text{BCl}_3/10\text{N}_2$  (center), or  $10\text{BCl}_3/5\text{N}_2$  (bottom).

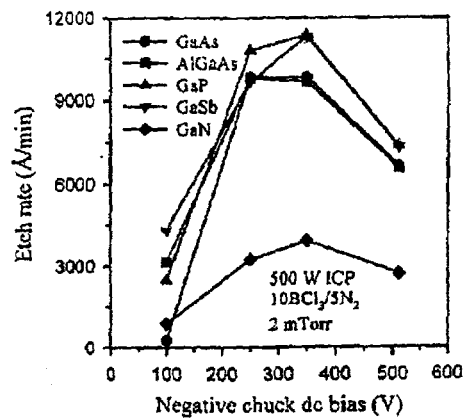
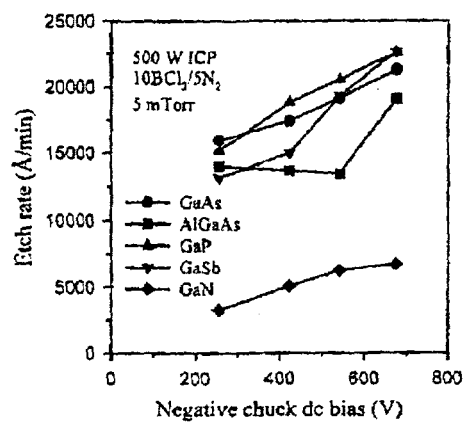
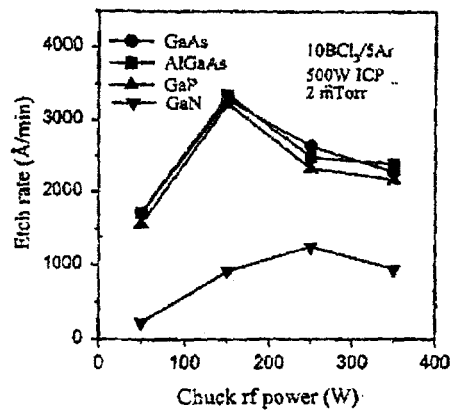


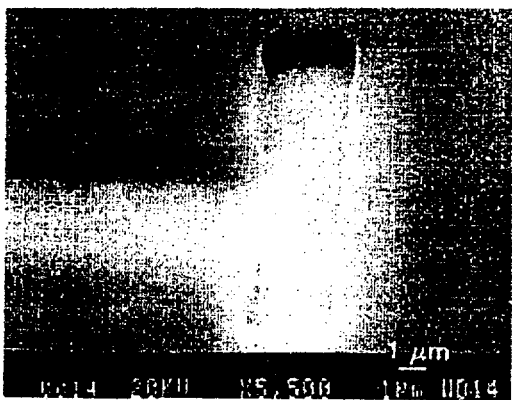
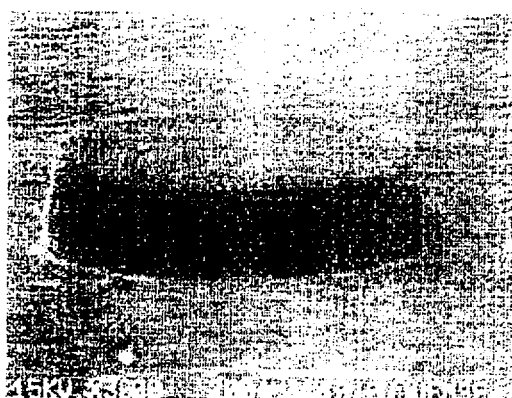
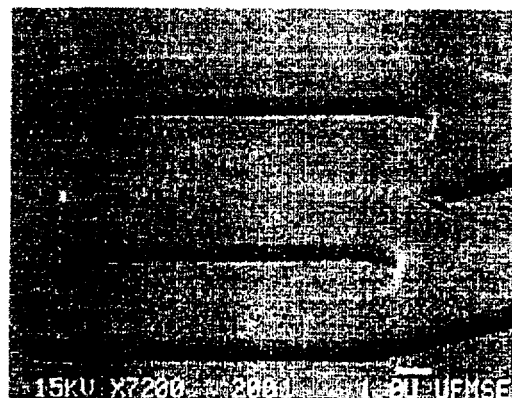


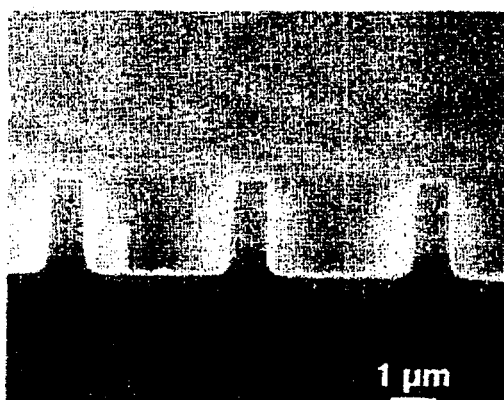
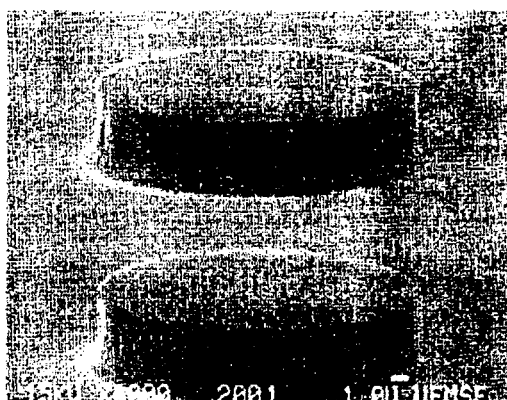
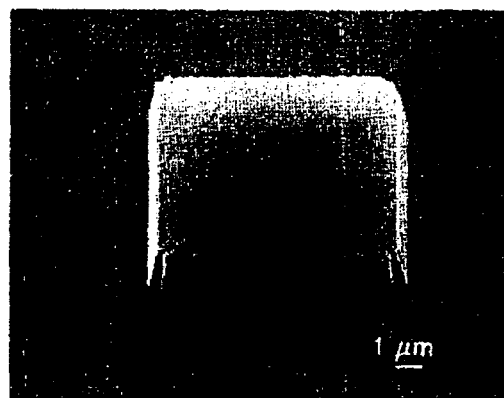
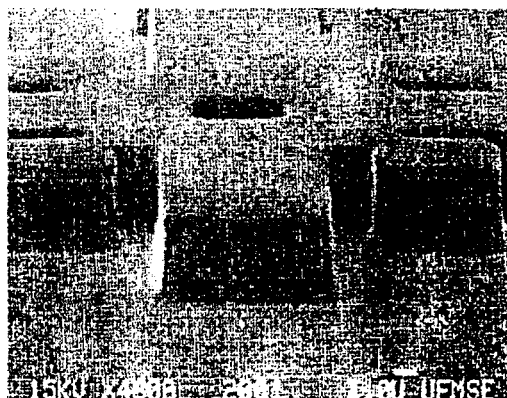


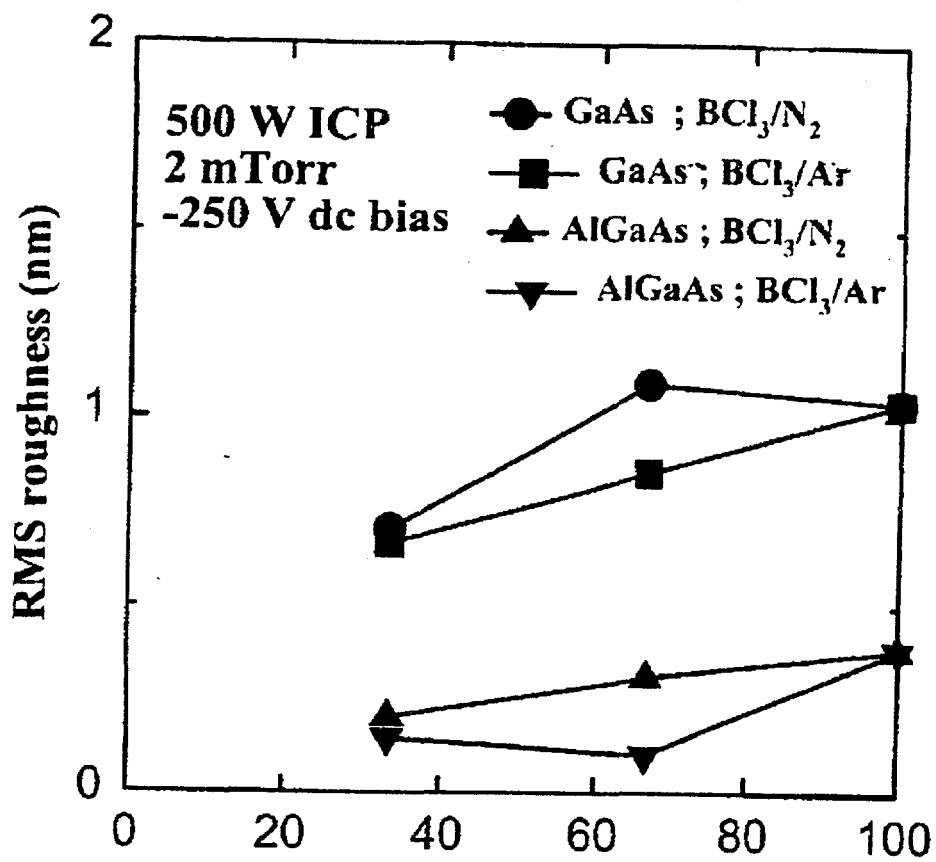




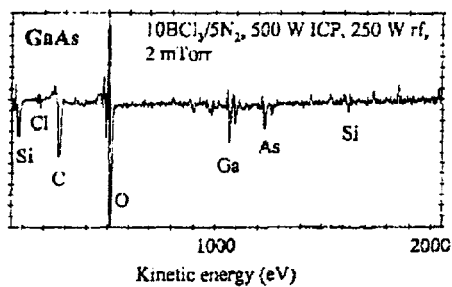
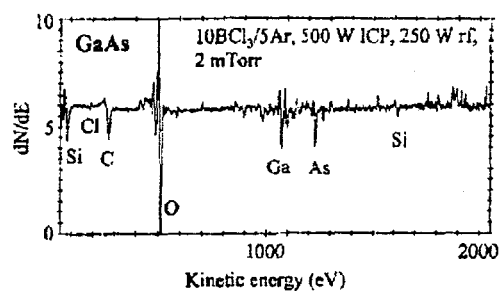
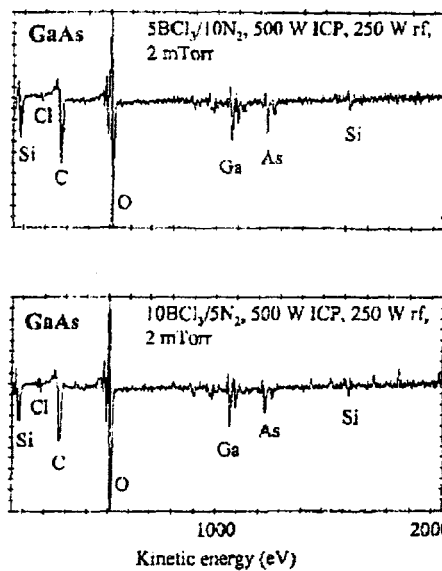
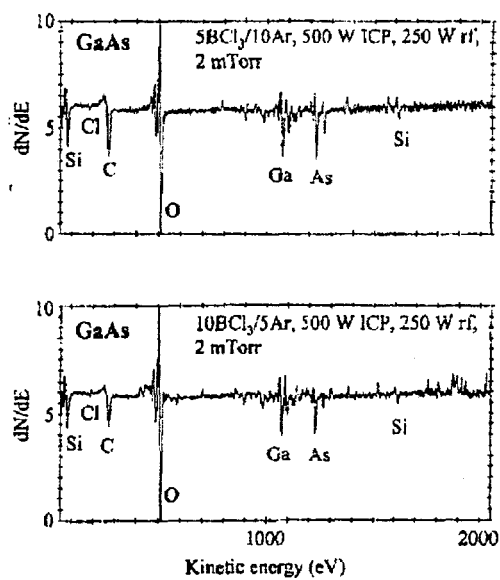








% BCl<sub>3</sub> (total flow rate of BCl<sub>3</sub> + N<sub>2</sub> or Ar is 15 sccm)



Peak to peak

