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Inductively Coupled Plasma Etching in ICl- and IBr-Based Chemistries: Part II. InP, InSb, InGaP and InGaAs

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ABSTRACT

A parametric study of Inductively Coupled Plasma etching of InP, InSb, InGaP and InGaAs has been carried out in ICl/Ar and IBr/Ar chemistries. Etch rates in excess of 3.1 μm/min for InP, 3.6 μm/min for InSb, 2.3 μm/min for InGaP and 2.2 μm/min for InGaAs were obtained in IBr/Ar plasmas. The ICP etching of In-based materials showed a general tendency: the etch rates increased substantially with increasing the ICP source power and rf chuck power in both chemistries, while they decreased with increasing chamber pressure. The IBr/Ar chemistry typically showed higher etch rates than ICl/Ar, but the etched surface mophologies were fairly poor for both chemistries.

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INTRODUCTION

The dry etching of III-V compounds is experiencing a resurgence of interest, largely due to the need to achieve high-resolution, anisotropic etching in device applications. This etching has a variety of requirements, such as fast etch rate for creation of deep ($\geq$ 1 μm) trenches, high selectivity for one material over another (e. g., InGaAs over AlInAs) or, conversely, equi-rate etching for these materials.

There are two basic classes of gas mixtures used for the etching of III-V materials.[1,2] The first is based on Cl or Br, particularly the former because Ga and other group III chloride are volatile at relatively low temperature, as opposed to the stable gallium fluorides. It is common, then, to use Cl_2-based etching for III-V materials, in contrast to the F-based etching prevalent for Si. The second general class of gas mixture is based on methane or ethane and H_2.[3] This has attracted considerable recent attention for etching both Ga- and In-based semiconductors. This nonchlorinated mixture shows controlled, smooth, highly anisotropic etching of all III-V materials.

Etch rates for the In-based materials with Cl_2 containing gases are considerably slower than for GaAs due to the fact that $InCl_x$ is less volatile (boiling point of $InCl_3$ at atmosphere is 600 °C) than $GaCl_x$ (boiling point of $GaCl_3$ is 201 °C) if the sample temperature is kept low during the plasma exposure. Much faster and smoother etching of InP and related materials are obtained at elevated temperatures ($\geq$ 100 °C), where desorption of the group III chlorides becomes easier. However, in general this is impractical in many device processing sequences.

Smooth etching at low rates of all of the III-V materials including In-based compounds is obtained with CH_4/H_2 or C_2H_6/H_2 mixtures, provided that the CH_4-to-H_2

ratio is kept between approximately 1:3. For high CH_4 concentration, polymer deposition on the sample leads to micromasking and rough surfaces, whereas at high H_2 concentrations there is a preferential loss of P or As relative to In or Ga, and this also leads to rough surface morphologies. Hydrogen passivation during CH_4/H_2-based plasma etching of electronic materials can be another important problem which causes degradation of device performance.

To overcome the limitations of existing etch methods, in particular to achieve higher etch rates for InP related compounds, new plasma sources, which operate at much higher ion densities ($> 10^{11}$ cm^{-3}, compared to $\sim 10^9$ cm^{-3} for RIE tools), have been introduced. These sources also operate at relatively low pressures (1 mTorr, or $\sim 3x10^{13}$ atoms/cm^3) and thus the ion-to-neutral ratios are vastly different than in the older reactors. The question that we have addressed in this research is, Can high density plasma sources (i.e. ECR or ICP) achieve new etch regimes to solve the existing problems for pattern transfer in electron materials, especially In-based compounds? And, if the answer is yes, what is the mechanism?

InP was chosen as the prototypical material that requires development of new etch regimes, because it has an involatile product ($InCl_3$) in Cl_2-based plasma chemistries, but alternative chemistries such as CH_4/H_2 have many drawbacks such as the low etch rates and hydrogen passivation discussed earlier. Prior to this current work there has been very little published on high density etching of InP. Constantine et al.[4,5] used ECR $Cl_2/CH_4/H_2/Ar$ plasmas in conjunction with elevated substrate temperatures (130-150 °C) to obtain etch rates of $\sim$ 1 μm/min for forming through-wafer vias. The purpose of the CH_4 was for sidewall passivation to minimize undercut and H_2 was added to try to obtain

equi-rate removal of In and P since at elevated temperatures there is generally faster removal of the former in Cl_2-based plasmas.[4] By adding H_2, they were able to remove P as PH_3.

Somewhat later, Pang et al. was able to demonstrate very high etch rates for InP (up to 4 μm/min) in an ECR Cl_2/Ar discharge at quite low source powers (100-200 W).[6] The control of temperature in their system was not well-defined, and it appears a large amount of the etch-rate enhancement was due to sample heating. It appears to us possible to use the very high ion fluxes available in ECR or ICP sources to prevent formation of the chlorinated selvedge layer that is a feature of RIE Cl_2 etching of InP and thus to achieve a new high-rate regime that avoid all of the disadvantages of the CH_4/H_2 plasma chemistry.[7-9]

It is expected that Cl_2-based plasma chemistry yield the following overall etch reactions with InP:

$$InP + 3Cl_2 \rightarrow InCl_3 + PCl_3 \quad (1)$$

$$4InP + 9Cl_2 + 3H_2 \rightarrow 4InCl_3 + 2PH_3 + 2PCl_3 \quad (2)$$

These equations assume complete reaction to form the fuly chorinated or hydrogenated products, and thus there is an assumption of a high neutral gas density and of the absence of ion bombardment that might desorb partially reacted products by sputtering.[9-15]

In two pioneering papers, McNevin[12,14] examined, firstly, purely chemical etching of InP in Cl_2 (i.e. no ions). For temperatures < 430 K, there was no etching, but at higher temperatures the surface is covered by a mixture of $InCl_2$ and P, as measured by AES. For low Cl_2 pressures, the desorbed etch products were $InCl_2$, InCl and P_4 (the latter

is predominantly a result of surface decomposition at elevated temperature). For high Cl_2 pressures, more fully chlorinated products were desorbed - $InCl_3$, $InCl_2$ and PCl_3. At these temperatures in the absence of a Cl_2 flux, the evaporation products were P_2, P_4 and In.[12,14]

When ions were introduced into the system by creating a Cl_2 plasma, etching was observed even at 300 K, with the etch products being $InCl_2$, InCl and P_4 at low Cl_2 pressures. Note that these are the same products seen at much higher temperatures in the absence of ion bombardment. McNevin's conclusion was that the ions essentially provided a thermal pulse to the surface, and produced reactions that normally would have required much higher temperatures.[14]

Hou et al.[10] produced a similar study on Cl_2 reaction with GaAs. In the absence of a plasma and with a low substrate temperature the main products were $GaCl_3$ and $AsCl_3$, while at high surface temperature the main products were $GaCl_3$ and As_4. Furukata et al.[15] examined the temperature dependence of etch rates for both InP and GaAs in Cl_2 and found activation energies of 7.7 kcal/mol for the former and 13.9 (at >400 °C) and 7.1 kcal/mol (at < 200 °C) for the latter. The results for InP did not even closely match the enthalpies for $InCl_3$ (39.4 kcal/mol), $InCl_2$ (24 kcal/mol) or InCl (27.2 kcal/mol),[14,16] while for GaAs the results were closer to the value for $GaCl_3$ (11.4 kacl/mol) and GaCl and $GaCl_2$ (~ 18 kcal/mol).[10,17] In our particular high density sources we observe the PCl_3 and daughter fragments fairly readily with mass spectrometry, but do not see the $InCl_x$ products under normal circumstances. It is generally believed for neutral/ion flux ratio of > 10 and nominal room temperature processing that the dominant products for GaAs are $GaCl_3$ and $AsCl_3$, and that mass spectrometry detects the daughter

fragments.[10,18-21] Similarly for I_2 etching of GaAs over the temperature range 270 - 330 °C, the major products gas GaI_3 and AsI_3.[22]

Vernon et al.[11] published a detailed study of the effects of Cl_2 pressure and substrate temperature on the etch rate of InP in Cl_2 gas. At high temperatures (> 150 °C) the etch rate was limited by Cl_2 mass transport to the surface, while at lower temperatures the etch rate was a function of Cl_2 sticking coefficient and the stoichiometry of the products (i.e. $InCl_3$, PCl_3 vs. InCl, P_2/P_4). A very surprising result was that the interaction energy between $InCl_3$ and InP was lower than between $InCl_3$ and itself. Above a particular substrate temperature T_s^*, $InCl_3$ desorbs rapidly and etch rate is high and surface morphology is good. As the temperature is lowered, $InCl_3$ islands form, and below T_s^* there can be complete $InCl_3$ coverage and the etch rate follows the $InCl_3$ vapor pressure. However, at T_s^* islands of $InCl_3$ and bare InP co-exist, but the bare InP etches at a rate approximately 15 times faster than the islands regions, leading to rough surfaces.

These results have direct relevance to the situation in high density plasma etching of InP in Cl_2-based chemistries. They clearly indicate that the ion-neutral ratio, which determines the Cl_2 coverage and the localized surface temperature in the first 10 - 30 Å will control the etch rate and surface morphology provided we can provide an optimum window of ion flux to incident Cl neutral flux. This is equally clearly not possible in conventional RIE systems because of the low ion density (~ 10^9 cm^{-3}) and high neutral density (~ 1 % dissociation of 100 mTorr of gas, i.e. 3 x 10^{13} cm^{-3} atomic chlorine, or an ion-to-neutral ratio of 3.3 x 10^{-5}). By contrast in a high density tool the ion density is typically ~ 3 x 10^{11} cm^{-3}, with a dissociated percentage of ~ 25 % of 1 mTorr, i.e. 0.75x10^{13} atomic chlorine, or an ion-to-neutral flux ~ 4 x 10^{-2}, or 3 orders of magnitude

higher than in the RIE tool. Our current tenet was that this completely different plasma regime should enable us to achieve new etch processes for InP, and thus avoid all the drawbacks of the CH_4/H_2 chemistry, and of the need for elevated substrate temperatures with RIE.

In the previous paper we examined ICP etching of Ga-based semiconductors.[23] In this work, the influence of ICl/Ar and IBr/Ar chemistries on the ICP etching of In-based compounds (InP, InSb, InGaP and InGaAs) has been studied for various plasma parameters. Plasma composition, rf chuck power and ICP source power were varied to examine their effects on the etch rates, dc bias and ion fluxes, and morphology. The ICP ICl/Ar and IBr/Ar discharges resulted in high etch rates for the In-based compounds, resulting in somewhat faster etch rates with IBr/Ar chemistry.

EXPERIMENTAL

Fe-doped InP and nominally undoped InSb wafers were taken from Czochralski-grown bulks. Epitaxial layers of $In_{0.5}Ga_{0.5}P$ and $In_{0.53}Ga_{0.47}As$ were grown on GaAs and InP wafers, respectively by Metal Organic Molecular Beam Epitaxy or Metal Organic Chemical Vapor Deposition. Samples were masked with Apiezon wax, and etching and subsequent characterizations were carried out as described in the previous paper.[23]

RESULTS AND DISCUSSION

Figure 1 shows the effect of plasma composition on etch rates of InP, InSb, InGaP and InGaAs in IBr/Ar and ICl/Ar discharges at 5 mTorr, 750 W source power and 250 W rf chuck power. In the ICl/Ar plasmas the etch rates of InP, InSb and InGaAs increased up to 33.3 % ICl and decreased thereafter, while that of InGaP increased with increasing ICl content (Fig. 1, top). However, in the IBr/Ar discharges InSb and InGaP showed maximum etch rates at 33.3 % IBr, while InP and InGaAs showed an increase in etch rate with IBr percentage (middle). The etch rates are proportional to the interhalogen content in both chemistries, indicating that etching of GaAs in either chemistry is more attributed to chemical etching by increased concentrations of reactive neutrals than ion-assisted sputtering. The maximum etch rates obtained at 750 W source power, 250 W rf chuck power and 5 mTorr were: 1) 2.2 μm/min for InP, 1.7 μm/min for InSb, 1.3 μm/min for InGaAs and 0.8 μm/min for InGaP in the ICl/Ar chemistry, and 2) in the IBr/Ar plasma, 3.1 μm/min for InP, 3.6 μm/min for InSb, 2.3 μm/min for InGaP and 2.2 μm/min for InGaAs. The greater etch rates with IBr/Ar than with ICl/Ar may be attributed to relatively low volatilities of etch products such as $InCl_x$ (for example, $InCl_3$ boils at 600 °C, but $InBr_3$ sublimes).[24] It is also interesting to see that the fall-off in etch rates is more drastic with IBr/Ar than with ICl/Ar plasmas. This may be due to the increased dc-bias voltages or ion bombardment energies in the former (Fig. 1, bottom). The increased self-bias voltage enhances the desorption of the reactive species at the substrate surface prior to etch reactions. At the same time the decreased ion fluxes due to the increased dc biases contribute in part to the decrease of etch rate at higher concentrations of etch gases.

In general the etch characteristics are significantly affected by the ICP source power or ion density. Figure 2 shows the effect of ICP source power on etch rates, dc bias voltages, and ion fluxes at the sheath edge for ICl/Ar (top) and IBr/Ar discharges (middle) with constant flow rates of etch gases at 2 sccm ICl or IBr and 13 sccm Ar. During these runs the chamber pressure and the rf chuck power were held constant at 5 mTorr and 250 W, respectively. The etch rates of all materials increased substantially with the ICP source power in both chemistries, except the InSb etch rate at 750 W in IBr/Ar. These results indicate that the increase in etch rates with increasing the source power is mainly due to the higher concentration of reactive species in the plasma, suggesting a reactant-limited regime, and to higher incident ion flux to the substrate surface. Both chemistries showed similar variations of dc-bias voltages and ion fluxes at the sheath edge. (Fig. 2, bottom).

Figure 3 shows the effect of rf chuck power on the etch rates, dc bias, and ion flux at the sheath edge at 750 W ICP power, 5 mTorr and 2 sccm ICl or IBr and 13 sccm Ar. As with the GaAs and related compounds, ICP etch characteristics showed a general tendency: etch rates for all materials except InSb increased substantially in both ICl (top) and IBr (middle) discharges as the rf power or the ion-bombarding energy increased. The dc-bias volatge increased monotonically from - 74 to -308 V with varying the chuck power from 50 to 350 W, resulting in an enhancement of sputter desorption of etch products due to the increased ion bombardment energies (bottom).

The effect of reactor pressure on etch rate, etch yield, dc bias and ion flux in ICl/Ar plasmas is shown in Fig. 4. Experiments were performed at constant source power (750 W) and chuck power (250 W). InSb showed a maximum etch rate at 10 mTorr,

while other materials showed decreased etch rates with increasing the pressure. The tendency of increase or decrease in etch rate with pressure indicates that there exists a pressure which divides the etch mechanism between mass-transfer limited and redeposition-of-etch products limited regimes. Etch yield data together with dc biases and ion fluxes at the sheath are shown in the lower part of the figure.

The surface morphologies were examined using AFM for etched samples. Figure 5 shows the AFM results for InGaP etched at 750 W ICP power, 250 W rf chuck power and 5 mTorr in 2ICl/13Ar (top) and 2IBr/13Ar (bottom) discharges. The etched surface of InGaP showed better morphology with ICl/Ar (rms roughness 7.4 nm) than with IBr/Ar (rms value 27.8 nm), while InP showed quite rough surfaces with both chemitsries (rms roughness > 10nm uner all conditions). These results indicate that these chemistries are not suited for mesa etching applications because of the rough surfaces, but are promising for through-wafer via etching.

SUMMARY AND DISCUSSION

Inductively Coupled Plasma etching of InP, InSb, InGaP and InGaAs has been carried out in ICl/Ar and IBr/Ar chemistries. The effects of plasma composition, ICP source power, rf chuck power and chamber pressure on etch rate, etch yield, dc-bias voltage and ion flux at the sheath edge were examined. Very high rates suitable for via hole formation were obtained for all In-containing materials. In the ICl/Ar plasmas, the etch rates of InP, InSb and InGaAs showed maxima depending on interhalogen content, while InGaP etch rate increased etch rates with plasma composition. However, in the IBr/Ar discharges InSb and InGaP showed maximum etch rates at 33.3 % IBr; InP and

InGaAs showed an increase in etch rate with IBr content. The etch rates of all materials generally increased substantially with the ICP source power in both chemistries. Higher etch rates of In-based materials (except InSb in ICl/Ar) were also obtained with higher rf chuck powers, while etch rates were decreased with increasing chamber pressure.

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REFERENCES

1. S. J. Pearton, U. K. Chakrabarti, and W. S. Hobson, J. Appl. Phys., 66, 2061 (1989).
2. E. M. Omeljanovsky, A. V. Pakhomov, A. Y. Polykov, O. M. Borodina, E. A. Kozhukhova, A. U. Nashelski, S. V. Yakobson, and V. V. Novikova, Solid State Communications, 72, 409 (1989).
3. M. Moehrle, Appl. Phys. Lett., 56, 542 (1990).
4. C. Constantine, C Barratt, S. J. Pearton, F. Ren, J. R. Lothian, W. S. Hobson, A. Katz, C. W. Yang, and P. C. Chao, Electron. Lett., 29, 984 (1993).
5. C. Constantine, C Barratt, S. J. Pearton, F. Ren, and J. R. Lothian, Appl. Phys. Lett., 61, 2899 (1992); Electron. Lett., 28 1749 (1992).
6. S. Thomas III, K. K. Ko, and S. W. Pang, J. Vac. Sci. Technol., A13, 894 (1995); S. Thomas III, E. W. Beog, and S. W. Pang, J. Vac. Sci. Technol., B14, 1807 (1996).
7. J. W. Lee, J. Hong, and S. J. Pearton, Appl. Phys. Lett., 68, 847 (1996).
8. J. Kainal, S. Sotier, and G. Franz, J. Electrochem. Soc., 142, 2418 (1995).
9. D. L. Melville, J. G. Simmons, and D. A. Thompson, J. Vac. Sci. Technol., B11, 2028 (1993).
10. H. Hou, z. Zhang, S. Chen, C. Su, W. Yan, and M. Vernon, Appl. Phys. Lett., 55, 801 (1989).
11. M. Vernon, T. R. Hayes, and V. M. Donnelly, J. Vac. Sci. Technol., A10, 3499 (1992).
12. S. C. McNevin, J. Vac. Sci. Technol., B4, 1216 (1986).

13. V. M. Donnelly, D. L. Flamm, C. W. Tu, and D. E. Ibbotson, J. Electrochem. Soc., 129, 2533 (1982).

14. S. C. McNevin, , J. Vac. Sci. Technol., B4, 1227 (1986); Ext. Abstr. Of the 18th Intl. Conf. On Solid State Devices and Materials (1986), pp. 721-722.

15. N. Furukata, H. Miyamoto, A. Okamoto, and K. Okata, J. Appl. Phys., 65, 168 (1989).

16. Y. Kuniya and M. Hosaka, J. Cryst. Growth, 28, 385 (1975).

17. M. Balooch, D. R. Olander, and W. J. Siekhaus, J. Vac. Sci. Technol., B4, 704 (1986).

18. M. S. Ameen and T. M. Mayer, J. Appl. Phys., 63, 1152 (1988).

19. S. C. McNevin and G. E. Becker, J. Appl. Plys., 58 , 4670 (1985).

20. C. Su, M. Xi, Z. G. Dai, M. F. Vernon, and B/ E/ Bent, Surf. Sci., 282, 357 (1993).

21. C. R. Eddy, Jr., O. J. Gembocki, D. Leonhardt, V. A. Shamamian, R. T. Holen, B. D. Thomas, J. E. Butler, and S. W. Pang, J. Elctron. Mater., 26, 2310 (1997).

22. K.-C. Wang and E. A. Ogryzlo, , J. Vac. Sci. Technol., B10, 668 (1992).

23. Y. B. Hahn, H. Cho, K. B. Jung, E. S. Lambers, C. R. Abernathy, S. J. Pearton, W. S. Hobson, and R. J. Shul, Plasma Chem. Plasma Proc., submitted (1998).

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

Figure Captions

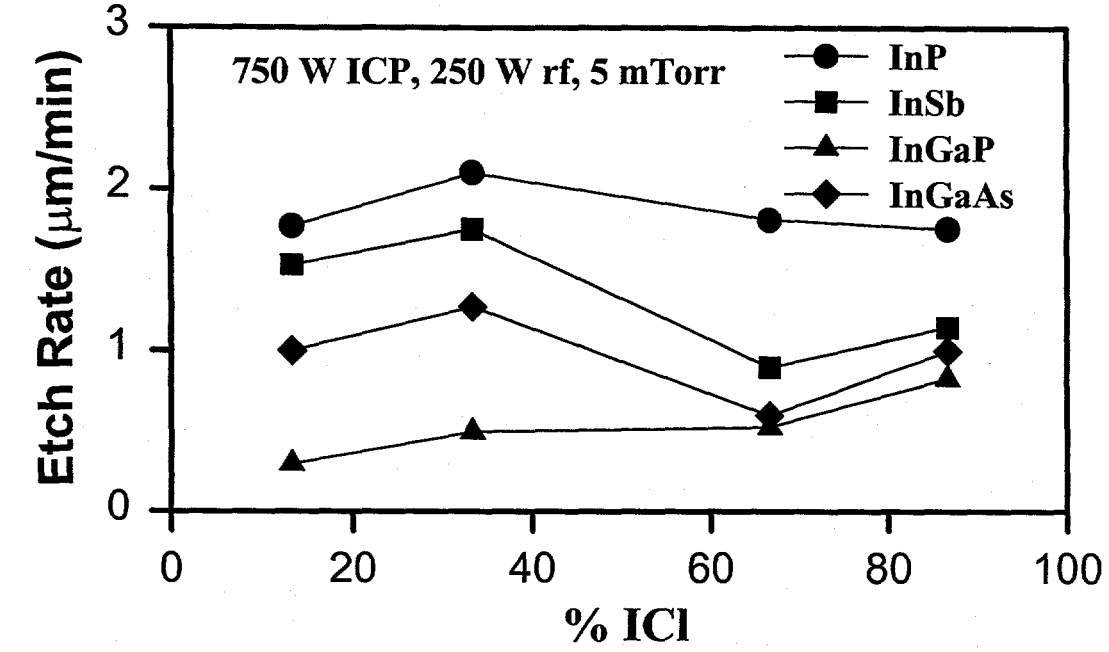
Figure 1. Effect of plasma composition on etch rates in ICl/Ar (top) and IBr/Ar (middle) plasma chemistries, and dc bias and ion flux at the sheath (bottom).

Figure 2. Effect of ICP source power on etch rates in ICl/Ar (top) and IBr/Ar (middle) plasma chemistries, and dc bias and ion flux at the sheath (bottom).

Figure 3. Effect of rf chuck power on etch rates in ICl/Ar (top) and IBr/Ar (middle) plasma chemistries, and dc bias and ion flux at the sheath (bottom).

Figure 4. Effect of process pressure on etch rates in ICl/Ar (top) plasma chemistry, and dc bias and ion flux at the sheath (bottom).

Figure 5. AFM scans for InGaP etched in ICl/Ar (top) and IBr/Ar (bottom) plasmas.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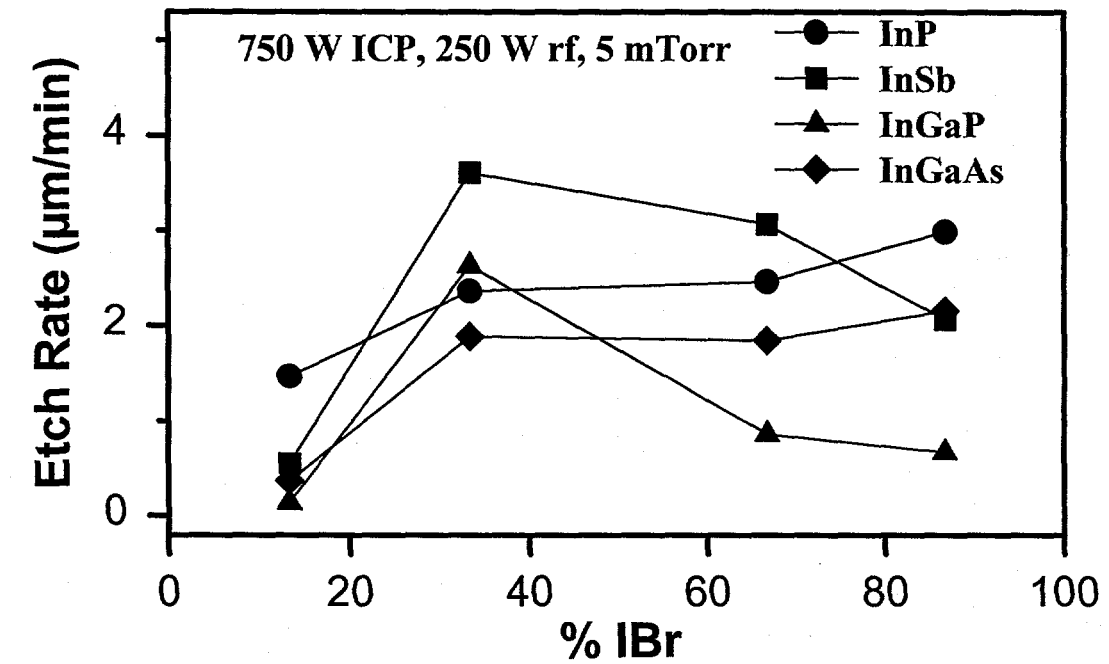
InP
InSb
InGaP
InGaAs
Etch Rate (μm/min)
% ICl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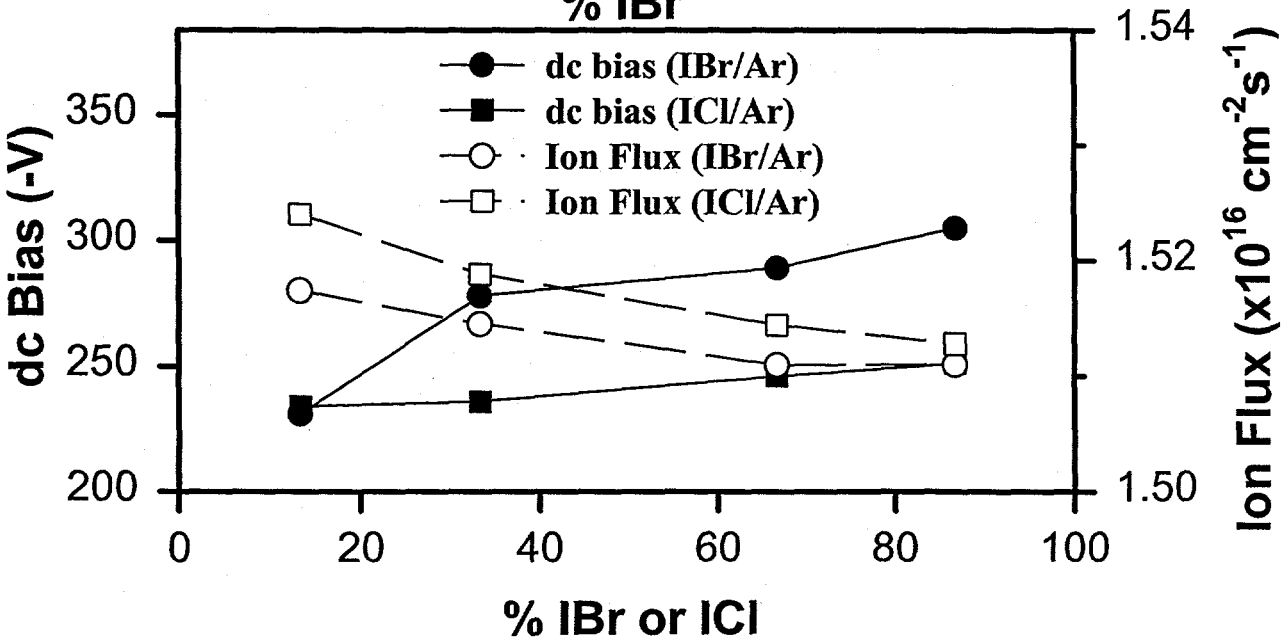
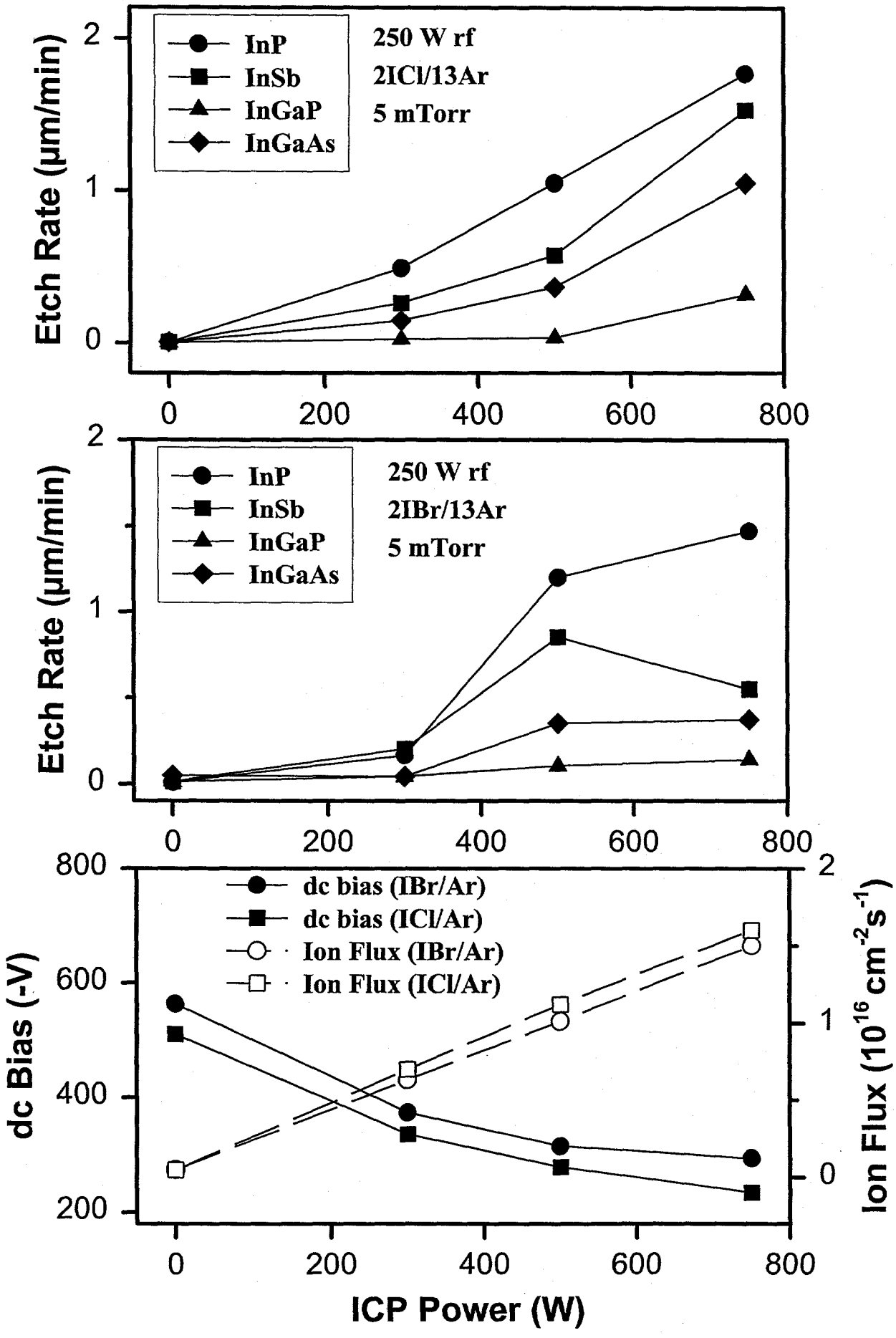
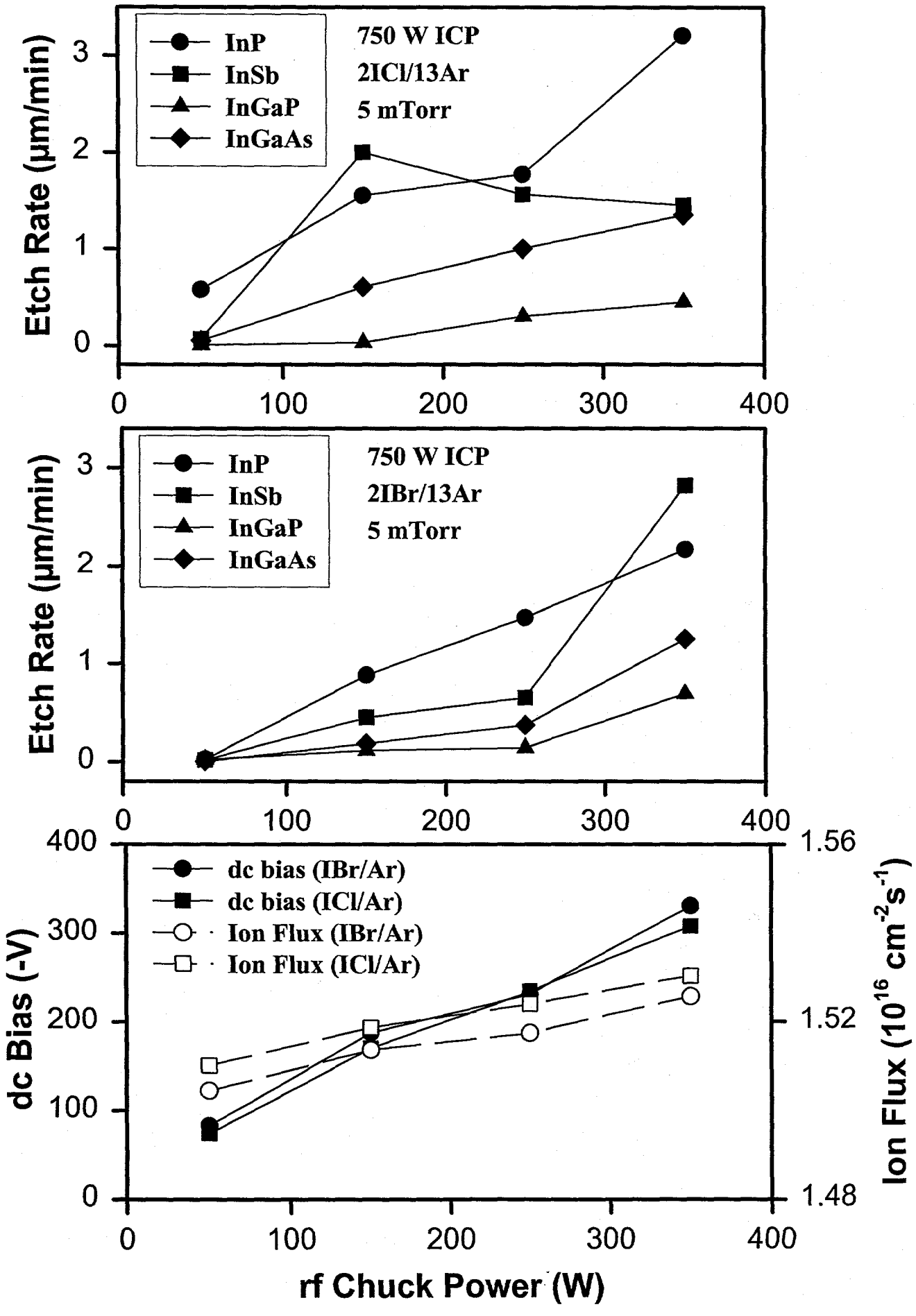
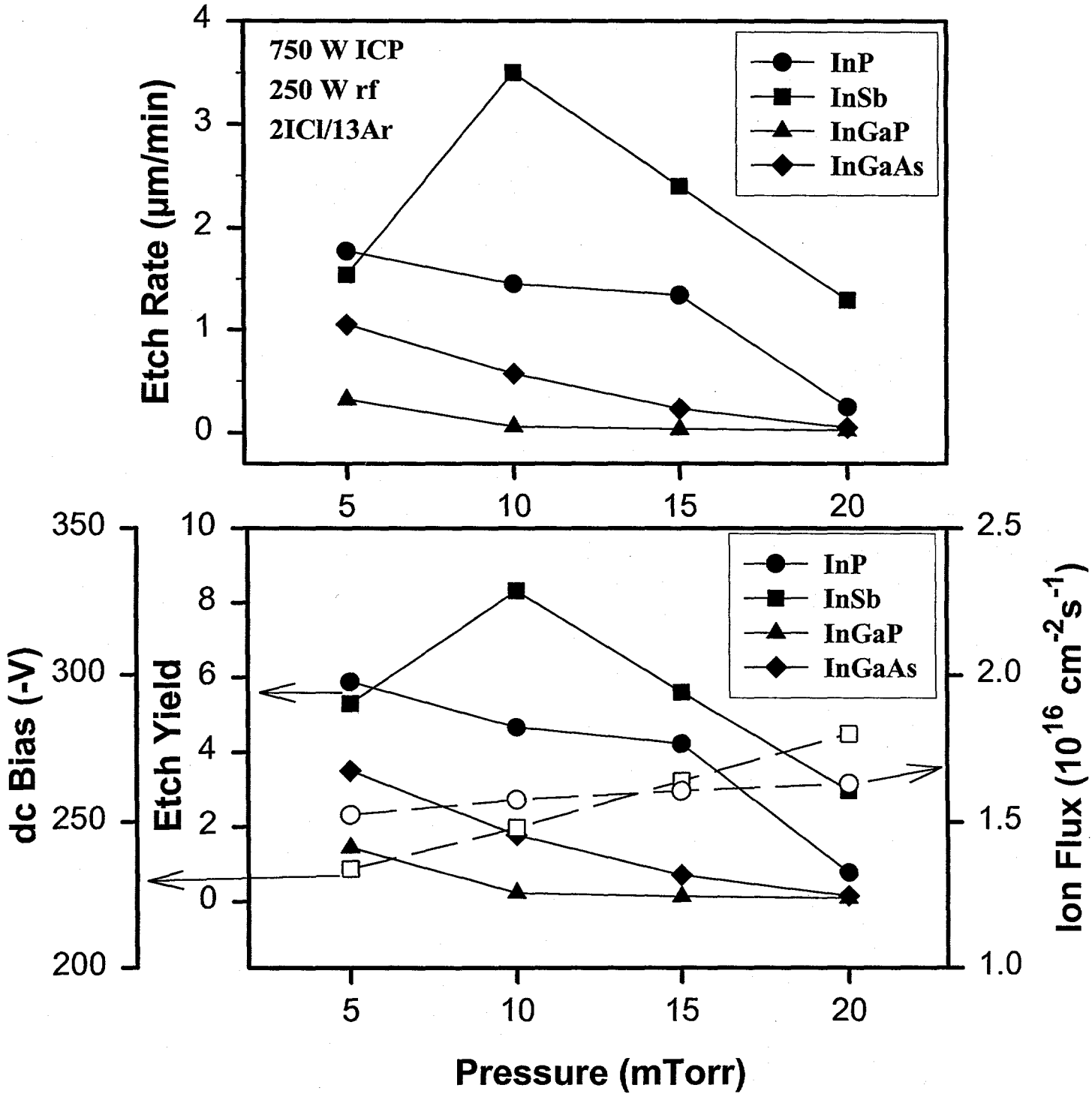
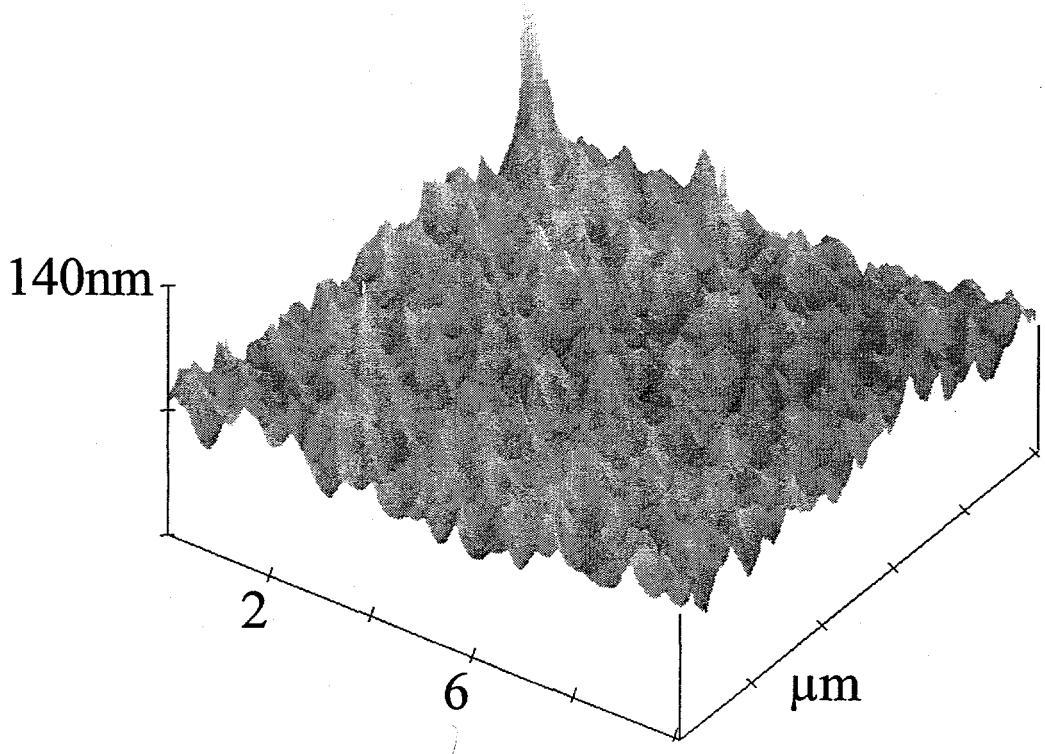
InP
InSb
InGaP
InGaAs
Etch Rate (μm/min)
% IBr


dc bias (IBr/Ar)
dc bias (ICl/Ar)
Ion Flux (IBr/Ar)
Ion Flux (ICl/Ar)
dc Bias (-V)
Ion Flux (x10^16 cm^-2 s^-1)
% IBr or ICl

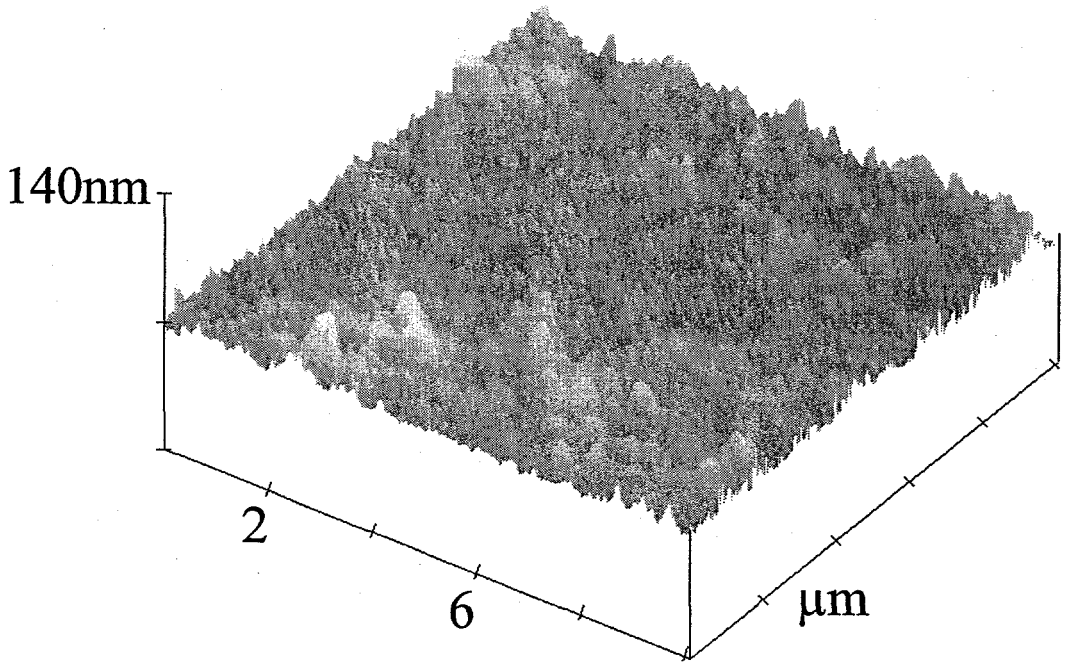

InP
InSb
InGaP
InGaAs
250 W rf
2ICl/13Ar
5 mTorr
Etch Rate (μm/min)
0
1
2
0
200
400
600
800
InP
InSb
InGaP
InGaAs
250 W rf
2IBr/13Ar
5 mTorr
Etch Rate (μm/min)
dc bias (IBr/Ar)
dc bias (ICl/Ar)
Ion Flux (IBr/Ar)
Ion Flux (ICl/Ar)
dc Bias (-V)
Ion Flux (10^{16} $cm^{-2}s^{-1}$)
200
400
600
800
ICP Power (W)


InP
InSb
InGaP
InGaAs
750 W ICP
2ICl/13Ar
5 mTorr
Etch Rate (μm/min)
0
1
2
3
0
100
200
300
400
InP
InSb
InGaP
InGaAs
750 W ICP
2IBr/13Ar
5 mTorr
Etch Rate (μm/min)
0
1
2
3
0
100
200
300
400
dc bias (IBr/Ar)
dc bias (ICl/Ar)
Ion Flux (IBr/Ar)
Ion Flux (ICl/Ar)
dc Bias (-V)
0
100
200
300
400
1.48
1.52
1.56
Ion Flux (10^{16} $cm^{-2}s^{-1}$)
0
100
200
300
400
rf Chuck Power (W)


750 W ICP
250 W rf
2ICl/13Ar
InP
InSb
InGaP
InGaAs
Etch Rate (μm/min)
Etch Yield
dc Bias (-V)
Ion Flux (10^{16} $cm^{-2}s^{-1}$)
Pressure (mTorr)



2ICl/13Ar
RMS Roughness = 7.4nm



2IBr/13Ar
RMS Roughness = 27.8nm