

INDUCTIVELY COUPLED PLASMA ETCHING OF III-V SEMICONDUCTORS IN BCl₃-BASED CHEMISTRIES : PART II : InP, InGaAs, InGaAsP, InAs AND AlInAs

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ABSTRACT

A parametric study of etch rates and surface morphologies of In-containing compound semiconductors (InP, InGaAs, InGaAsP, InAs and AlInAs) obtained by BCl₃-based Inductively Coupled Plasmas is reported. Etch rates in the range 1,500 - 3,000 Å/min. are obtained for all the materials at moderate source powers (500 W), with the rates being a strong function of discharge composition, rf chuck power and pressure. Typical root-mean-square surface roughness of ~5 nm were obtained for InP, which is worse than the values obtained for Ga-based materials under the same conditions (~1 nm). The near surface of etched samples is typically slightly deficient in the group V element, but the depth of this deficiency is small (a few tens of angstroms).

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INTRODUCTION

Laser diodes operating at 1.3 or 1.55 μm are the basis of telecommunication systems and employ InGaAsP active regions with InGaAs contact layers. The AlInAs/InGaAs/InP heterostructure system is of interest for high speed bipolar transistors and modulation-doped field effect transistors, and InAs is useful for Hall sensors⁽¹⁻³⁾. While the Ga-based materials described in part I of this paper are readily dry etched in Cl₂-containing plasma chemistries, In-containing compound semiconductors present difficulties in trying to obtain efficient and equi-rate removal of the group V lattice elements and the In⁽⁴⁻¹⁵⁾. Under conventional reactive ion etching conditions there is difficulty in desorbing the relatively involatile InCl_x etch products in Cl₂ discharges unless the sample is heated to $> 240^\circ\text{C}$ ^(4, 9, 10, 16). Even at elevated temperature where acceptable etch rates are obtained, the sidewall profiles lead to be sloped⁽⁴⁾. To avoid these problems the most commonly used plasma chemistry is CH₄/H₂⁽¹⁷⁾, which is a universal etchant for In-based semiconductor. This produces smooth pattern transfer, but suffers from low etch rates (< 100 nm/min), hydrogen passivation of near-surface dopants and polymer deposition within the chamber. Under high density conditions it has proven essentially impossible to avoid preferential loss of the group V element from the surface with the CH₄/H₂ chemistry, and in some cases it is even possible to observe In-droplets⁽¹⁸⁾.

For these reasons there is strong interest in developing high density plasma etch process for the In-containing compound semiconductors using chlorine-based chemistries and without sample heating, since the latter precludes use of photoresist masks. Previous results on Electron Cyclotron Resonance (ECR) Cl₂ or BCl₃ etching of InP, InGaAs and InGaP have shown that under some conditions it is possible to achieve practical etch rates while maintaining a high surface quality^(10, 19). Most of the development effort on high density plasma sources has turned away from ECR toward inductively coupled geometries because of their superior uniformity, the existence of more mature auto-tuning networks at these frequencies and the absence of bulky and expensive electromagnets^(20, 21). A key question therefore is whether chlorine-containing plasma chemistries operated under Inductively Coupled Plasma (ICP) conditions can provide practical room-temperature etch rates for In-based semiconductors, together with high quality surfaces.

In this paper we describe a parametric study of BCl₃-based ICP etching of five different In-containing materials (InP, InAs, InGaAs, InGaAsP and AlInAs). The experimental parameters

varied were discharge composition, ICP source power, pressure and dc chuck bias. We find that reasonably smooth (root-mean-square roughness ≤ 5 nm) surfaces can be achieved at maximum rates in the range 2 - 5,000 Å/min.

EXPERIMENTAL

The following samples were employed in this study: Fe-doped semi-insulating (100) InP substrates grown by the Czochralski process; nominally undoped ($n \sim 10^{16}$ cm $^{-3}$), (100) InAs substrates grown by the Czochralski process; nominally undoped ($n \sim 5 \times 10^{15}$ cm $^{-3}$) In_{0.53}Ga_{0.47}As, Al_{0.48}In_{0.52}As or InGaAsP ($\lambda = 1.3$ μm) all grown lattice-matched to InP by either Metal Organic Molecular Beam Epitaxy (MOMBE)⁽²²⁾ or Metal Organic Chemical Vapor Deposition (MOCVD)⁽²³⁾. All samples were patterned with a Shipley photoresist.

All of the etching was performed in the system described in the previous paper⁽²⁴⁾, and similar characterization methods were employed.

RESULTS AND DISCUSSION

Figure 1 (top) shows etch rates for two of the materials in BCl₃/N₂ ICP discharges as a function of discharge composition at fixed pressure (2 mTorr), source power (500 W) and dc self-bias (-250 V). We do not observe the sharp maxima in etch rates seen for the Ga-based materials at a discharge composition of ~33% N₂ by flow⁽²⁴⁾. The difference is most likely due to the fact that the etch rates for In-based materials are not limited by the supply of chlorine neutrals, but rather by the desorption of the InCl_x etch products. The results in Figure 1 are therefore consistent with the simple picture of increasing etch rates as BCl₃ is introduced into the plasma chemistry, and a gradual reduction at high BCl₃ percentages due to a lower ion density in the discharge (note that a lower rf power is required to sustain -250 V chuck bias for pure BCl₃ conditions, indicating a decreased positive ion density). Etch yield data is shown at the bottom of the Figure 1. The calculations for etch yield will be described elsewhere⁽²⁵⁾.

The etch rate data for BCl₃/Ar and BCl₃/H₂ discharges are shown in Figure 2. The results for BCl₃/Ar are fairly similar to those for BCl₃/N₂, which is expected from the previous discussion.

The rates with BCl_3/H_2 are significantly lower than for the other two chemistries due to the less effective sputter desorption of the products and the lower chlorine neutral density.

The influence of ICP source power on etch rate is shown in Figure 3. For the BCl_3/N_2 chemistry at high BCl_3 percentage (shown in the top of the Figure) the rates increase essentially linearly with this power, as ion flux to the surface increases. At lower BCl_3 percentages (shown in the center of the Figure) the etch rates saturate or decrease at high source power, where reactant-limited conditions apply. Since BCl_3/Ar discharges contain less atomic chlorine, these conditions are reached at lower source power (bottom of the Figure).

The effect of process pressure at fixed dc chuck bias is shown in Figure 4. The results are similar for both BCl_3/N_2 and BCl_3/Ar mixtures, with the rates decreasing almost linearly with increasing pressure due to a lower ion density resulting from recombination.

As with the Ga-based materials, there was a general tendency for In-material etch rates to increase with chuck power (or dc chuck bias) due to more efficient ion-assisted product desorption, followed by a saturation or even reduction as the chlorine neutral desorption prevents reaction with the semiconductor surface (Figure 5). At higher pressures (5 mTorr) in the BCl_3/N_2 mixture we do not observe this behavior (lower part of the Figure) since there is a higher chlorine density under these conditions.

While the root-mean-square (RMS) roughness for etched surfaces of Ga-based materials measured by AFM were ≤ 1 nm, and the surfaces were essentially featureless when examined by SEM, the results were not as good for the In-based materials. Figure 6 shows SEM micrographs of InP (top, left and right) and InGaAs (bottom, left and right) features formed by BCl_3/N_2 (left, top and bottom) or BCl_3/Ar (right, top and bottom) discharges. The sidewalls are somewhat more sloped than for the Ga-based materials etched under the same conditions, and the surfaces slightly rougher. The sidewall roughness originates from the photoresist mask, which is replicated into the semiconductor¹⁶. To quantify the surface morphology, AFM measurements were performed. Figure 7 shows RMS values as a function of BCl_3 percentage in BCl_3/N_2 and BCl_3/Ar by flow. The latter typically produces slightly better morphologies, but for both plasma chemistries the RMS values are 3 - 5 times rougher than unetched control samples.

It is generally difficult to produce InP with a stoichiometric surface after dry etching because of the disparity in chemical volatility of the respective In and P etch products and in the weight of the In and P atoms if there is a strong sputter component⁴. Figure 8 shows AES surface scans

of InP after etching in 5 $\text{BCl}_3/10\text{N}_2$ (top left), 10 $\text{BCl}_3/5\text{N}_2$ (bottom left), 5 $\text{BCl}_3/10\text{Ar}$ (top right) or 10 $\text{BCl}_3/5\text{Ar}$ (bottom right). There is oxygen present from the native oxide that forms upon exposure to ambient and adventitious carbon. The two main features common to all the data are the presence of detectable chlorine-containing residues and a slight P deficiency. The amount of chlorine is small (~1 at %), but larger than in the case of the Ga-based materials described earlier. However previous publications on Cl_2 -based etching of InP under RIE conditions have shown residual chlorine concentrations at least an order of magnitude larger, which emphasizes the efficiency of the higher ion flux in ICP tools in removing InCl_x species and preventing build-up of a selvedge layer. To more fully examine the stoichiometry of the near-surface region of the etched samples, AES depth profiling was performed. As shown in Figure 9, the In and P signals come to their stoichiometric values within approximately 1.5 minutes of sputtering time, equivalent to ~75 Å depth.

SUMMARY AND CONCLUSIONS

BCl_3 -based chemistries operated under ICP conditions appear attractive for hydrogen-free etching of In-containing III-V materials at rates much higher than is possible with CH_4/H_2 . The etched surface morphologies are not as good as those obtained on Ga-based materials, but RMS roughness of ~5 nm are typical on InP etched several microns deep. The near-surface region is typically group-V-deficient to a few tens of angstrom, and small quantities of Cl-residues are detectable by AES. Our past experience has shown that these can be removed by water or solvent rinsing⁽¹⁶⁾. We do not observe the sharp maxima in etch rates with composition in BCl_3/N_2 discharges that is reported for Ga-based materials, since the neutral atomic chlorine concentration is not limiting the etch rate of the In-containing materials. The most important factor in the latter case is the ion-neutral ratio, since too low an ion flux will allow a chlorinated selvedge layer to form, which prevents etching, while too high an ion flux produces predominantly physical sputtering, with its attendant problems. The ICP tool provides effective pattern transfer for the In-containing materials.

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Figure Captions

Figure 1. Etch rate (top) and etch yield (bottom) of In-based semiconductors as a function of BCl_3 percentage in BCl_3/N_2 ICP discharges at fixed source power (500 W), pressure (2 mTorr) and dc self-bias (-250 V).

Figure 2. Etch rates of In-based semiconductors as a function of BCl_3 percentage in BCl_3/Ar or BCl_3/H_2 ICP discharges at fixed source power (500 W), pressure (2 mTorr) and dc self-bias (-250 V).

Figure 3. Etch rates of In-based semiconductors as a function of ICP source power in BCl_3/N_2 or BCl_3/Ar ICP discharges of different composition..

Figure 4. Etch rates of In-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).

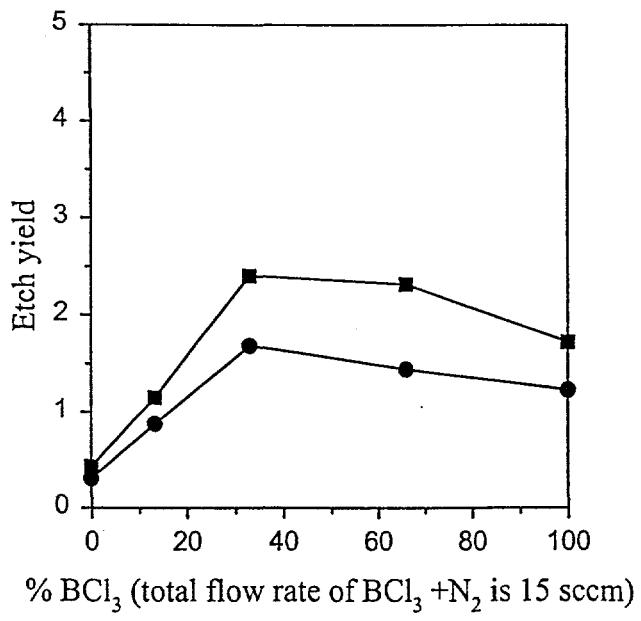
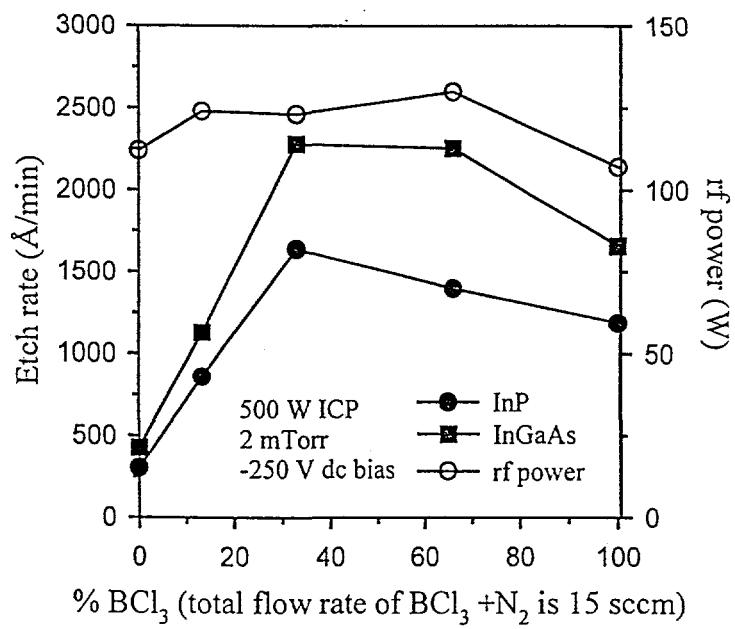
Figure 5. Etch rates of In-based semiconductors as a function of rf chuck power or dc chuck bias in BCl_3/Ar or BCl_3/N_2 ICP discharges at fixed source power (500 W) and pressures of 2 - 5 mTorr.

Figure 6. SEM micrographs of features etched into InP (top) and InGaAs (bottom) with 500 W source power, 250 W rf chuck power, 2 mTorr, discharges of either $10\text{BCl}_3/5\text{N}_2$ (right) or $10\text{BCl}_3/5\text{Ar}$ (left).

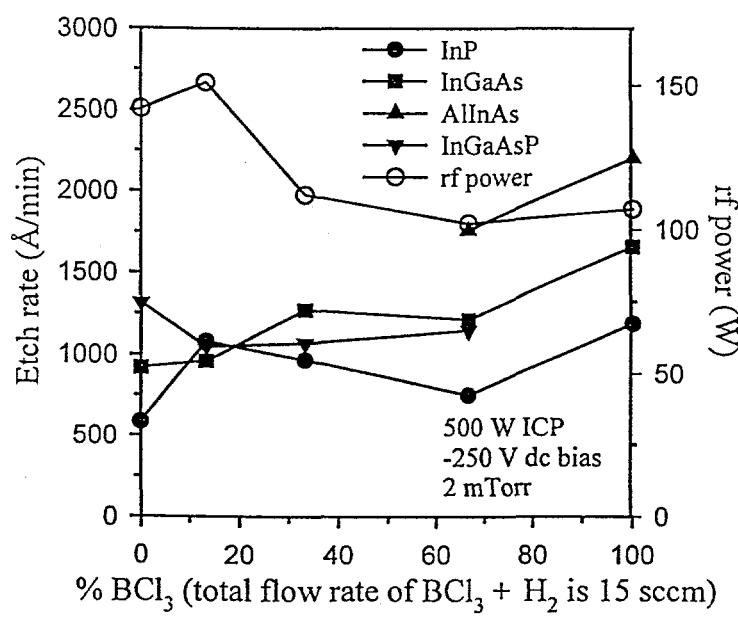
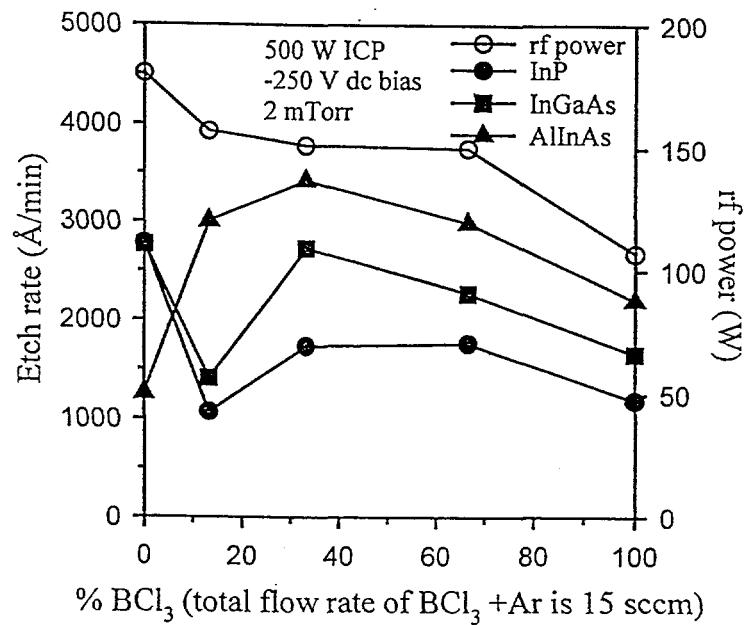
Figure 7. RMS roughness measured by AFM for InP etched with BCl_3/N_2 or BCl_3/Ar ICP discharges as a function of discharge composition at fixed source power (500 W), pressure (2 mTorr) and dc self-bias (-250 V).

Figure 8. AES surface scans of InP etched in 2 mTorr, 500 W source power, -250 V dc bias discharges of $5\text{BCl}_3/10\text{N}_2$ (top left), $10\text{BCl}_3/5\text{N}_2$ (bottom left), $5\text{BCl}_3/10\text{Ar}$ (top right) or $10\text{BCl}_3/5\text{Ar}$ (bottom right).

Figure 9. AES depth profiles of InP etched in 2 mTorr, 500 W source power, -250 V dc bias discharges of 10BCl₃/5Ar (top), 5BCl₃/10N₂ (center), or 10BCl₃/5N₂ (bottom).

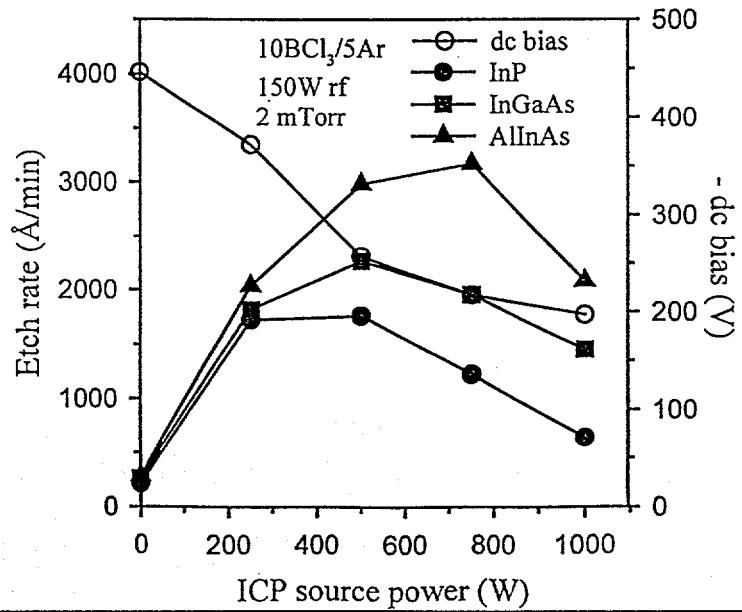
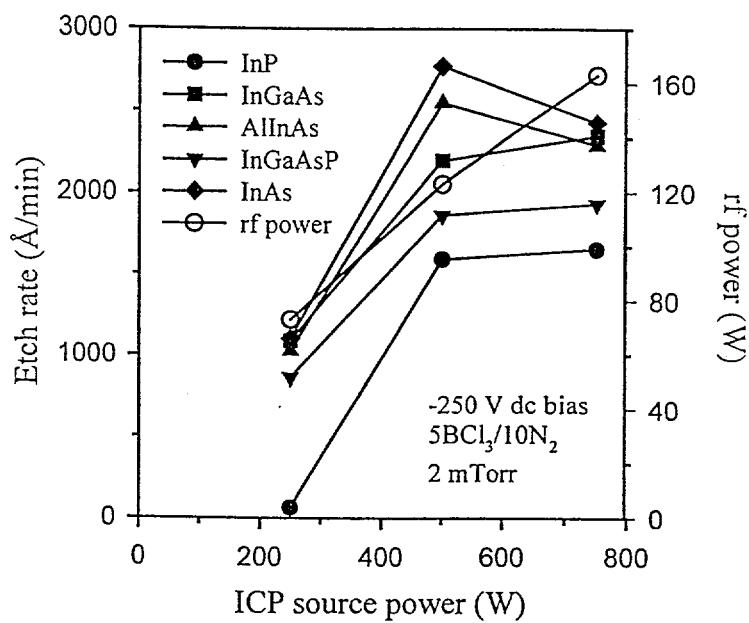
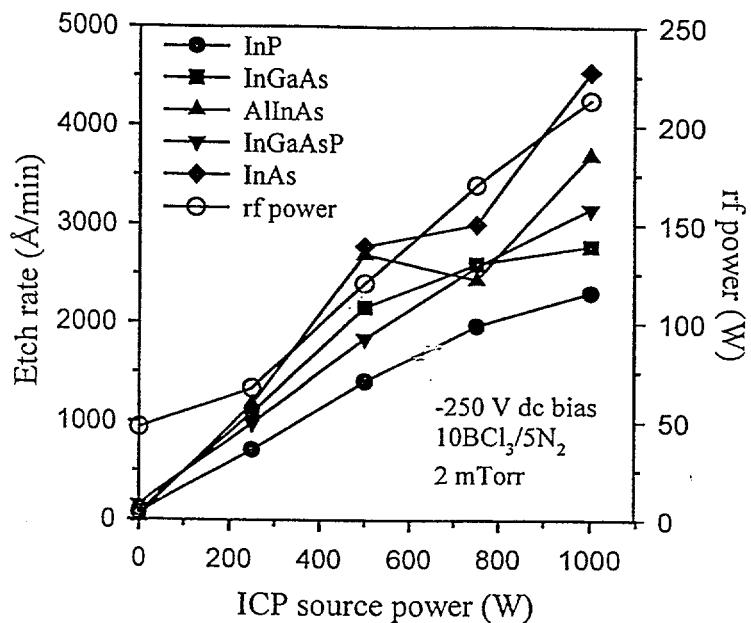


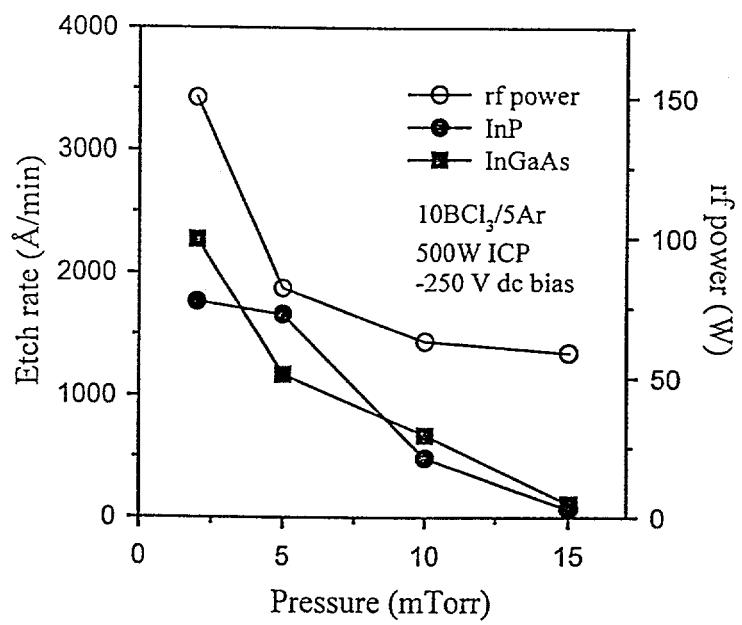
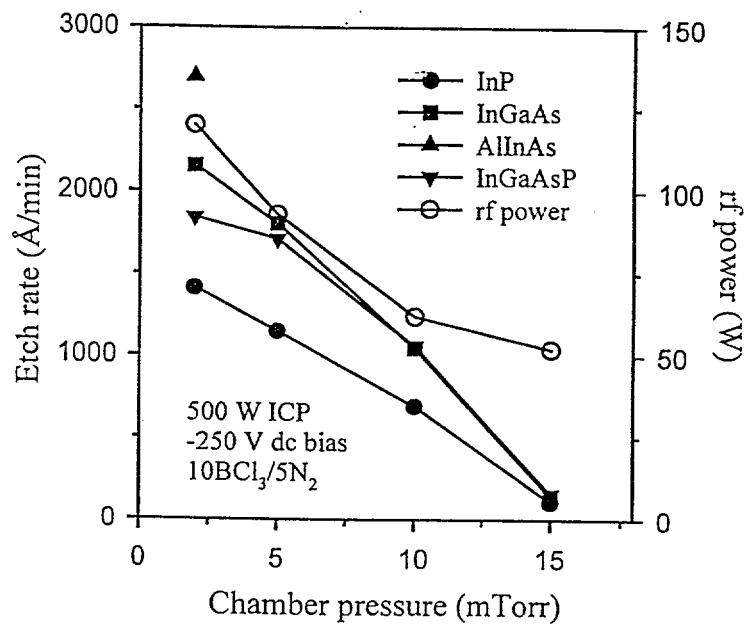
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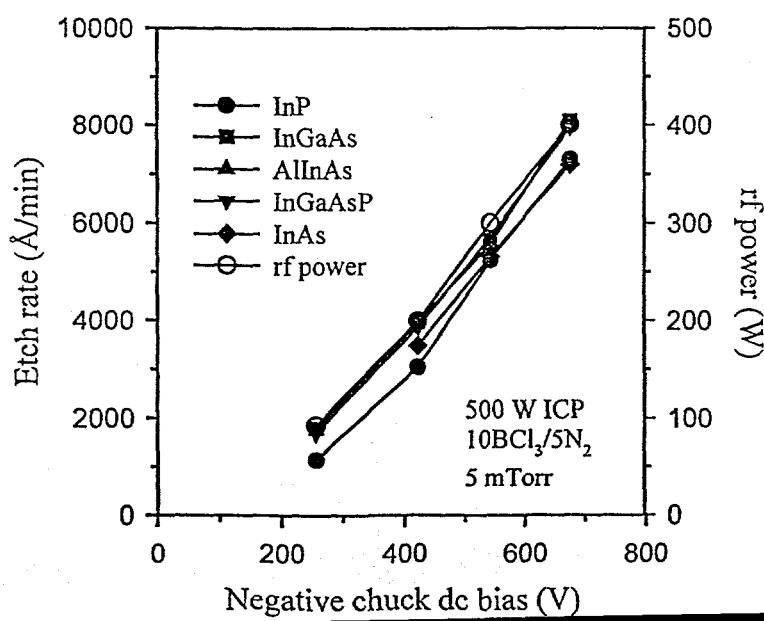
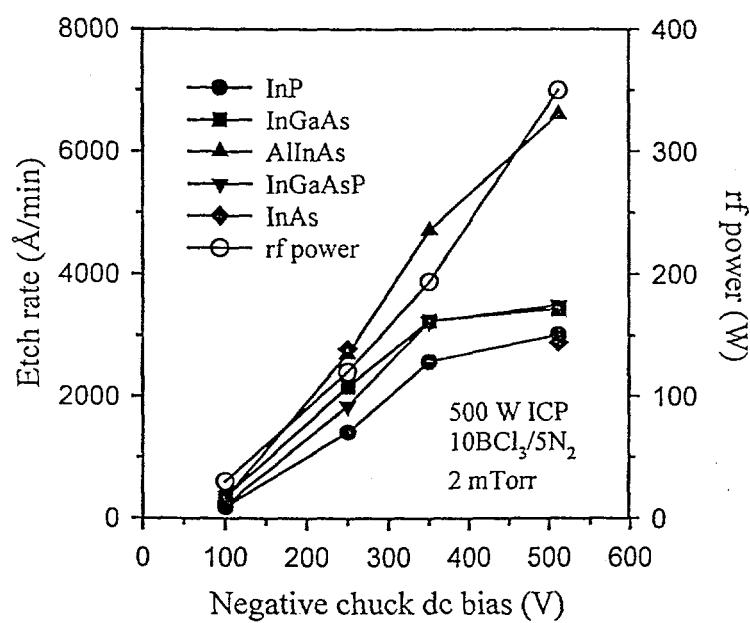
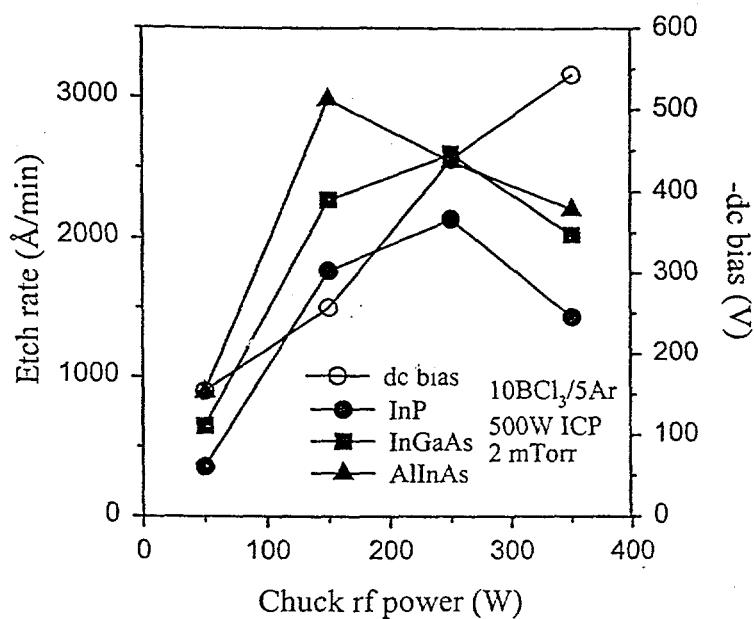
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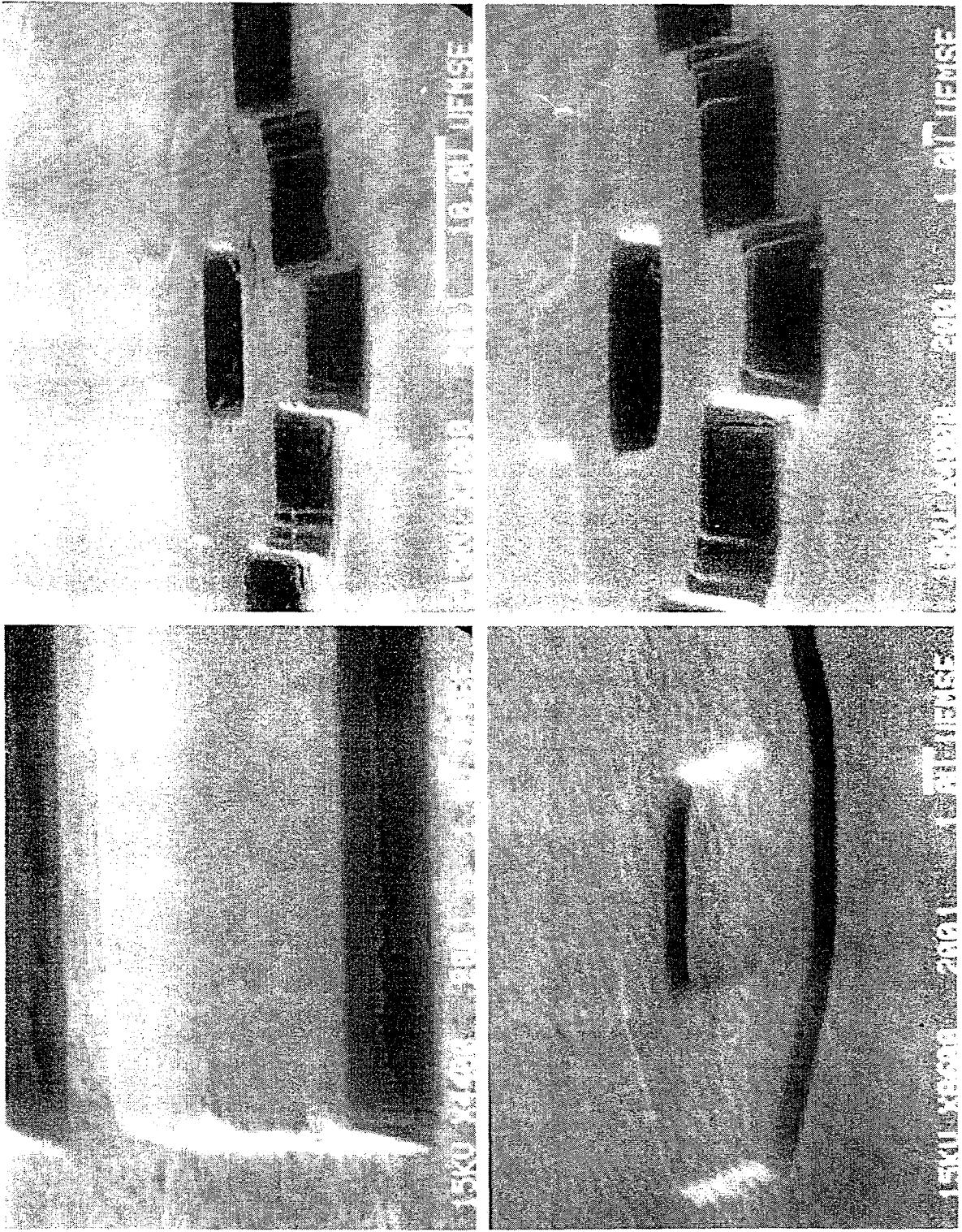


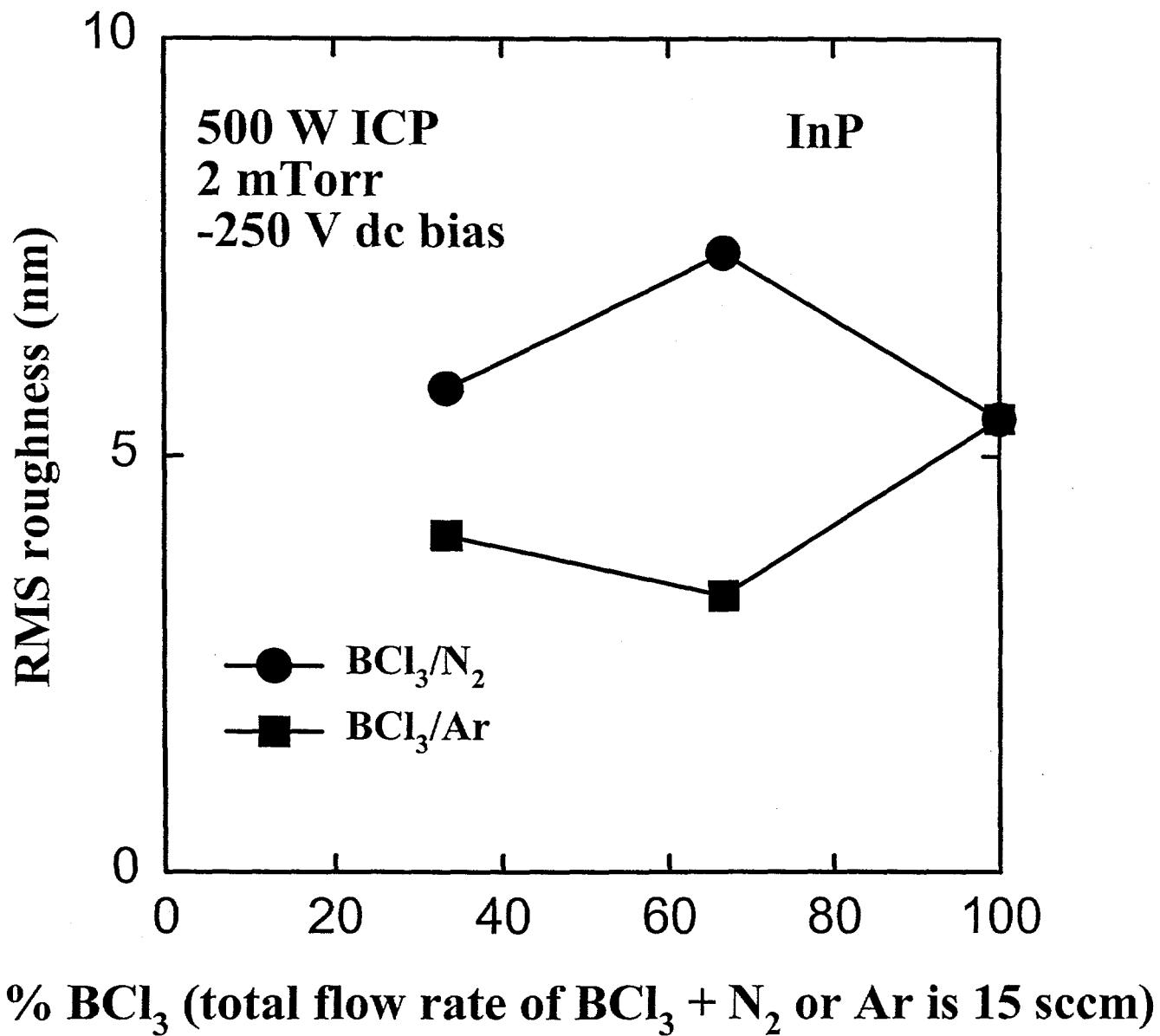


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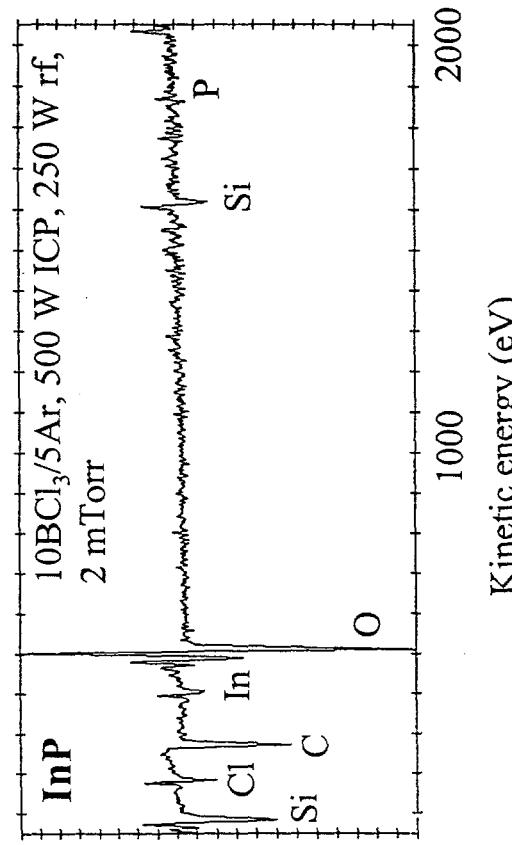
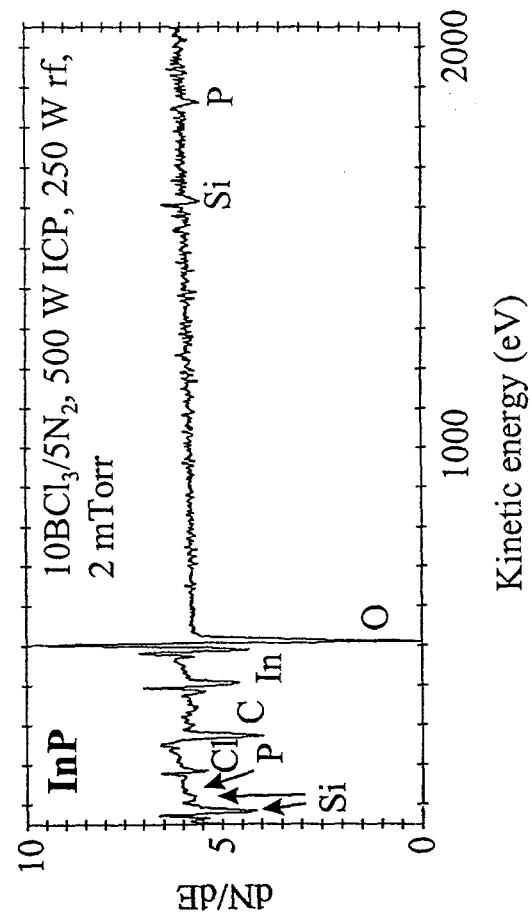
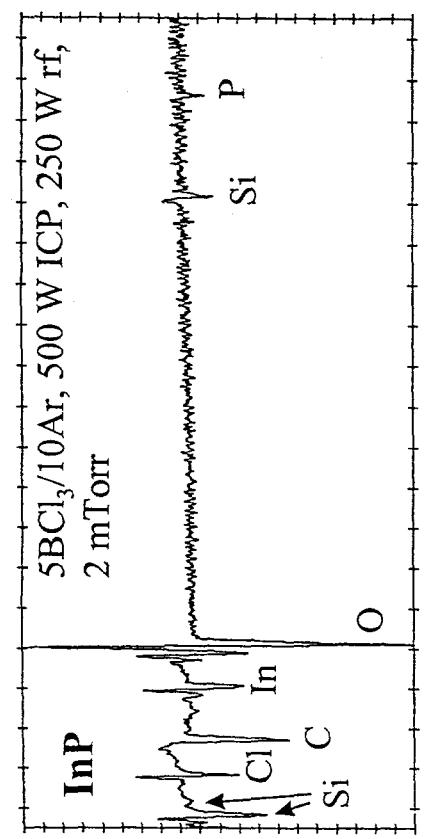
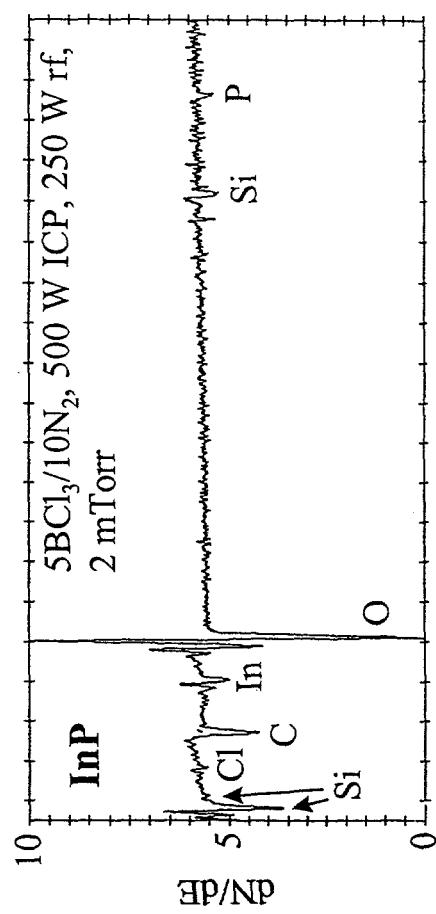
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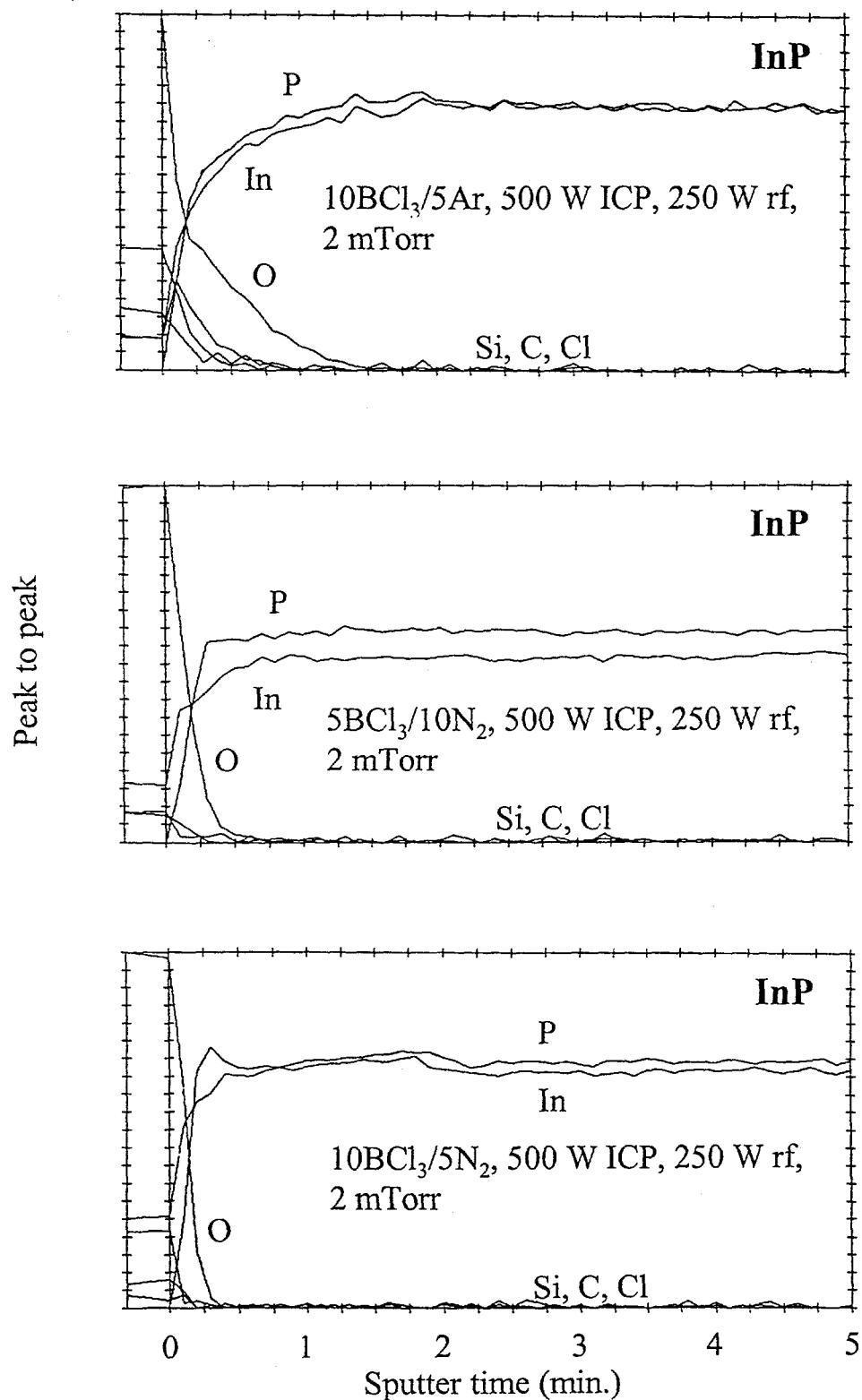
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Kinetic energy (eV)

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