

**EFFECT OF INERT GAS ADDITIVE SPECIES ON Cl₂ HIGH DENSITY
PLASMA ETCHING OF COMPOUND SEMICONDUCTORS:
PART I. GaAs AND GaSb**

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ABSTRACT

The role of the inert gas additive (He, Ar, Xe) to Cl₂ Inductively Coupled Plasmas for dry etching of GaAs and GaSb was examined through the effect on etch rate, surface roughness and near-surface stoichiometry. The etch rates for both materials go through a maximum with Cl₂ % in each type of discharge (Cl₂/He, Cl₂/Ar, Cl₂/Xe), reflecting the need to have efficient ion-assisted desorption of the etch products. Etch yields initially increase strongly with source power as the chlorine neutral density increases, but decrease again at high powers as the etching becomes reactant-limited. The etched surfaces are generally smoother with Ar or Xe addition, and maintain their stoichiometry.

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INTRODUCTION

The spontaneous chemical etch rates of III-V semiconductors at room temperature in Cl_2 or other halogens is negligible, and practical removal rates are only obtained under ion-assisted conditions.⁽¹⁻²⁰⁾ It is common to include a noble gas additive such as Ar to a halogen-based plasma in order to facilitate the ignition of the discharge at low pressures and also to enhance the efficiency of etch product desorption by ion bombardment. There has been little investigation of the effect of this noble gas species on the etching characteristics of compound semiconductors.

In this paper we report on a study of Cl_2/He , Cl_2/Ar and Cl_2/Xe dry etching of GaAs and GaSb, the two main Ga-based III-V semiconductors. In part II of the paper we discuss the results for In-based materials, which are a special case because of difficulty in removing the InCl_x etch products. There is an increasing interest in GaSb-based devices such as infrared detectors, ultra-high speed electronics such as heterojunction bipolar transistors and laser diodes operating in the $\sim 2 \mu\text{m}$ range. Precise etch processes are required for these devices, and Cl_2 -based plasma chemistries offer the most effective approach because of the high volatility of both Ga and Sb chlorides. Similar comments apply to GaAs, which forms the basis of red light-emitting diodes and low power high speed electronics for personal communication devices. In terms of their effect on the etching characteristics of GaAs and GaSb in Cl_2 Inductively Coupled Plasma (ICP), we find that He and Xe have somewhat different characteristics than Ar.

EXPERIMENTAL

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The samples used for etching in this work are: semi-insulating undoped (100) GaAs and undoped (100) GaSb substrates grown by the Czochralski process. The samples were patterned with Apiezon wax and etched in a Plasma-Therm ICP 790 system. The temperature of the back-side cooled chuck was held at 23 °C. The plasma composition was varied between 0 and 86.7 % Cl₂, rf chuck power between 50 and 350 W, and ICP source power between 300 and 1000 W. The process pressure was held constant at 5 mTorr, while the total flow rate of Cl₂-additive gas was 15 sccm. Etch rates were calculated from stylus profilometry measurements of the etched samples after the removal of the mask material. The error of these measurements is approximately $\pm 5\%$. The morphology and near-surface chemistries of the etched samples were examined by atomic force microscopy (AFM) operating in tapping mode with Si tip, and Auger Electron Spectroscopy (AES), respectively.

RESULTS AND DISCUSSION

Figure 1 shows the effect of Cl₂ concentration on etch rates obtained in Cl₂/He, Cl₂/Ar and Cl₂/Xe discharges at 5 mTorr, 750 W source power and 250 W rf chuck power. All three noble gases showed similar trends: for GaAs and GaSb, an increase in etch rates up to 13 % Cl₂ and a decrease thereafter. The attainable maximum etch rates were $\sim 1 \mu\text{m}/\text{min}$ for GaAs with all three chemistries and $\sim 4 \mu\text{m}/\text{min}$ for GaSb with Cl₂/Xe. Although GaSb showed the highest etch rate with Cl₂/Xe discharges (bottom), there is no clear advantage in terms of etch rates. The decrease in etch rates at higher percentages of Cl₂ is believed because the etching process may be limited by mass

transfer of ions from the plasma bulk to the substrate surface. Figure 2 shows the effect of Cl_2 content on etch yield and dc-bias voltage for the case of Cl_2/Ar discharge. Increase in dc bias with Cl_2 content implies that the electronegative Cl_2 is decreasing the positive ion density in the discharges, and thus partly supports the assumption of a mass-transfer limited etching process at higher Cl_2 concentrations.

The effect of ICP source power on etch rates of GaAs and GaSb are shown in Fig. 3. The etch rate of GaAs increased monotonically with increasing the source power in the Cl_2/He plasma, but with Cl_2/Ar it decreased substantially at higher ICP power (1000 W). For the case of the Cl_2/Xe plasma (bottom), the etch rates of both materials increased up to 750 W and remained constant thereafter. The increase in etch rate with increasing source power is mainly due to the higher concentration of reactive species in the plasma and higher ion flux to the substrate surface. However, the decrease in etch rate with further increase of the ICP power is attributed either to lower ion energies or ion-assisted desorption of the reactive species at the substrate surface prior to etch reactions.

The etch yield, ion flux and dc-bias voltage are significantly affected by the ICP source power. Typical results are shown in Fig. 4 for the case of Cl_2/Ar . The ion flux at the sheath and the etch yield defined as number of atoms etched per ion were described in detail elsewhere.²¹ The etch yields of GaAs and GaSb are a strong function of the source power, leading to a reactive chemical-driven etch mechanism up to 750 W ICP power (Fig. 4, top). The dc bias of the sample chuck was substantially decreased up to 750 W as the ICP power increased mainly due to the monotonic increase in ion density, and maintained constant thereafter (bottom).

Figure 5 shows the effect of rf chuck power on the etch rates, obtained with Cl₂/He (top), Cl₂/Ar (middle) and Cl₂/Xe (bottom) plasmas at 750 W ICP power and 5 mTorr. The etch rates of both materials increased up to 250 W and remained constant beyond 250 W, except that of GaSb with Cl₂/He at 350 W rf power. The increase in etch rate with increasing the chuck power can be attributed to enhanced sputter desorption of etch products as well as dominant physical sputtering of the III-V compounds. However at higher rf power (> 250 W), due to increased ion bombardment energy the sputter desorption of adspecies of reactive Cl ions or atoms from the substrate surface may compete with the sputter desorption of etch products, leading to a relatively constant etch rates at higher chuck powers. The effect of the chuck power on etch yield, dc-bias voltage and ion flux at the sheath is shown in Fig. 6 for the case of etching with Cl₂/Ar. The etch yield of GaSb increased with the rf power (top). GaAs showed an increase in etch yield up to 150 W and maintained a constant value beyond 150 W, implicating that the chemical-assisted etching is dominant. The dc bias increased monotonically with increasing rf chuck power from 50 to 350 W, but the ion flux at the sheath edge increased slightly (bottom), indicating that the main role of the chuck power is to increase the ion energy.

Figure 7 shows AFM scan results of the GaAs surfaces etched with Cl₂/He (top), Cl₂/Ar (middle) and Cl₂/Xe (bottom) chemistries at 750 W ICP power, 250 W rf chuck power and 5 mTorr, respectively. It is seen that the Cl₂/He discharge shows the worst morphology, but all additive gases resulted in quite smooth surfaces that are fairly similar to unetched controls (rms roughness 0.7 - 1.1 nm).

In addition to the surface smoothness, equi-rate removal of group III and V components or their corresponding etch products are very important to guarantee the stoichiometry of the etched surface. Figures 8 and 9 show the AES surface scans and depth profiles of GaAs etched in, respectively, Cl_2/Ar and Cl_2/Xe plasmas at 750 W ICP power, 250 W chuck power and 5 mTorr. Although not illustrated, the Cl_2/He chemistry showed similar AES scan results to Cl_2/Xe . There is oxygen present that grows on the samples in the course of transfer from the ICP chamber to the AES system and also carbon contamination due to the exposure to surrounding air. As shown in the depth profiles of Figs. 8 and 9, the etched surfaces with all Cl_2 -based plasmas are chemically quite clean without having chlorine contamination. It is also seen from the AES scans that the etched surfaces remain stoichiometric, indicating equi-rate of removal of group III and V components in all plasma chemistries.

SUMMARY AND DISCUSSION

The influence of noble additive gases such as He, Ar and Xe in the ICP etching of GaAs and GaSb was carried out for various plasma parameters. The etch rates were greatly affected by ICP source power, rf chuck power and chlorine concentration. The influence of the additive gases was ~~much~~^{very} dependent on the particular III-nitride material. The etch rates or etch yields of GaAs and GaSb were significantly affected ~~with~~^{by} the ICP source power, leading to a chemical-driven etch mechanism up to 750 W ICP power. The etch rates increased up to 250 W rf chuck power and remained relatively constant thereafter. All three noble gases showed a similar trend: the etch rates of GaAs and GaSb

increased up to 13 % Cl₂ and decreased thereafter. The maximum etch rates obtained were ~ 1 $\mu\text{m}/\text{min}$ for GaAs with all three chemistries and ~ 4 $\mu\text{m}/\text{min}$ for GaSb with Cl₂/Xe. The etched surface of GaAs with Cl₂/He, Cl₂/Ar and Cl₂/Xe showed very smooth morphologies (rms roughness 1.9 - 5.8 nm). The AES analysis showed the equi-rates of removal of group III and V components, and revealed the stoichiometry of the etched surface.

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Figure Captions

Figure 1. Effect of chlorine percentage (by flow) on etch rates of GaAs and GaSb with Cl₂/He (top), Cl₂/Ar (middle) and Cl₂/Xe (bottom) plasma chemistries for fixed source power (750 W), rf chuck power (250 W) and pressure (5 mTorr).

Figure 2. Effect of chlorine percentage (by flow) on etch yields of GaAs and GaSb, and dc-bias voltage with the Cl₂/Ar plasma chemistry.

Figure 3. Effect of ICP source power on etch rates of GaAs and GaSb with Cl₂/He (top), Cl₂/Ar (middle) and Cl₂/Xe (bottom) plasma chemistries (5 mTorr, 250 W rf chuck power).

Figure 4. Effect of ICP source power on etch yields of GaAs and GaSb (top), and dc-bias voltage and ion flux at the sheath edge (bottom) with the Cl₂/Ar plasma chemistry.

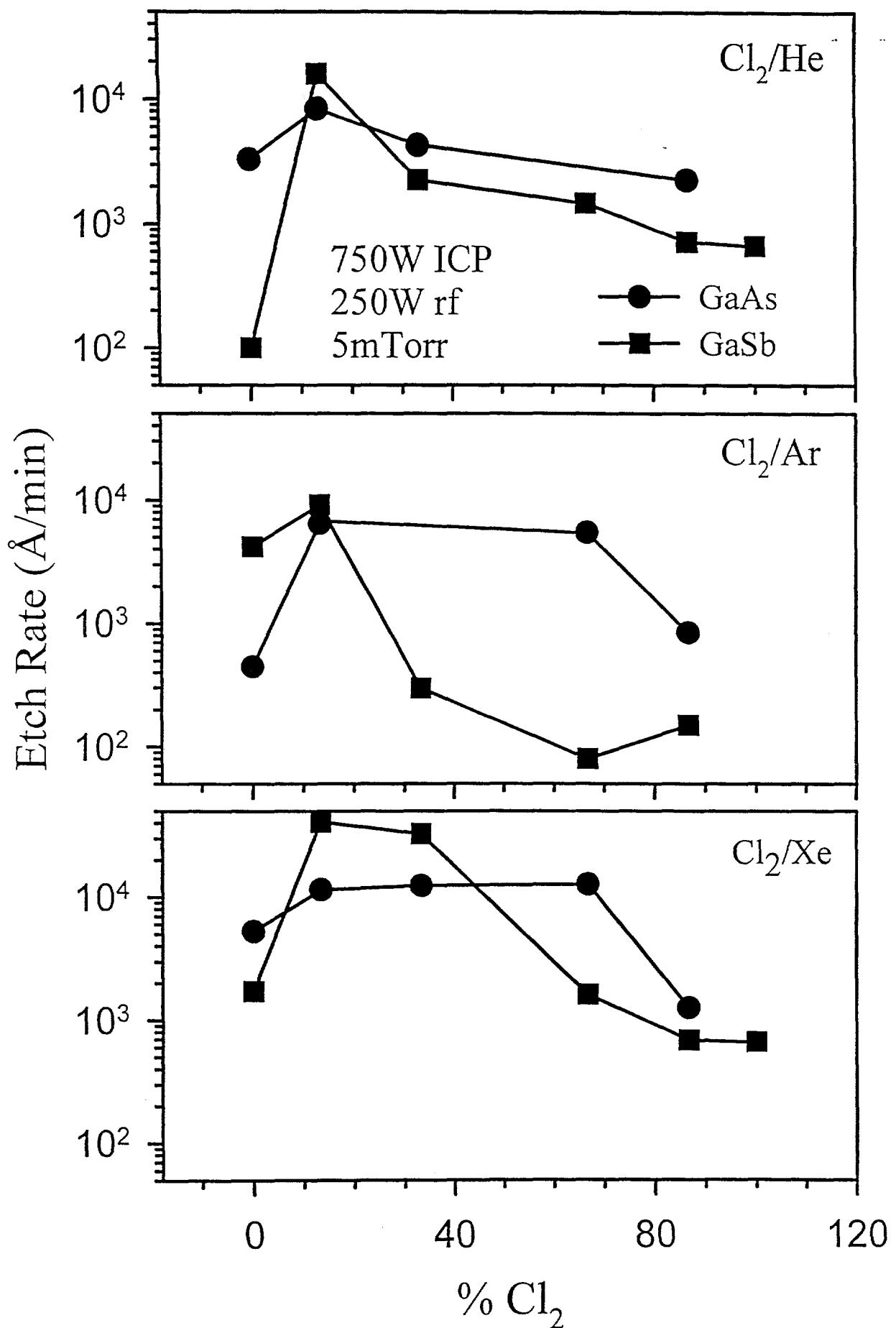
Figure 5. Effect of rf chuck power on etch rates of GaAs and GaSb with Cl₂/He (top), Cl₂/Ar (middle) and Cl₂/Xe (bottom) plasma chemistries (750 W source power, 5 mTorr).

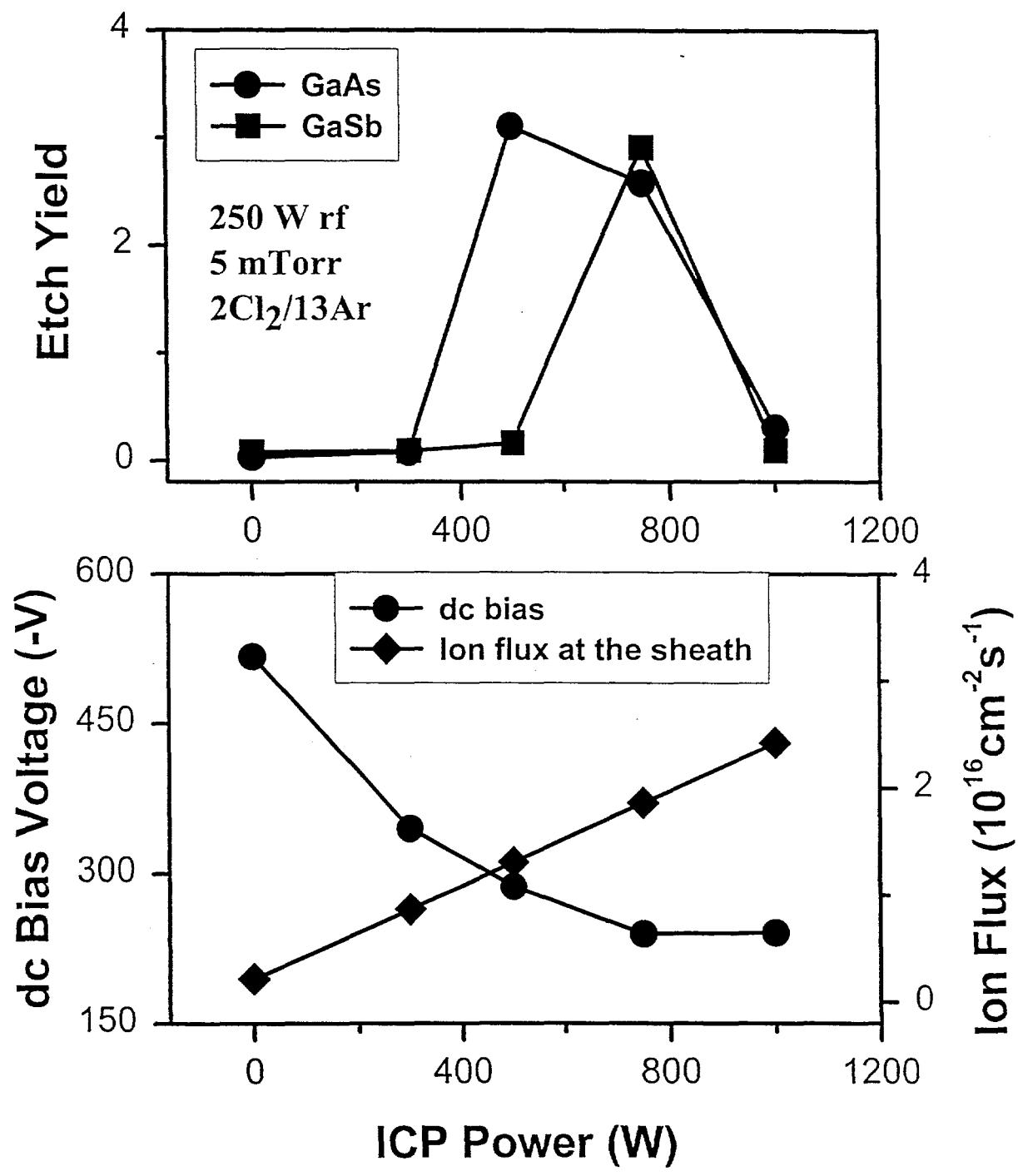
Figure 6. Effect of rf chuck power on etch yields of GaAs and GaSb (top), and dc-bias voltage and ion flux at the sheath edge (bottom) with the Cl₂/Ar plasma chemistry.

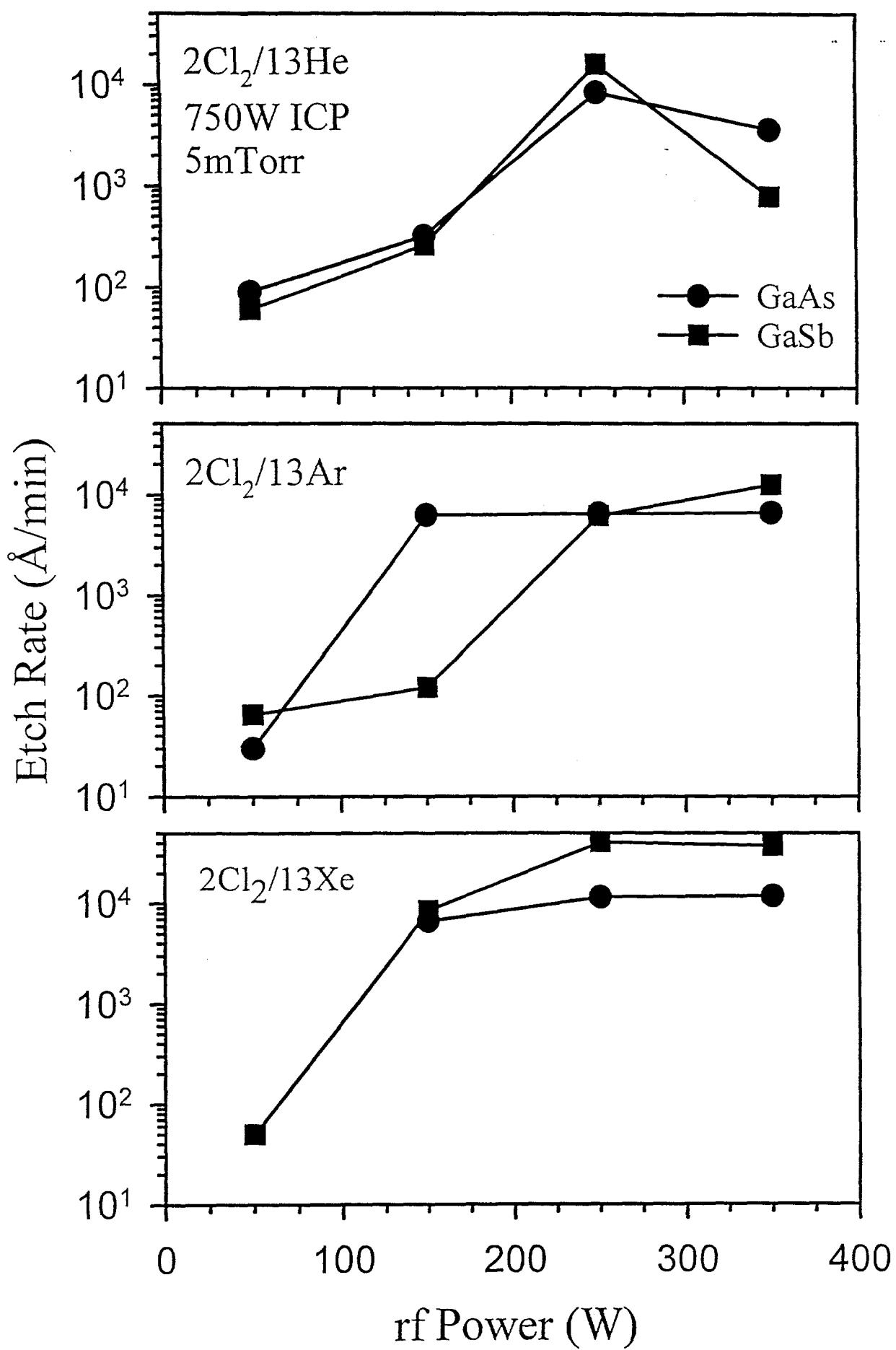
Figure 7. AFM scans for GaAs etched in Cl₂/He (top), Cl₂/Ar (middle) and Cl₂/Xe (bottom) plasmas.

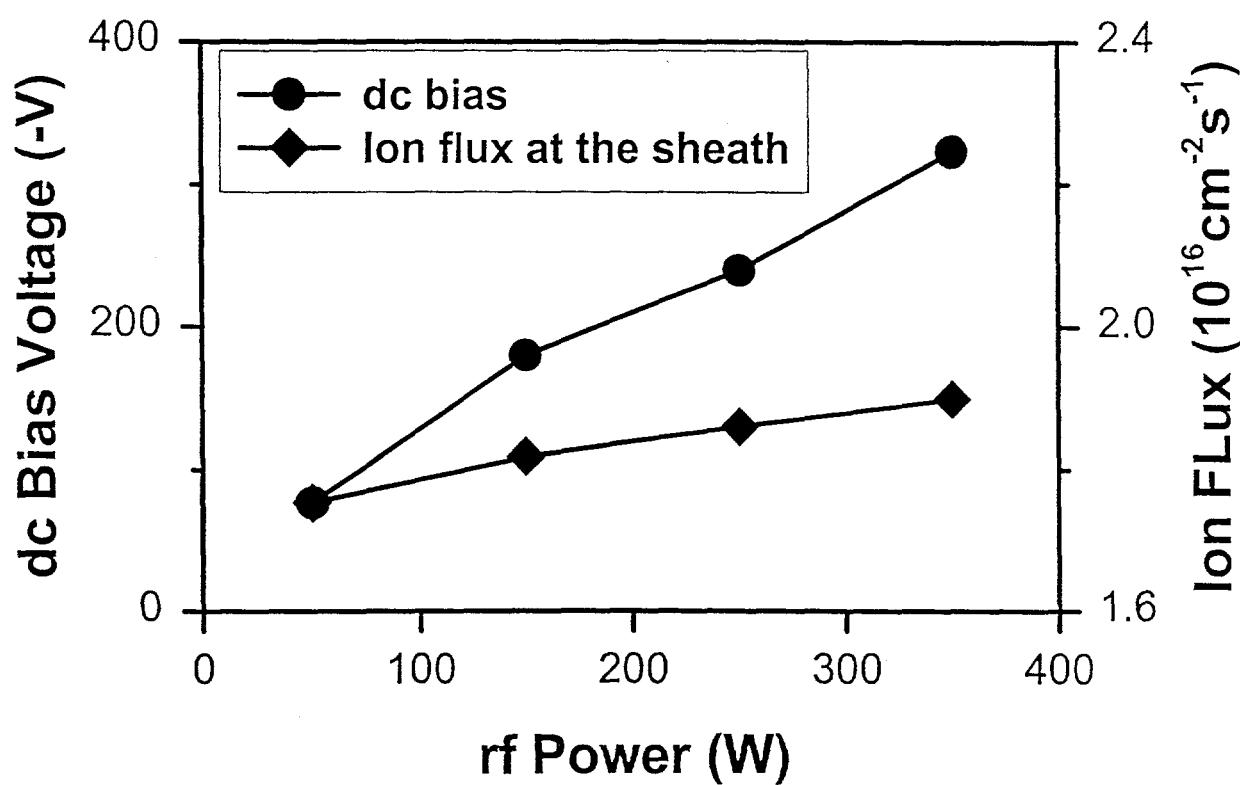
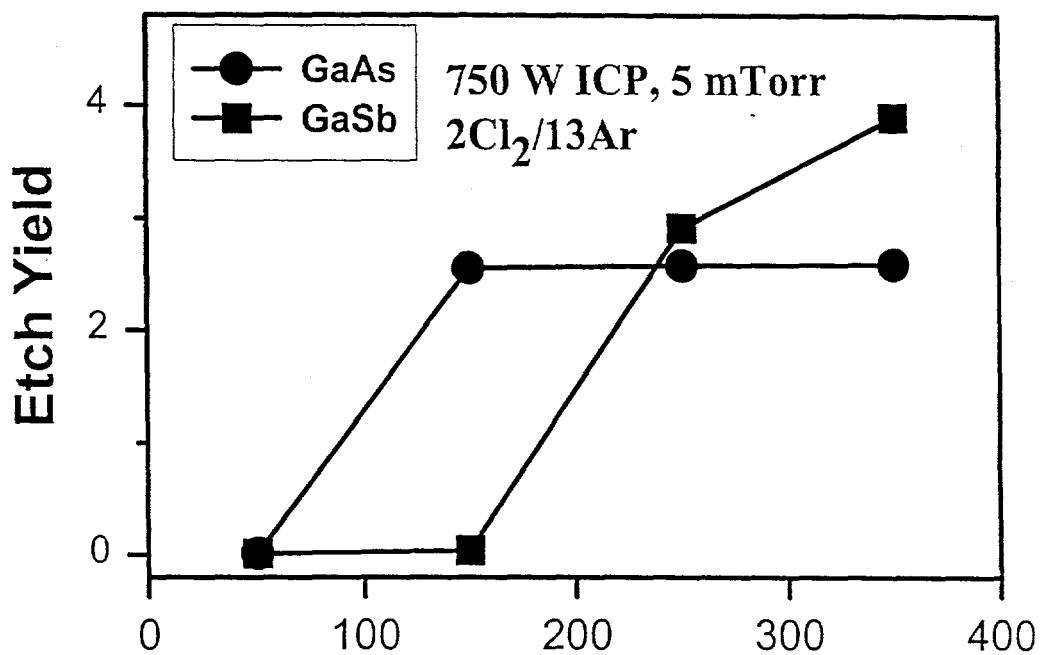
Figure 8. AES surface scan (top) and depth profile (bottom) of GaAs etched in Cl₂/Ar plasma at 750 W source power, 250 W rf chuck power and 5 mTorr.

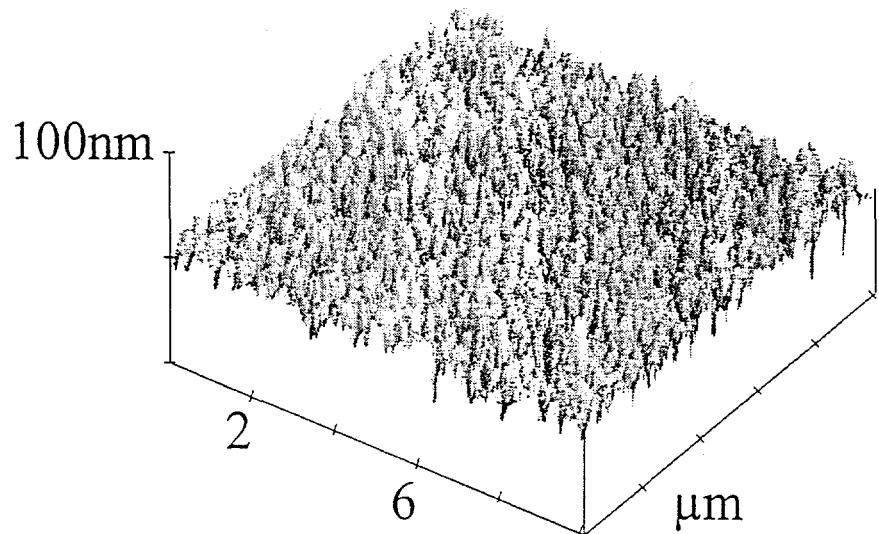
Figure 9. AES surface scan (top) and depth profile (bottom) of GaAs etched in Cl₂/Xe plasma at 750 W source power, 250 W rf chuck power and 5 mTorr.



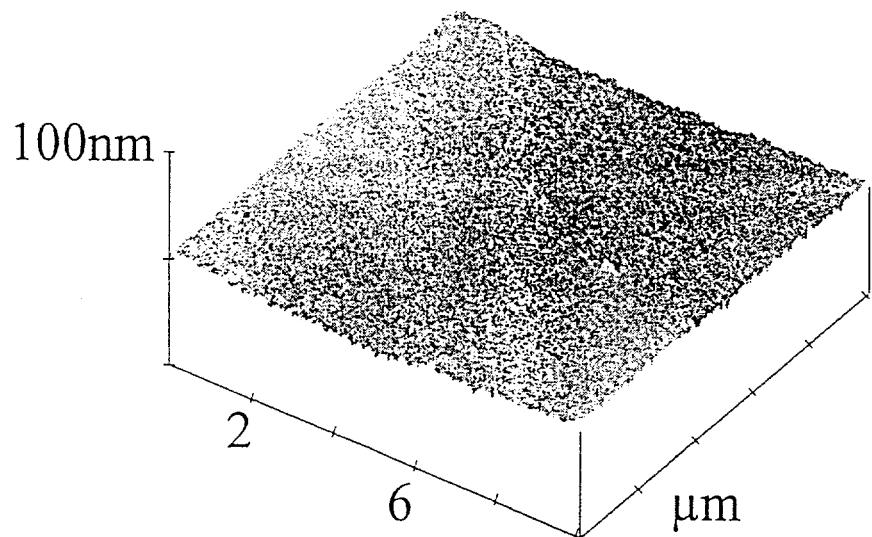




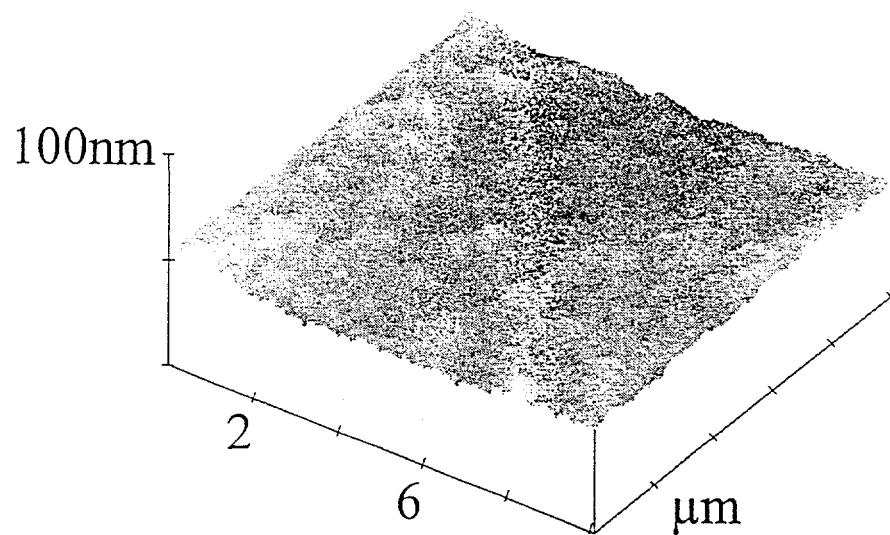




$2\text{Cl}_2/13\text{He}$
RMS Roughness
5.8nm



$2\text{Cl}_2/13\text{Ar}$
RMS Roughness
1.9nm



$2\text{Cl}_2/13\text{Xe}$
RMS Roughness
2.1nm

