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IN-SITU MONITORING OF ETCH BY-PRODUCTS DURING REACTIVE ION BEAM ETCHING OF GaAs IN CHLORINE/ARGON

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ABSTRACT

Mass spectrometry of the plasma effluent during Reactive Ion Beam Etching (RIBE) of GaAs using an Inductively Coupled Plasma (ICP) source and a Cl_2/Ar gas chemistry shows that $AsCl_3$, $AsCl_2$ and AsCl are all detected as etch products for As, while $GaCl_2$ is the main signal detected for the Ga products. The variation in selective ion currents for the various etch products has been examined as a function of chuck temperature (30-100^{o}C), percentage Cl_2 in the gas flow, beam current (60-180 mA) and beam voltage (200-800 V). The results are consistent with $AsCl_3$ and $GaCl_3$ being the main etch product species under our conditions, with fragmentation being responsible for the observed mass spectra.

INTRODUCTION

Comparatively little is known about the etch products for III-V semiconductors in high density plasmas, The prototypical system is Cl_2/GaAs, where extensive work on high vacuum (10^{-6} - 10^{-7} Torr) molecular beam experiments have identified the dominant etch products to be $GaCl_3$ and $AsCl_3$ for neutral-ion flux ratios >10 and nominal room temperature conditions.(1-5) In the temperature range up to ~300^{O}C only $GaCl_3$, $AsCl_3$ and As reaction products were observed. At higher temperatures $GaCl_3$ and As_4 were dominant.(1) McNevin(6) published a Cl_2/GaAs data base for the ΔH_f and S^O values for all the potential etch products in this system and also found that $GaCl_3$ and $AsCl_3$ should be the main products (eg. enthalpies for the mono-, di- and tri-chlorides of Ga were -14.6, -54.5 and -99 kCal/mol respectively at 298K). Ion-enhanced etching conditions produce removal rates for GaAs in Cl_2 plasmas approaching those of Langmuir free evaporation(7), suggesting the ions provide enough local energy deposition to overcome kinetic barriers to the free evaporation process. Sugata and Asakawa(8) found that the presence of Cl radicals lowered the temperature for the onset of etching of GaAs from ~300^{O}C in Cl_2, to <200^{O}C, while the addition of ions produced etching even at room temperature. This ion-assistance also drastically reduces the apparent activation energy for etching, leading to non-Arrhenius behavior.

Tadokoro et al.(9) and Asakawa and Sugata(10) examined Reactive Ion Beam Etching (RIBE) of GaAs with an Electron Cyclotron Resonance (ECR) source. Maximum etch rates were ~1.2μm·min^{-1} at 200V, but etch products were not examined. Eddy et.al.(11) studied the temperature, ion flux and ion energy dependence of GaAs surface chemistry in a Cl_2 ECR plasma and identified three mechanistic regions as a function of ion energy, namely thermal chemistry for <50eV, ion-assisted chemistry for 50-200eV and sputtering for >200eV.

In this paper we report on a study of the dependence of etch product intensity on plasma parameters in a RIBE system employing an Inductively Coupled Plasma (ICP) source. These sources have been identified as having numerous advantages over ECR sources, including ease of tuning, better scale-up capabilities and absence of costly electromagnets.(12-14) Our results are

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consistent with $AsCl_3$ and $GaCl_3$ again being the dominant etch products under high density RIBE conditions.

EXPERIMENTAL

Unpatterned, nominally undoped (100) GaAs substrates were used for all experiments. The samples were mounted on a resistively heated Mo stage in the custom-built RIBE system described previously.(15) In brief, the ion beams were generated in an ICP source equipped with dual pyrolitic-graphite grids for extraction. Grid-sample distance was approximately 35 cm. The mass spectrum sampled from the plasma was recorded as a function of ion current, ion energy, chuck temperature and Cl_2 percentage in the Cl_2/Ar gas flow (total flow held constant at 15 standard cubic centimeters per minute). As part of a separate study to be reported later, the etch rates, surface morphologies and near-surface composition of patterned samples were also measured.(16)

RESULTS AND DISCUSSION

A typical mass spectrum recorded for etching of GaAs in a Cl_2/Ar discharge at 30°C is shown in Figure 1. There are water and N_2 peaks from the residual vacuum in the system, peaks due to the plasma species (Cl, Cl_2, Ar) and peaks due to the GaAs etch products. The amu position of these species is shown in Table I. It is important to note that the overall spectrum is very similar to that reported by Eddy et al.(11) for ECR/RIE etching of GaAs, where the differentially pumped mass spectrometer sampling aperture was part of the rf-biasable etching platen, and thus we are confident of the validity of our approach. The most prevalent peaks are due to arsenic chlorides (AsCl at ~110, 112 amu, $AsCl_2$ at ~145, 147 and 149 amu, and $AsCl_3$ at ~180, 182 and 184 amu). The $GaCl_2$ peaks occur at ~139, 141 and 143 amu. Elemental Ga (69 and 71) and arsenic (75 amu) are difficult to separate from the molecular Cl_2 peaks at 70, 72 and 74 amu. Eddy et al.(11) suggested that additional peaks in the spectrum may be due to the parent molecule and subsequent fragmentation of $COCl_3$ formed by reaction in the plasma. The conclusion of these workers is that their spectrum (and by inference, ours) is consistent with $AsCl_3$ and $GaCl_3$ being the dominant products, since the cracking pattern of $GaCl_3$ is dominated by $GaCl_2$.

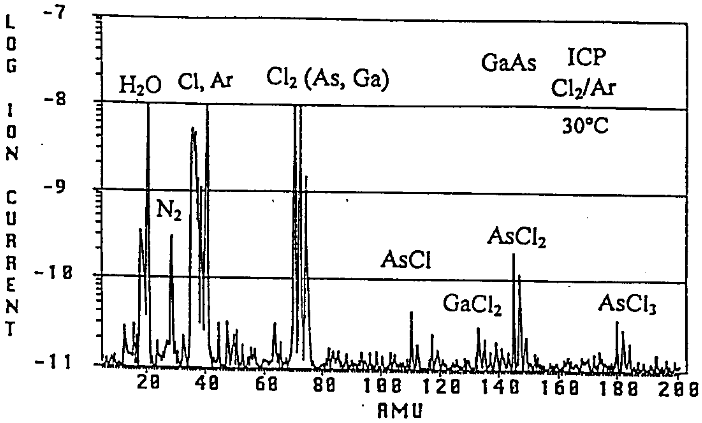

Figure 1. Typical mass spectrum obtained for RIBE-ICP Cl_2/Ar etching of GaAs at 30°C.

Table I. Possible etch by-products and their atomic mass units of GaAs etching in Cl_2 and Cl_2/Ar plasmas. Due to the presence of isotopes of Ga and chlorine, there are also satellite peaks, some of which we show in brackets.

Species	Atomic Mass Units
Ga	69.72 (71)
GaCl	106.45 (104)
$GaCl_2$	141 (139, 133, 145)
$GaCl_3$	176.45 (174, 178)
As	74.922
AsCl	110 (112)
$AsCl_2$	145.82 (147, 149)
$AsCl_3$	181.272 (180, 184)

This conclusion is supported by the data of Figure 2, which shows the mass spectra with (right) and without (left) GaAs samples in the chamber. From this type of data we were able to conclusively measure the dependence of etch product signal intensity on various plasma parameters.

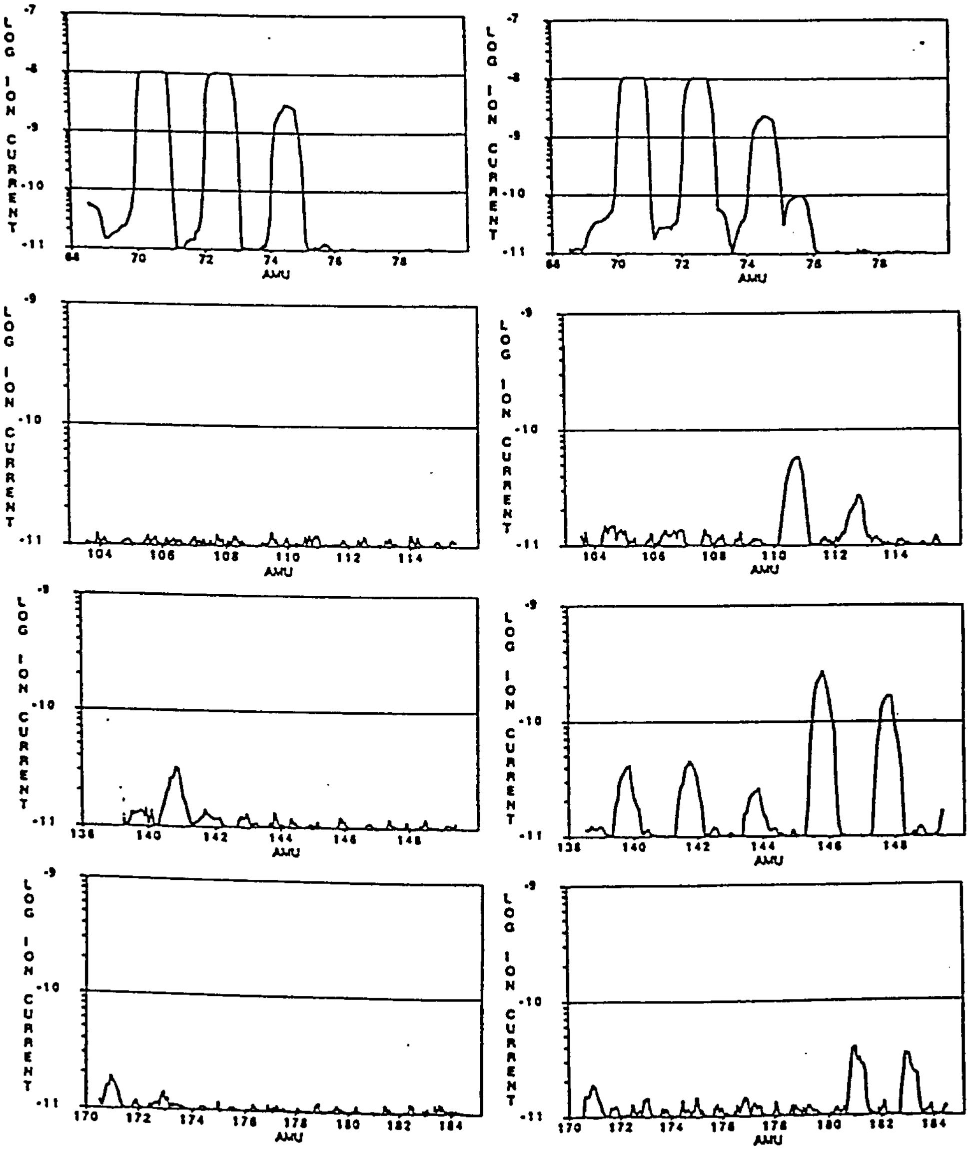

Figure 2. *In-situ* mass spectrometry data of GaAs (right) etched in the RIBE-ICP reactor under $7Cl_2/3Ar$, 100mA beam current and 600V beam voltage condition. The data is compared with the results obtained under the same plasma without GaAs in the reactor (left).

As beam voltage increased from -200 to -800 eV, the GaAs etch rate was found to increase from ~400Å·min^{-1} to ~2,000 Å·min^{-1} in 100 mA, $7Cl_2/3Ar$ discharges near room temperature. This was strongly correlated with the increase in product formation with ion energy (Figure 3). The correlation suggests ion-assisted processes are dominating the surface chemistry under these conditions. In both the etch product mass spectrometer signals and etch rate data there was a saturation at the highest beam voltages, which is probably indicative of a transition to a reactant-limited or physical sputtering dominated regime, as also found in ECR etching.$^{(11)}$

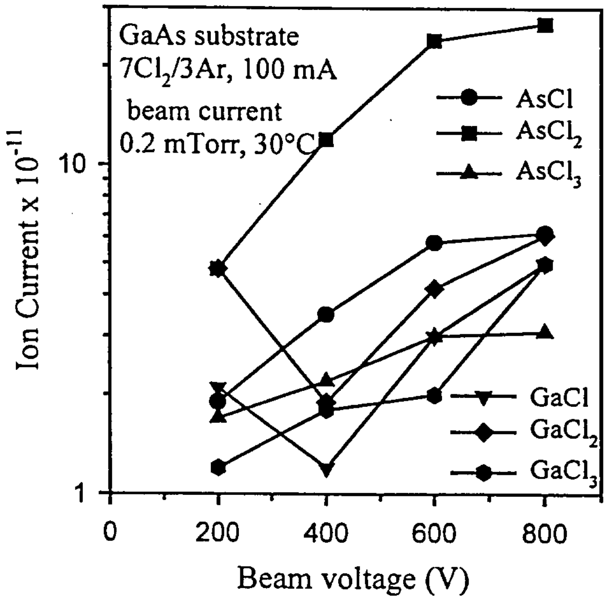

Figure 3. Variation of mass spectrometric signals for the various etch products as a function of beam voltage in $7Cl_2/3Ar$, 100mA discharges.

There was little dependence of either etch product mass peak intensity or GaAs etch rate on beam current, as shown for the former in Figure 4. This suggests that the rate is not flux-limited under these conditions. It is clear that sufficient fluxes of both neutral atomic chlorine and Ar^+ and Cl^+ and Cl_2^+ ions would be necessary to maximize etch product formation, and this appears to occur even at relatively low beam currents in the RIBE-ICP system.

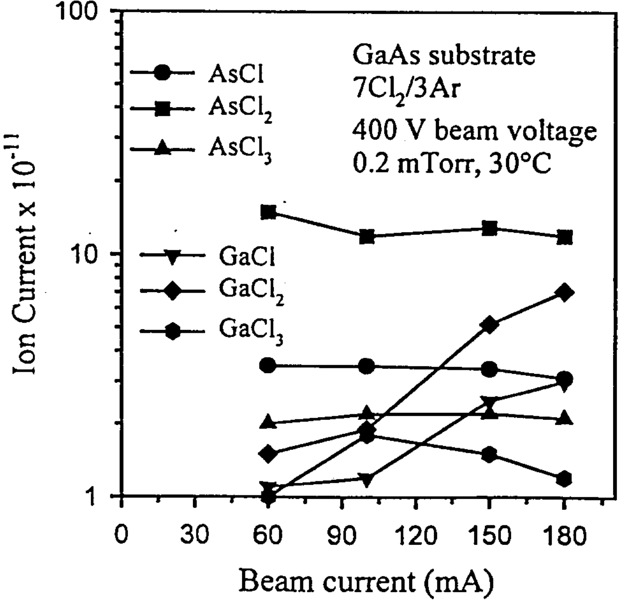

Figure 4. Variation of mass spectrometric signals for the various etch products as a function of beam current in $7Cl_2/3Ar$, 400V discharges.

Etch rates of GaAs initially increased as Cl_2 was added to a pure Ar plasma, and peaked at ~66% Cl_2 by flow before falling sharply for pure Cl_2 discharges. This emphasizes that the etching is ion-assisted, since for pure Cl_2 the positive ion density will be lower than for mixed Cl_2/Ar conditions. These trends are reflected in the etch product mass peak intensity data (Figure 5), although for most of the species there is an increased intensity for pure Cl_2 conditions. We are currently investigating if recombination in the plasma can account for this increase.

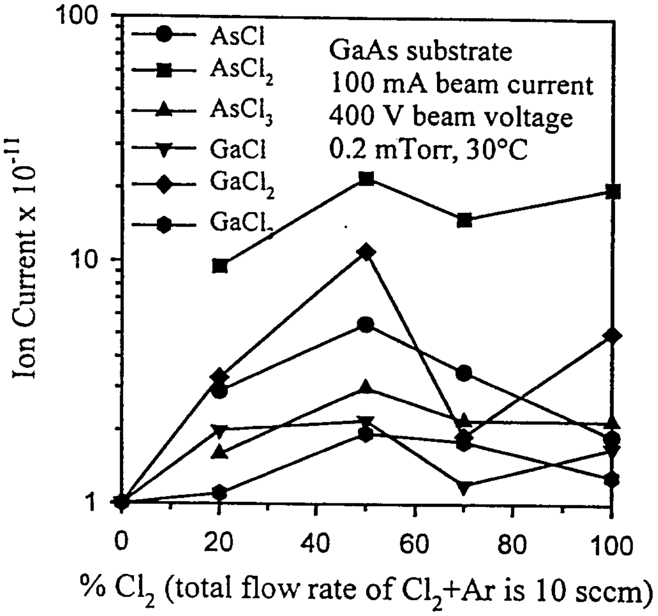

Figure 5. Variation of mass spectrometric signals for the various etch products as a function of percentage Cl_2 in Cl_2/Ar, 100mA, 400V discharges.

Chuck temperature was also found to have a strong influence on etch rate, with an increase from ~1,000 Å·min^{-1} at 30°C to ~4,200 Å·min^{-1} at 150°C for GaAs in $7Cl_2/3Ar$, 100mA, 400 V plasmas. This data was also reflected in the etch product mass peak intensity data (Figure 6), where all of the species increase with chuck temperature except the $AsCl_2$ fragment. We ascribe the increases in both etch rate and product signal intensity to the increased volatility of the $AsCl_3$ and $GaCl_3$ at higher temperatures.

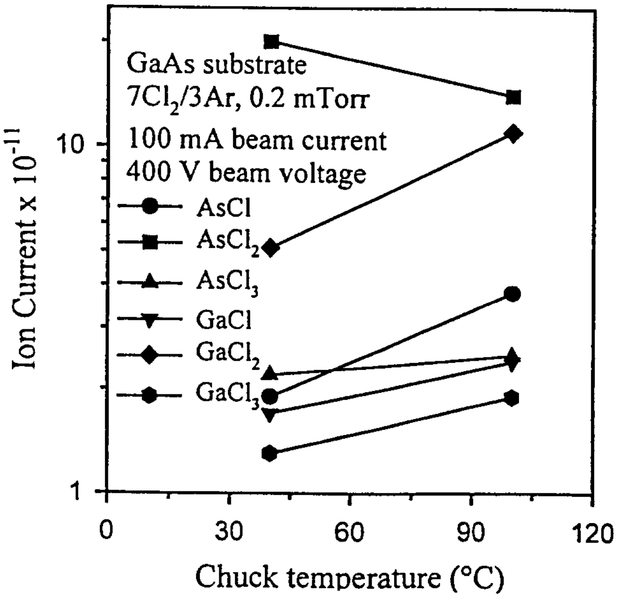

Figure 6. Variation of mass spectrometric signals for the various etch products as a function of chuck temperature in $7Cl_2/2Ar$, 100mA, 400V discharges.

CONCLUSIONS AND SUMMARY

Mass analysis of the etch product chlorides formed during RIBE-ICP Cl_2/Ar etching of GaAs shows that $GaCl_3$ and $AsCl_3$ are the dominant products. This result is consistent with recent work on ECR plasma etching of GaAs in Cl_2/Ar(11), and shows that high density plasmas accelerate etch rates predominantly by ion-neutral synergism and not by subverting the usual etch reactions.

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