

Reactive Ion Beam Etching of GaAs and Related Compounds in an Inductively Coupled Plasma of Cl₂-Ar Mixture

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ABSTRACT

Reactive ion beam etching (RIBE) of GaAs, GaP, AlGaAs and GaSb was performed in a Cl₂-Ar mixture using an Inductively Coupled Plasma (ICP) source. The etch rates and yields were strongly affected by ion energy and substrate temperature. The RIBE was dominated by ion-assisted etching at < 600 eV and by physical sputtering beyond 600 eV. The temperature dependence of the etch rates revealed three different regimes, depending on the substrate temperature: 1) sputtering-etch limited, 2) products-desorption limited, and 3) mass-transfer limited regions. GaSb showed the overall highest etch rates, while GaAs and AlGaAs were etched at the same rates. The etched features showed extremely smooth morphologies with anisotropic sidewalls.

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I. INTRODUCTION

In the fabrication of high frequency electronic devices as well as optoelectronic devices, it is critical to accurately control the pattern size, while minimizing damage created during the patterning process. As in Si-based semiconductor technology, the trend toward decreasing feature size has become an important issue and to this end various types of dry etching techniques have been under development.¹⁻¹³ One of the most flexible etching methods for GaAs and related compounds is reactive ion beam etching (RIBE).¹⁴⁻¹⁶ In contrast to conventional reactive ion etching (RIE), the ion energy and flux can be controlled independently in the RIBE system. In order to optimize etch rate and smooth etch morphology in the RIBE process, it is important to elucidate the effects of process variables such as beam voltage and current, etch gas concentration and substrate temperature, and to understand their relationship.

Most of recent works on the etching of III-V compounds have focused on understanding the dry etching process in terms of etch rate and surface morphology or etch profiles. Variations of ion energy and substrate temperature have been used mainly to control the etch characteristics. Little work has been reported to elucidate the RIBE process of III-V compounds by combining the effects of main variables such as beam voltage and current, substrate temperature and Cl_2 concentration, and by explaining the results in terms of etch yield together with etch rate, surface chemistry and etch products, especially for high density plasma sources.

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 has identified the dominant

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etch products to be GaCl_3 and AsCl_3 for neutral-ion flux ratios > 10 and nominal room temperature conditions.^{11,17-20} In the temperature range up to $\sim 300^\circ\text{C}$ only GaCl_3 , AsCl_3 and As reaction products were observed. At higher temperatures GaCl_3 and As_4 were dominant.¹¹ McNevin published a Cl_2/GaAs data base for ΔH_f° and S° values for all the potential etch products in this system and also found that GaCl_3 and AsCl_3 should be the main products (e.g. Enthalpies for the mono-, di- and tri-chlorides of Ga were -14.6, -54.5 and -99 kcal/mol, respectively, at 298K).²¹ Ion-enhanced etching conditions produce removal rates for GaAs in Cl_2 plasmas approaching those of Langmuir free evaporation,²² suggesting that ions provide enough local energy to overcome kinetic barriers to the free evaporation process. Sugata and Asakawa found that the presence of Cl radicals lowered the temperature for the onset of etching of GaAs from $\sim 300^\circ\text{C}$ in Cl_2 to $< 200^\circ\text{C}$, while the addition of ions produced etching even at room temperature.²³ This ion-assistance also drastically reduces the apparent activation energy for etching, leading to non-Arrhenius behavior.

Tadokoro et al.²⁴ and Asakawa and Sugata²⁵ examined reactive ion beam etching of GaAs with an Electron Cyclotron Resonance (ECR) source. Maximum etch rates were $\sim 1.2\ \mu\text{m}/\text{min}$ at 200 V, but etch products were not examined. Eddy et al.²⁶ studied the temperature, ion flux and ion energy dependence of GaAs surface chemistry in a Cl_2 ECR-RIE system and identified three mechanistic regions as a function of ion energy, namely thermal chemistry for $< 50\ \text{eV}$, ion-assisted chemistry for $50 - 200\ \text{eV}$, and sputtering for $> 200\ \text{eV}$.

In this study, to better understand the etch mechanism and to provide basic data required for optimizing the RIBE process, etching of GaAs, GaP, AlGaAs and GaSb were

carried out in a Cl_2 -Ar mixture under various conditions. Special attention was paid to identifying the etch mechanism and providing optimum conditions by analyzing the etch rate and yield, surface chemistry, and etch products.

II. EXPERIMENTAL

Unpatterned, nominally undoped (100) GaAs, GaP, GaSb substrates, and epitaxial $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ on 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 pyrolytic-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.

An UTI 100C residual gas analyzer (RGA) with a closed source for differential pumping was employed for etch product determination. All data were taken with gas introduced through a 1/4" id valve so that the RGA pressure matched the etch chamber pressure. (In other words, the pressure-reduction aperture was not used.) Etch rates were determined by stylus profilometry, while surface morphology was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Near-surface stoichiometry was measured by Auger Electron Microscopy (AES).

The standard etch conditions used in this study were 25 °C chuck temperature, 0.2 mTorr pressure, 400 V beam voltage, 100 mA beam current, and 70 % Cl_2 in Ar mixture, although each of these parameters was viewed in other cases.

III. RESULTS AND DISCUSSION

A. RIBE etch rate and yield

The effect of beam voltage on the etch rates and yields of GaAs, GaP, AlGaAs and GaSb were examined varying the beam voltage from 200 to 800 V, and the results are shown in Fig. 1. It is seen that the etch rate (Fig. 1, top) and etch yield, defined as number of atoms etched per incident ion (bottom), increase monotonically with increasing the ion energy up to 600 eV and then gradually increase at > 600 eV. This result suggests that the RIBE of GaAs, GaP, AlGaAs and GaSb is dominated by ion-assisted etching up to 600 eV ion energy and by physical sputtering beyond 600 eV. The transition at 600 eV from the ion-assisted to sputter etching leads to a conclusion that the incident ion energy has to be less than 600 eV to obtain the advantages of ion-assisted etching, i.e. high selectivity to mask materials and reduced ion damage. It is also interesting to see that the etch rate of GaSb is greater than any other compounds; GaAs and AlGaAs have the same etch rates; GaP shows overall lowest etch rates (Fig.1, top). The equirete etching of GaAs and AlGaAs is consistent with the previously reported results.^{4,14} It is worthwhile to see that GaAs and AlGaAs show almost the same etch yields mainly due to the same crystal structure of zinc blende (bottom).

Figure 2 shows the effect of beam current on the etch rate (top) and yield (bottom). The etch rates, except that of GaP, increased initially for currents up to 100 mA, mainly due to increased ion density and then remained relatively constant thereafter. However, the etch yield decreased monotonically as the ion current increased, indicating that the etching process is controlled overall by physical sputtering at higher beam currents. In

general, etch rates increase as the plasma density increases mainly due to higher concentrations of reactive species and higher ion flux which increases the bond breaking efficiency and the sputter desorption component of the etching mechanism. The relatively stabilized etch rates obtained in this study at beam currents greater than 100 mA are thus an unexpected result. The reason for this could be attributed to one or combined effects of saturation of reactive Cl at the substrate surface, desorption-limited regime formed at higher ion current, and redeposition of etch products.

Figure 3 shows the effect of Cl₂ concentration on etch rate (top) and yield (bottom). The etch rate and yield increased as Cl₂ concentration increased, reaching maxima at specific Cl₂ percentage (i.e., GaAs, AlGaAs and GaSb at 70 %; GaP at 50 %), and decreased to the lowest values at 100 % Cl₂. These results are unexpected and do not show the monotonic increase in plasma etching systems reported in the literature,^{14,27} but similar to those obtained by Shul et al. in an ECR etching system.⁷ The decrease in etch rate and yield at concentrations higher than 50 % Cl₂ for GaP and 70 % Cl₂ for GaAs, AlGaAs and GaSb may be attributed to less efficient sputter desorption of etch products from the surface, leading to a sputter-dominated etch mechanism. This result implies that optimization of the plasma chemistry is important in obtaining the desired anisotropic etch characteristics.

The effect of substrate temperature on etch rate and yield is shown in Fig. 4. It is seen that the etch rate (Fig. 4, top) and yield (bottom) have a stronger dependence on temperature compared to other variables. The etch rates and yields of GaP and GaSb increased monotonically as the chuck temperature increased from 25 to 100 °C, and increased gradually beyond 100 °C. However, GaAs and AlGaAs showed a gradual

increase in the etch rate and yield up to 75 °C, and substantial increase at > 75 °C. These results can be explained by analyzing the control steps of the overall etching process. For GaP and GaSb, the overall etch rate is controlled by desorption of etch products such as GaCl_x and SbCl_x at temperatures lower than 100 °C, and controlled by mass transfer of reactive Cl to the surface at > 100 °C. However, for GaAs and AlGaAs, the etch process is controlled by physical sputtering of etch products at < 75 °C, and by desorption of etch products such as GaCl_x, AlCl_x and AsCl_x at temperatures greater than 75 °C. Hence, based on the analysis of the temperature effect, we can identify three control regimes for the RIBE of GaAs and related compounds; 1) sputtering-etch limited region: the etch rate is relatively low and less dependent on temperature, 2) product-desorption limited region: the etch rate is strongly dependent on substrate temperature, and vertical profile and smooth surface may be obtained, and 3) mass-transfer limited region: the etch yield is still high, dependent on the transport of reactive Cl to the surface, but less dependent on temperature.

B. Etch morphology and etch profile

Etch morphology was examined using AFM for the GaAs samples etched at 25 °C, 0.2 mTorr, 100 mA and 7 sccm Cl₂/3 sccm Ar with varying beam voltage from 200 to 800 V, and the results are shown in Fig. 5. The root-mean-square (rms) roughness was less than or equal to 1 nm at < 600 eV, but was somewhat increased to 1.8 nm at 800 eV. It is worthwhile to note that the sub-nm roughness is pretty much same as the original polished wafer having ~1/2 nm roughness. Although not illustrated, the rms roughness at

150 °C and 180 mA were 1.8 and 1.6 nm, respectively, resulting in overall mirrorlike smoothness.

Figure 6 shows SEM micrographs of the GaAs etched at 25 °C (top) and AlGaAs etched at 150 °C (bottom), 0.2 mTorr, 400 eV, 100 mA, and 70 % Cl₂. The surface was extremely smooth and sidewalls were straight; the only features present were slight ripples in the AlGaAs sample that might be caused by pattern transfer of slightly rippled unetched surface (Fig. 6, bottom).

C. Surface chemistry and etch products

Figure 7 shows the AES spectra and elemental depth profile of the GaAs samples etched at various substrate temperatures, beam currents and Cl₂ concentrations. It is seen that the etched surface stoichiometry is almost the same for all cases, however the concentrations of residual chlorine and carbon are somewhat different. Compared to the AES spectrum for room-temperature etching (top left), the GaAs etched at 150 °C showed no Cl contamination, but substantial amount of carbon residue (top right). The increased amount of carbon contamination is likely from photoresist and the grid; the carbon reacts readily with etch byproducts at high temperature to form a polymer on the sidewall of the feature. The etch result obtained at 180 mA and 10 % Cl₂ (bottom right) showed similar AES spectrum to the one at 100 mA and 70 % Cl₂ (top left), except somewhat decreased in carbon content.

In-situ quadrupole mass spectrometer (QMS) was used to identify etch byproducts of GaAs, and results are shown in Figs. 8-10 in terms of peak intensity variation. The overall spectrum was very similar to that reported by Eddy et al.²⁶ 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 were due to arsenic chlorides (AsCl at ~ 110 , 112 amu, AsCl₂ at ~ 145 , 147 and 149 amu, and AsCl₃ at ~ 180 , 182 and 184 amu). The GaCl₂ peaks occurred at ~ 139 , 141 and 143 amu. Elemental Ga (69 and 71 amu) and arsenic (75 amu) were difficult to separate from the molecular Cl₂ peaks at 70, 72 and 74 amu. Eddy et al. suggested that additional peaks in the spectrum may be due to the parent molecule and subsequent fragmentation of COCl₃ formed by reaction in the plasma.²⁶ The conclusion of these work is that their spectrum (and by inference, ours) is consistent with AsCl₃ and GaCl₃ being the dominant products, since the cracking patterns of AsCl₃ and GaCl₃ are dominated by AsCl₂ and GaCl₂, respectively.

It is seen from Fig. 8 that the peak intensities increased overall as the ion energy increased up to 600 eV and saturated beyond 600 eV. As explained above, this is attributed to the ion-assisted etching at < 600 eV. It is also interesting to see that AsCl_x peaks are greater than GaCl_x peaks mainly due to lower boiling points and bond strength of AsCl_x than GaCl_x. As expected in the discussion of the effect of etch rate and yield (Fig. 2), the peak intensities of etch byproducts except of GaCl and GaCl₂ were relatively independent on the beam current (Fig. 9), implying that the etching of GaAs is dominated by physical sputtering at high ion current.

Figure 10 shows the effect of Cl₂ concentration on the peak intensities of the etch byproducts. It is seen that peak intensities increased with Cl₂ percentage to reach maxima at 50 % and decreased at > 50 %, which is consistent with the etch rates shown in Fig. 3.

Although not illustrated, the peak intensities of byproducts increased substantially with increasing substrate temperature, as expected in Fig. 4. Overall, combining the effects of beam voltage and current, Cl_2 concentration and substrate temperature, it is concluded that sufficient fluxes of both ions and reactive Cl neutrals are required to maximize the formation of etch byproducts.

IV. CONCLUSIONS

GaAs, GaP, AlGaAs and GaSb were etched in a novel reactive ion beam etching system in a Cl_2 -Ar mixture, using a high density ICP source. The influence of beam voltage and current, substrate temperature and Cl_2 concentration on etch rate was investigated. The etch rate and yield were strongly affected by ion energy and substrate temperature. The RIBE was dominated by ion-assisted etching at < 600 eV and by physical sputtering beyond 600 eV. However, the beam current was not an important variable to obtain anisotropic etching relative to the beam voltage. The etch rate and yield increased as Cl_2 concentration increased, reaching maxima for GaP at 50 % Cl_2 and at 70 % Cl_2 for GaAs, AlGaAs and GaSb, and decreased at higher percentages. The temperature dependency of RIBE rates revealed three control regimes, depending on the substrate temperature: 1) sputtering-etch limited, 2) product-desorption limited, and 3) mass-transfer limited regions. AFM and SEM analysis showed mirrorlike surfaces and anisotropic etching features. Mass analysis of the etch product chlorides formed during RIBE-ICP Cl_2/Ar etching of GaAs showed that GaCl_3 and AsCl_3 are the dominant products. This result is consistent with recent work on ECR-RIE of GaAs in Cl_2/Ar ,²⁶ and

shows that high density plasmas accelerate etch rates predominantly by ion-neutral synergism and not by subverting the usual etch reactions.

ACKNOWLEDGEMENTS

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Figure Captions

Fig. 1 Effect of beam voltage on etch rate and yield.

Fig. 2 Effect of beam current on etch rate and yield.

Fig. 3 Effect of chlorine concentration on etch rate and yield.

Fig. 4 Effect of substrate temperature on etch rate and yield.

Fig. 5 AFM scans of GaAs samples etched at various beam voltages.

Fig. 6 SEM photographs of GaAs at 25 °C (top) and AlGaAs etched at 150 °C (bottom), 400 eV, 100 mA, and 70 % Cl₂.

Fig. 7 AES spectra and elemental depth profile of GaAs after etching at various conditions.

Fig. 8 Effect of beam voltage on the QMS peak intensities of etch byproducts of GaAs.

Fig. 9 Effect of beam current on the QMS peak intensities of etch byproducts of GaAs.

Fig. 10 Effect of chlorine concentration on the QMS peak intensities of etch byproducts of GaAs.

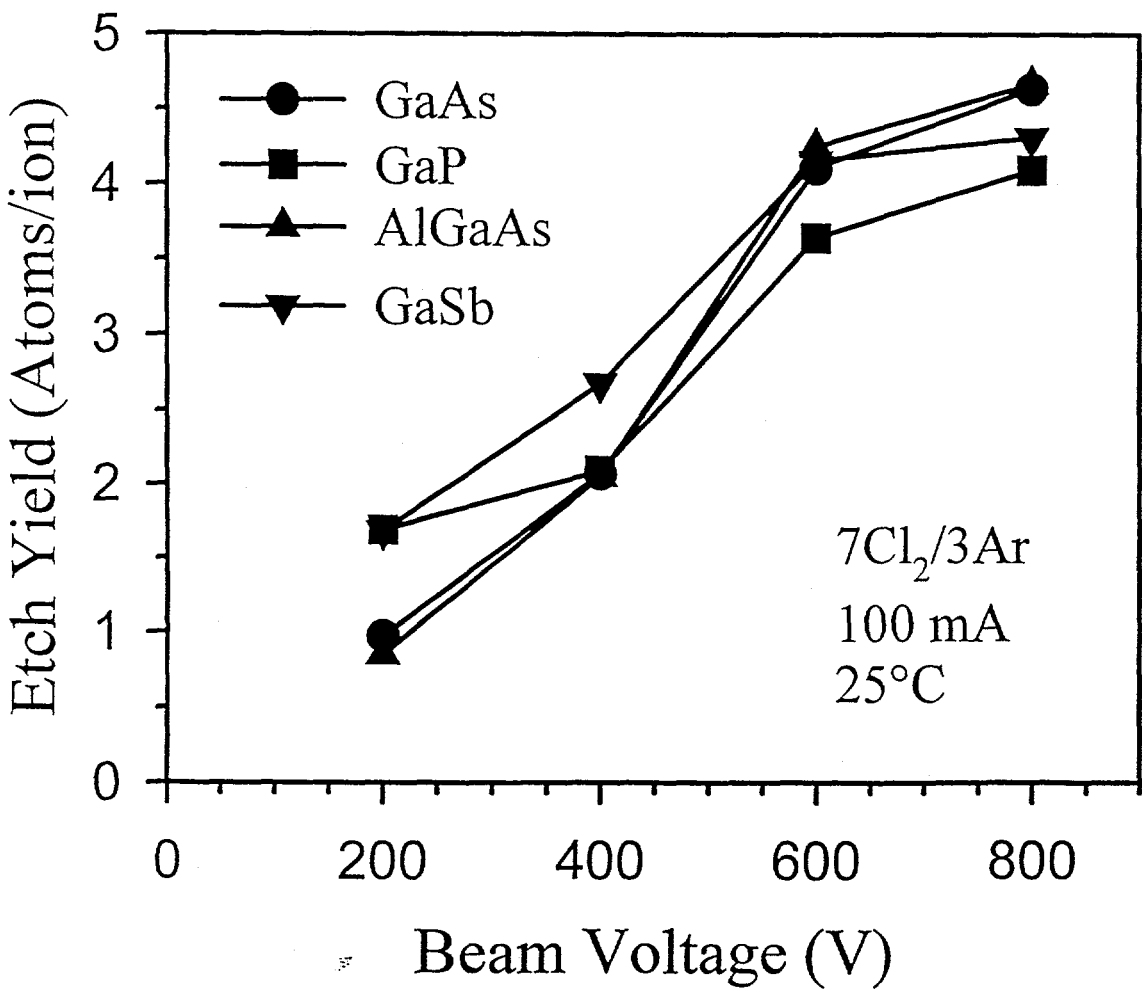
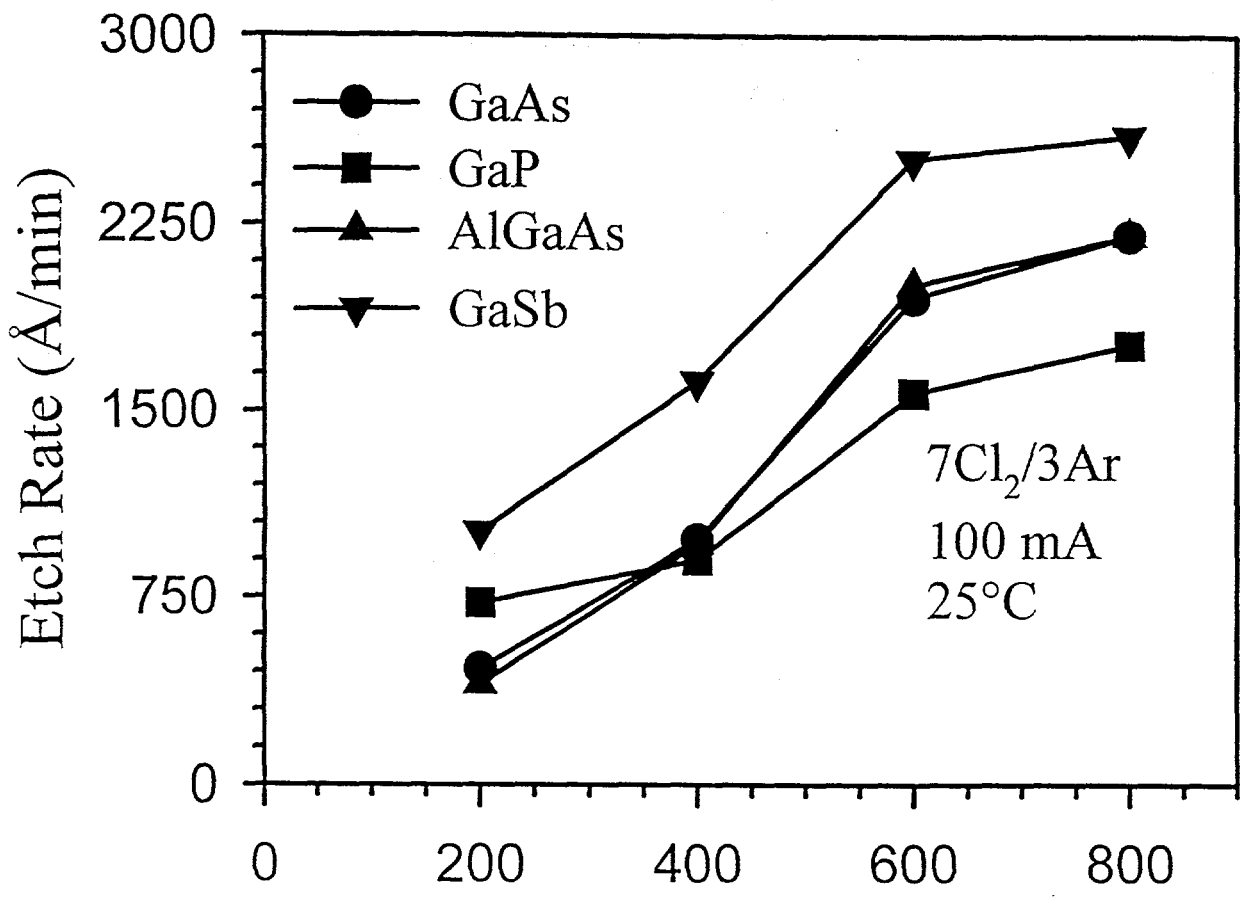


Fig. 1 G.B. Hahn et al.

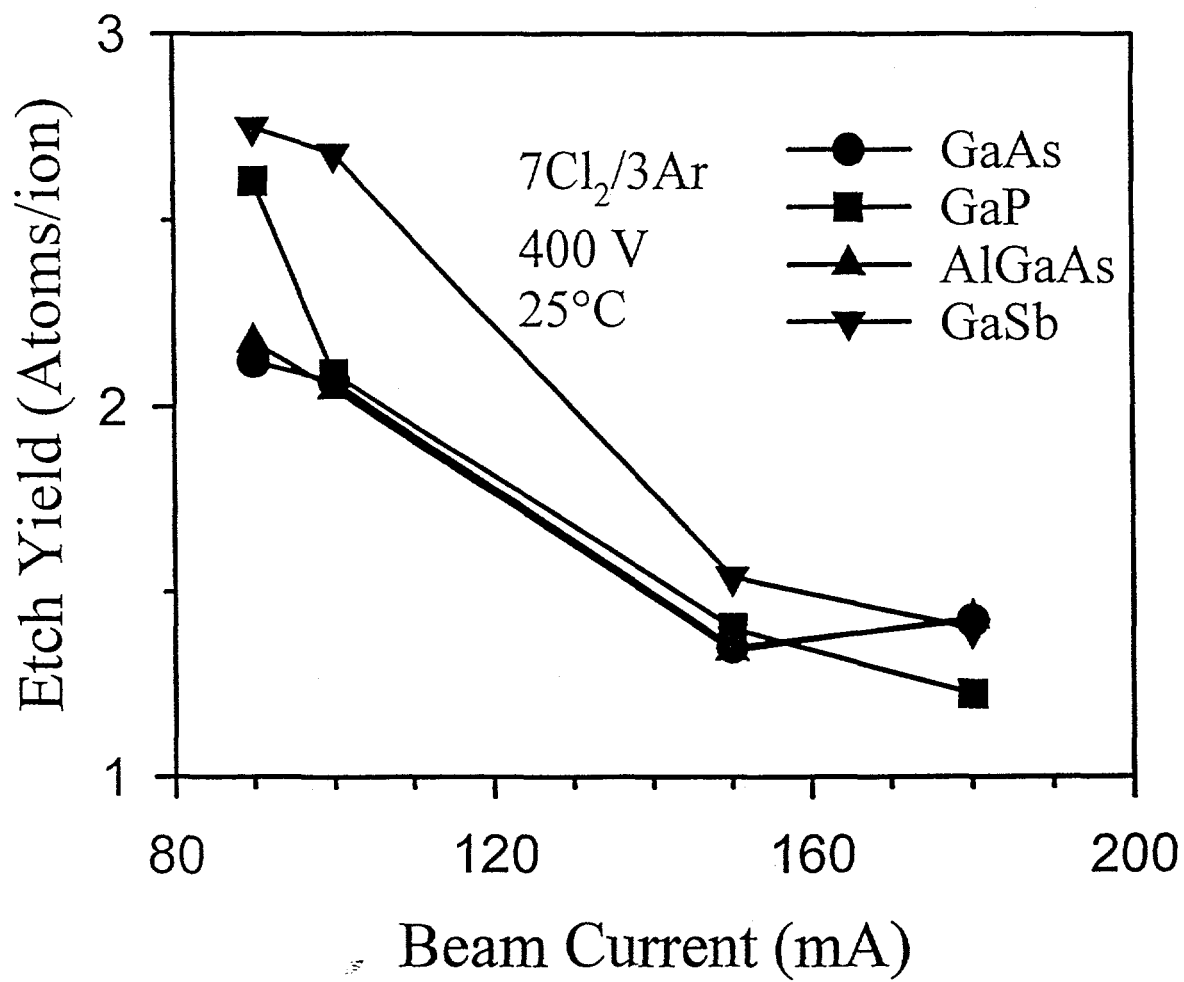
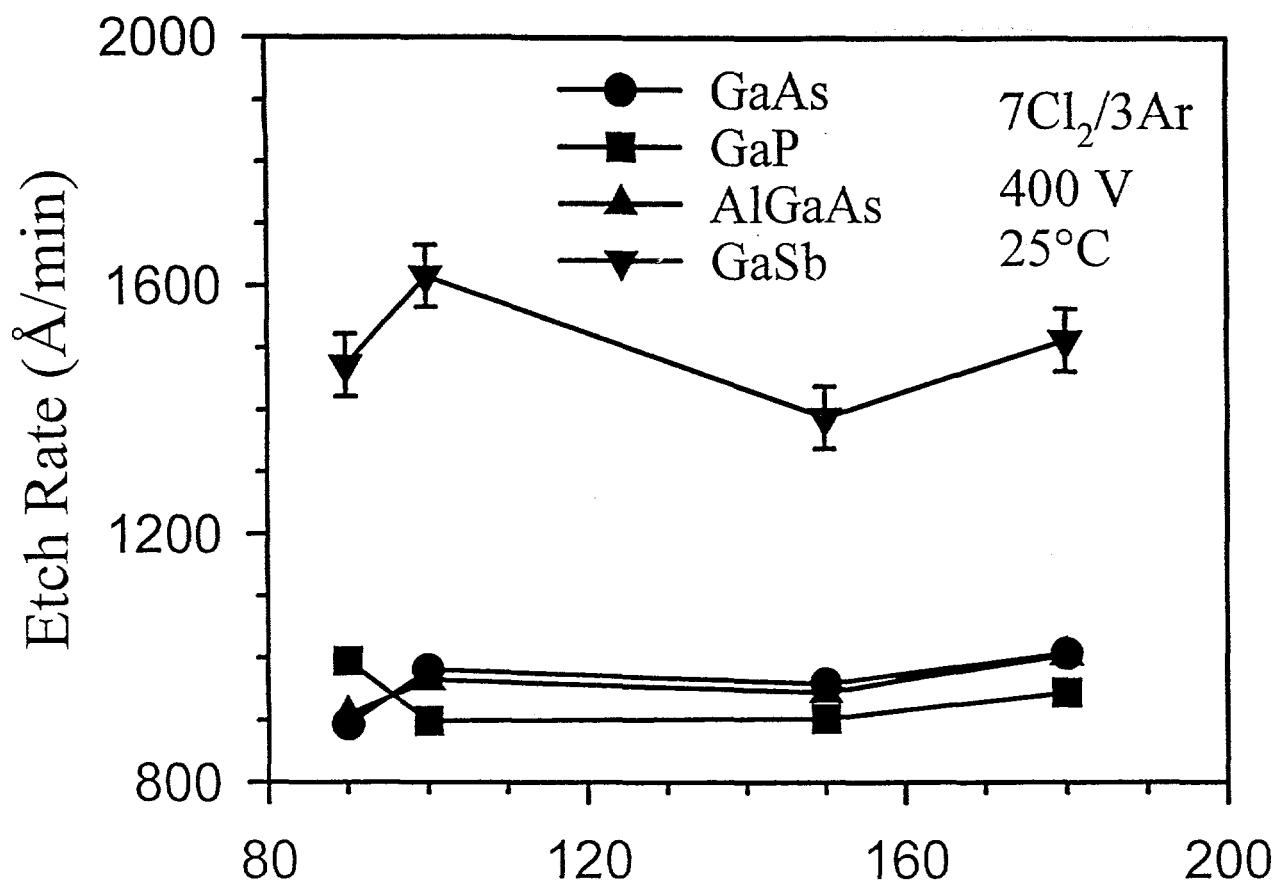


Fig. 2. Y. B. Hahn et al.

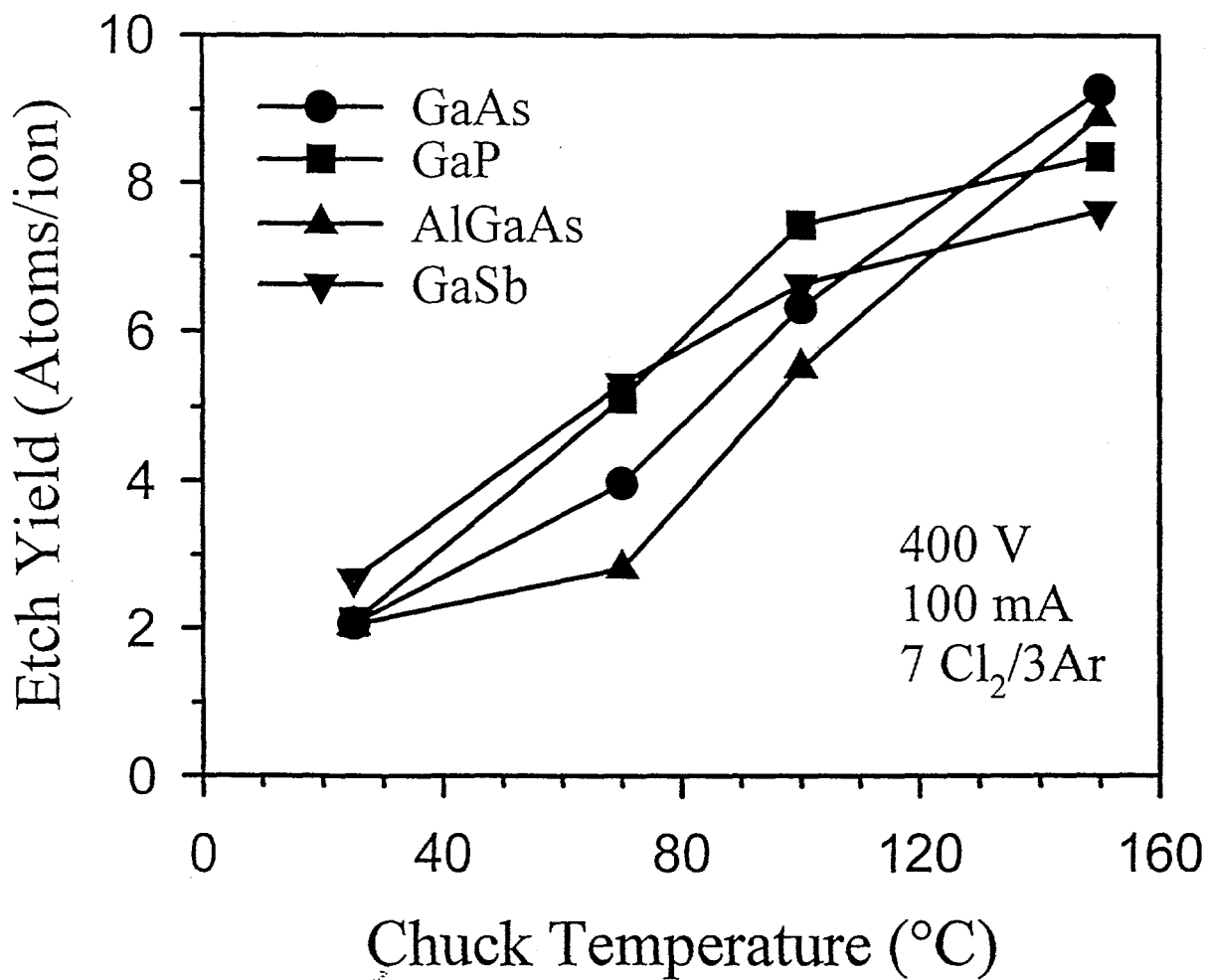
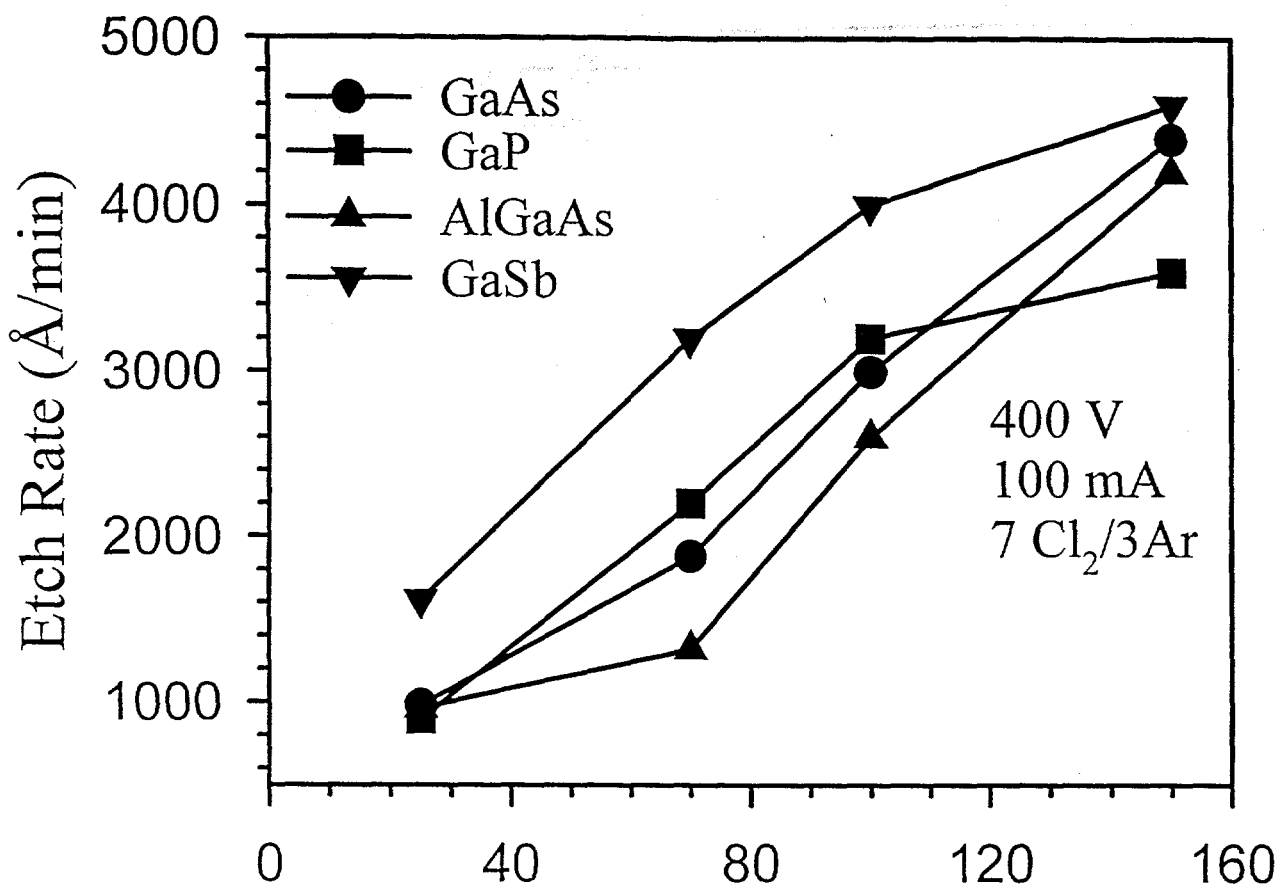
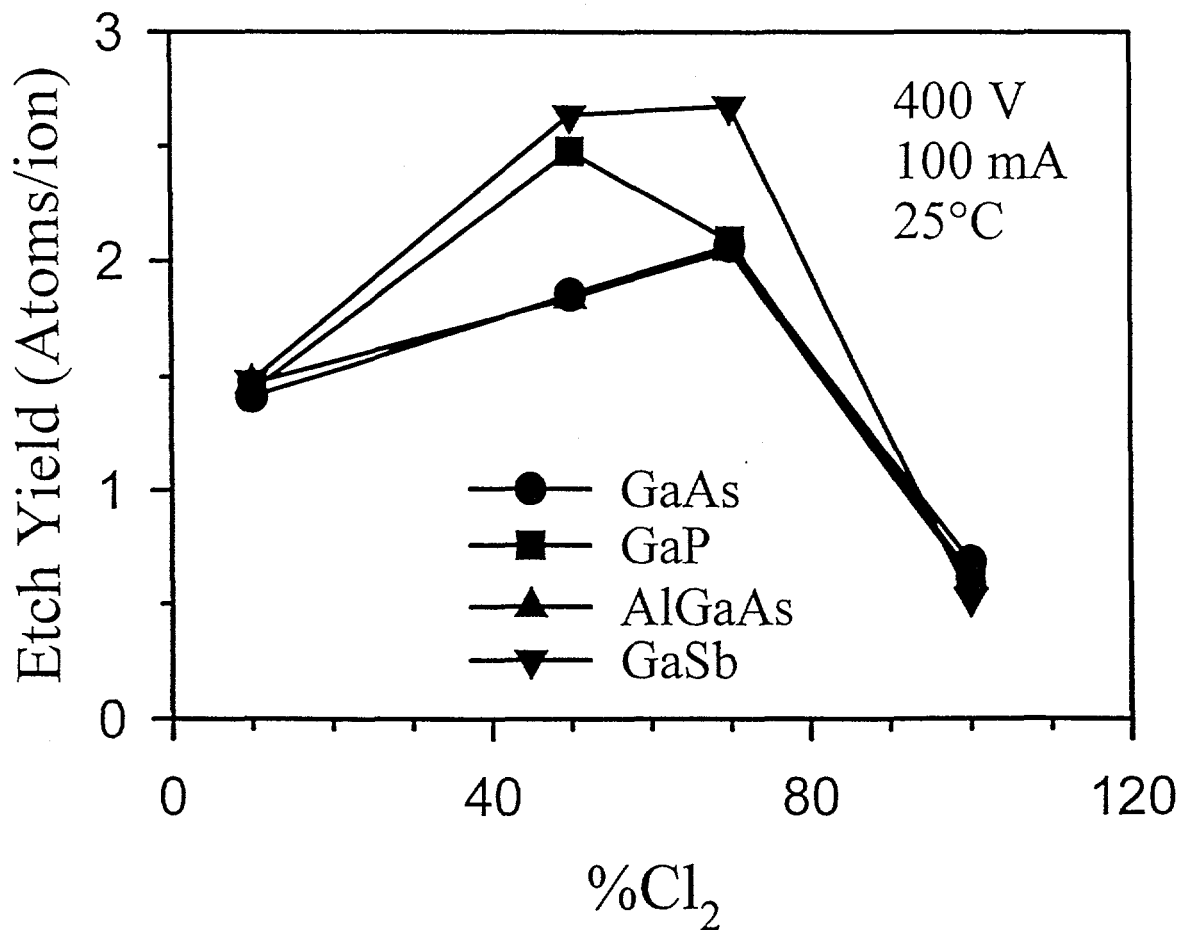
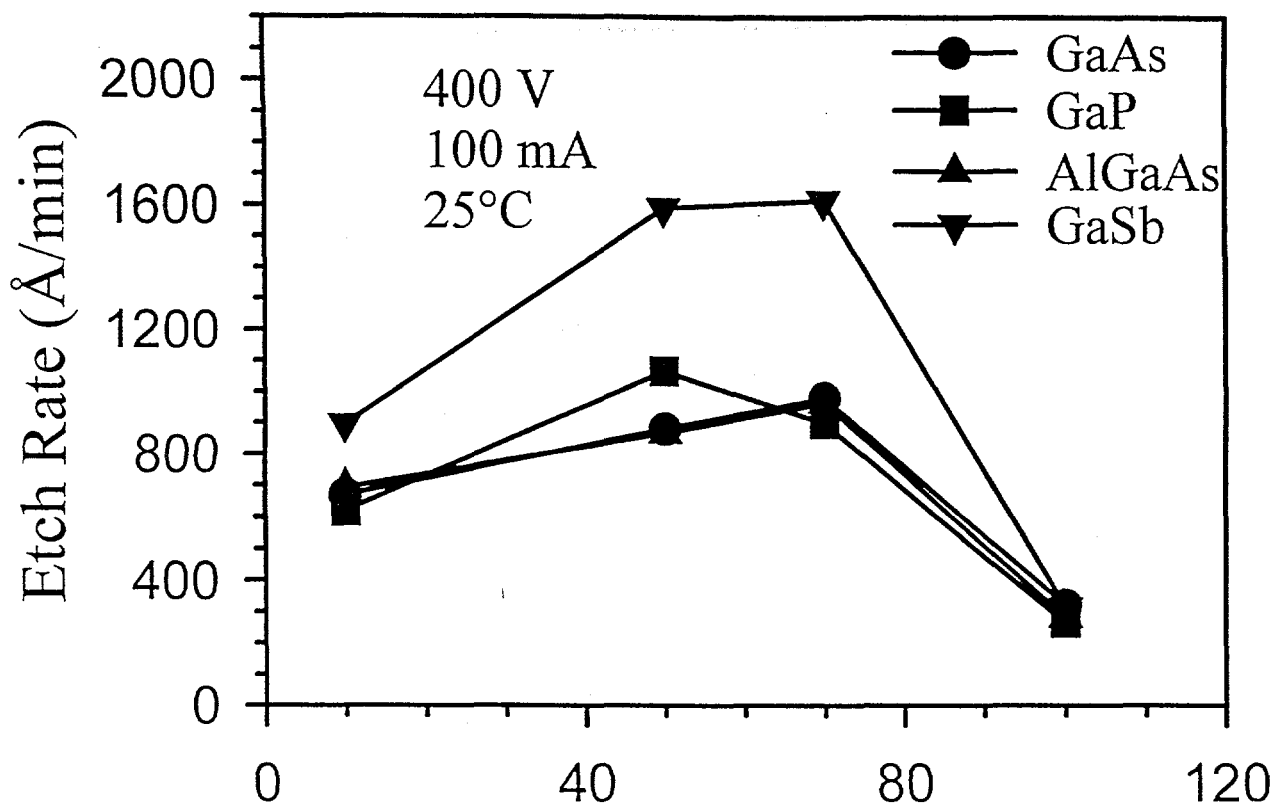


Fig 4. Y. B. Hahn et al.



(Total flow of Cl₂/Ar is 10 sccm)

Fig 3. Y. B. Hahn et al.

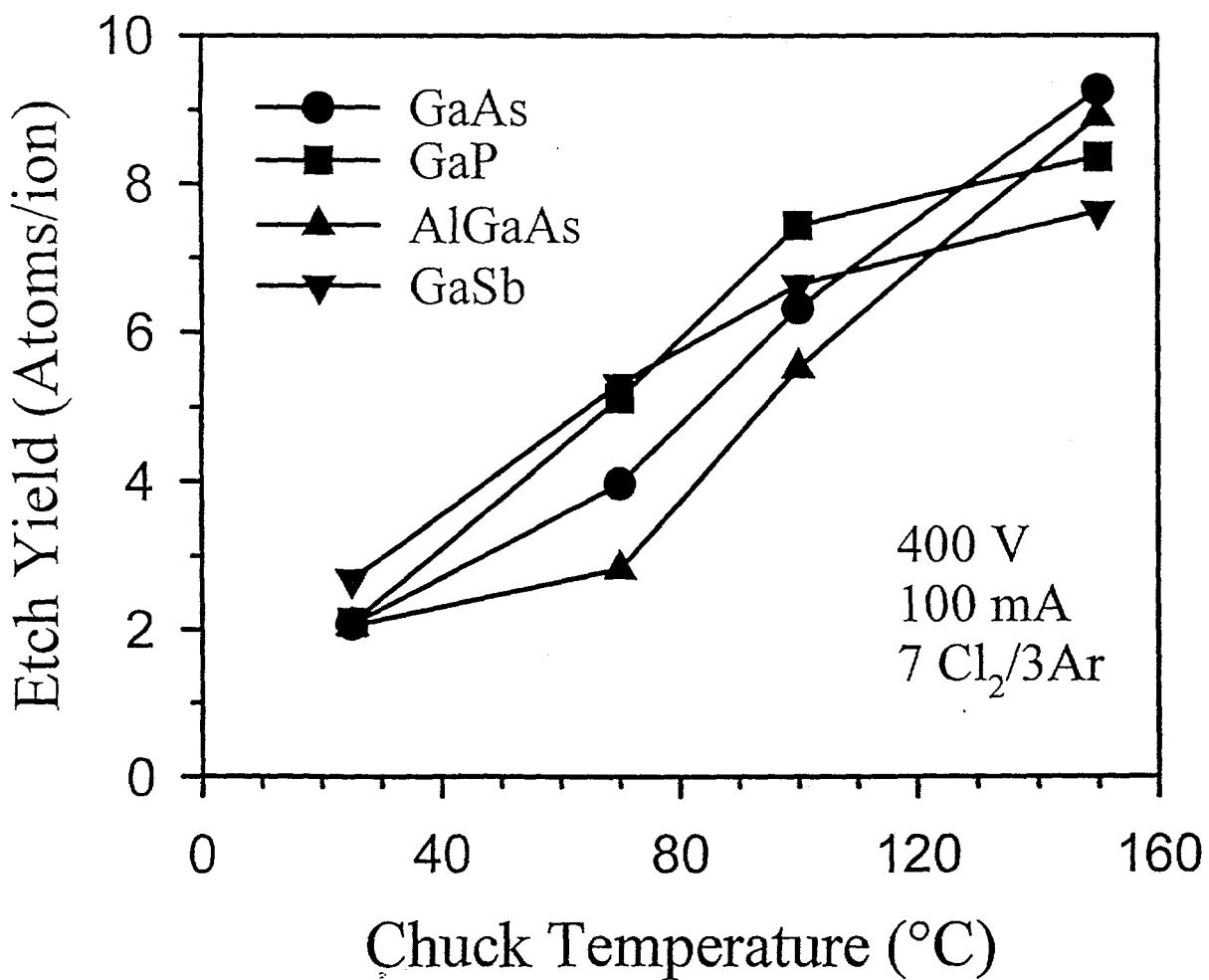
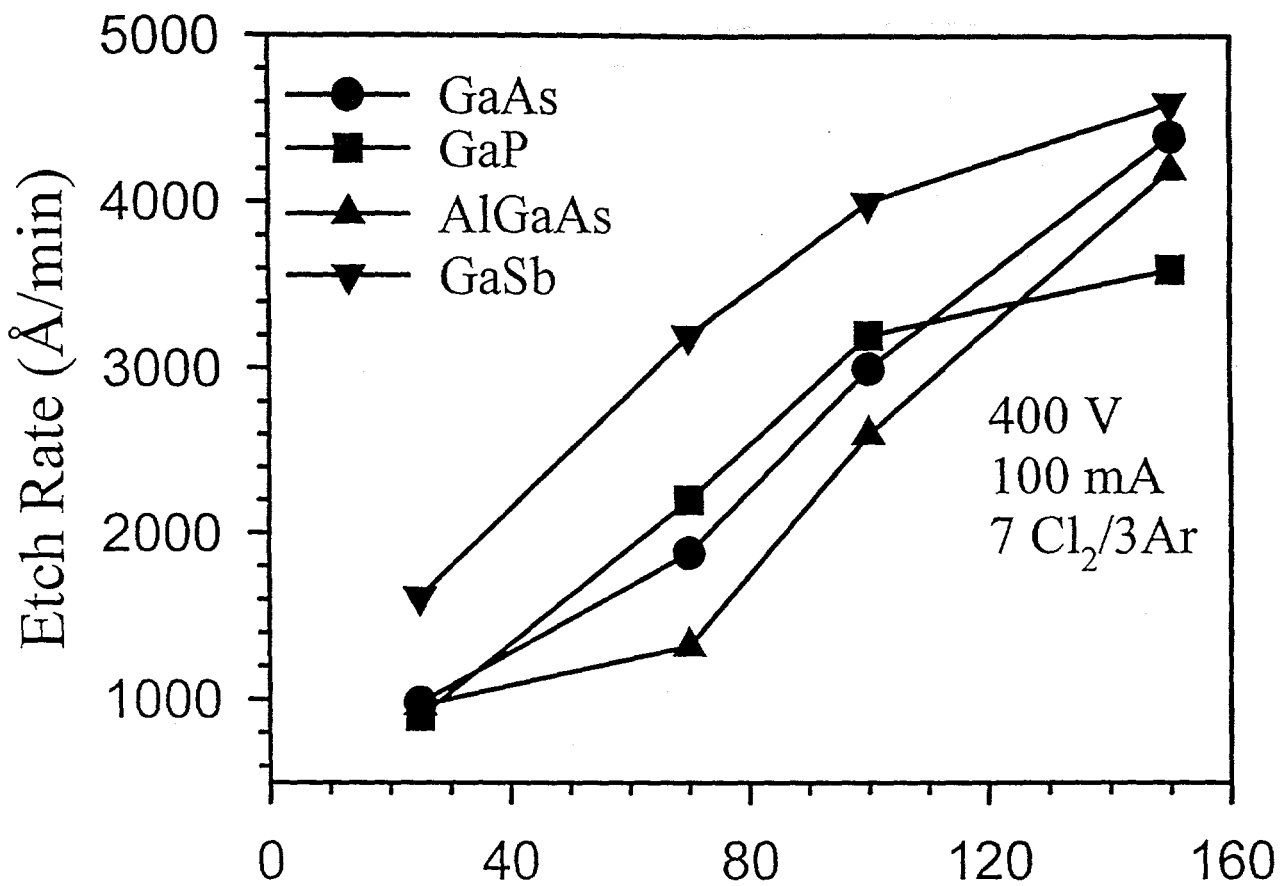
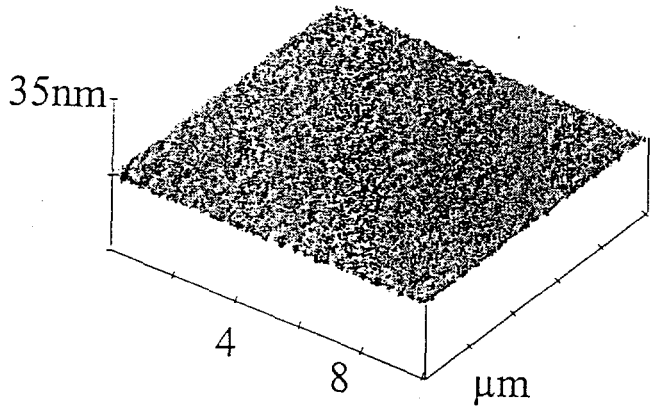
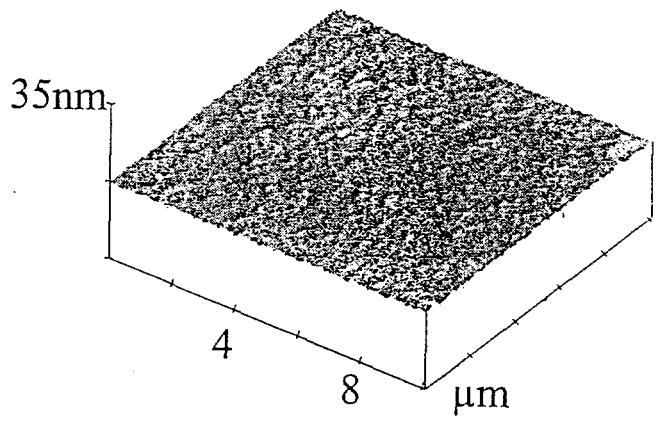


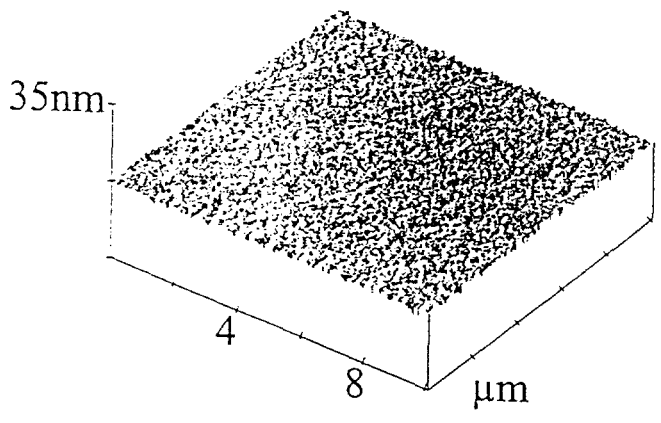
Fig 4. Y. B. Hahn et al.



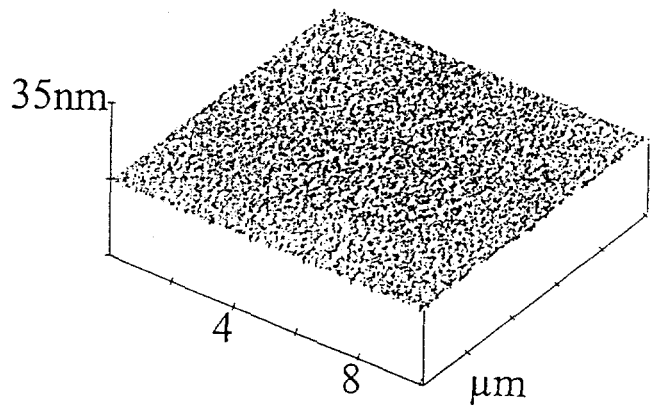
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400V, 0.9nm



600V, 1.0nm



800V, 1.8nm

Fig 5. Y. B. Hahn et al.

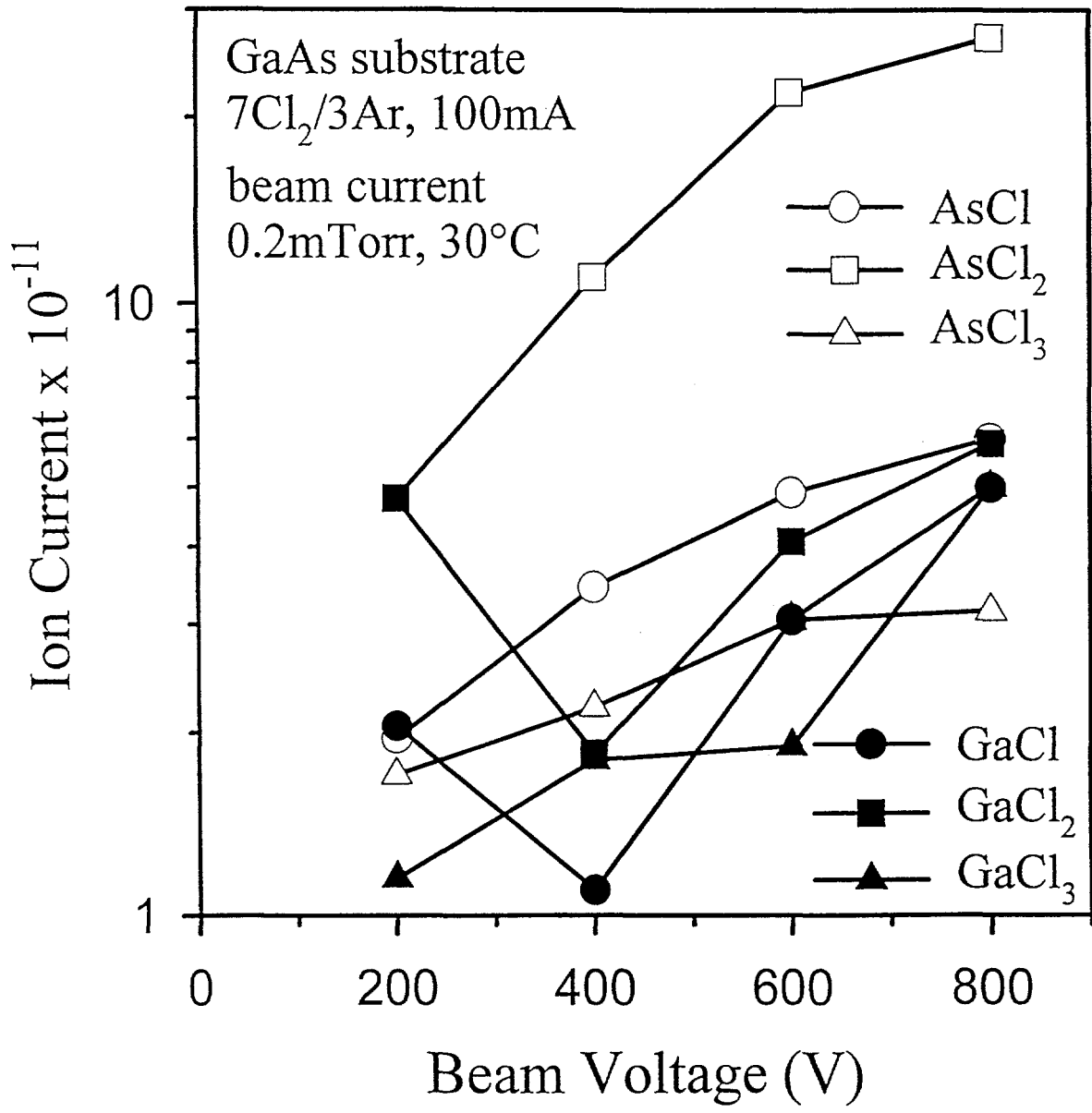


Fig 8. Y.S. Hahn et al.

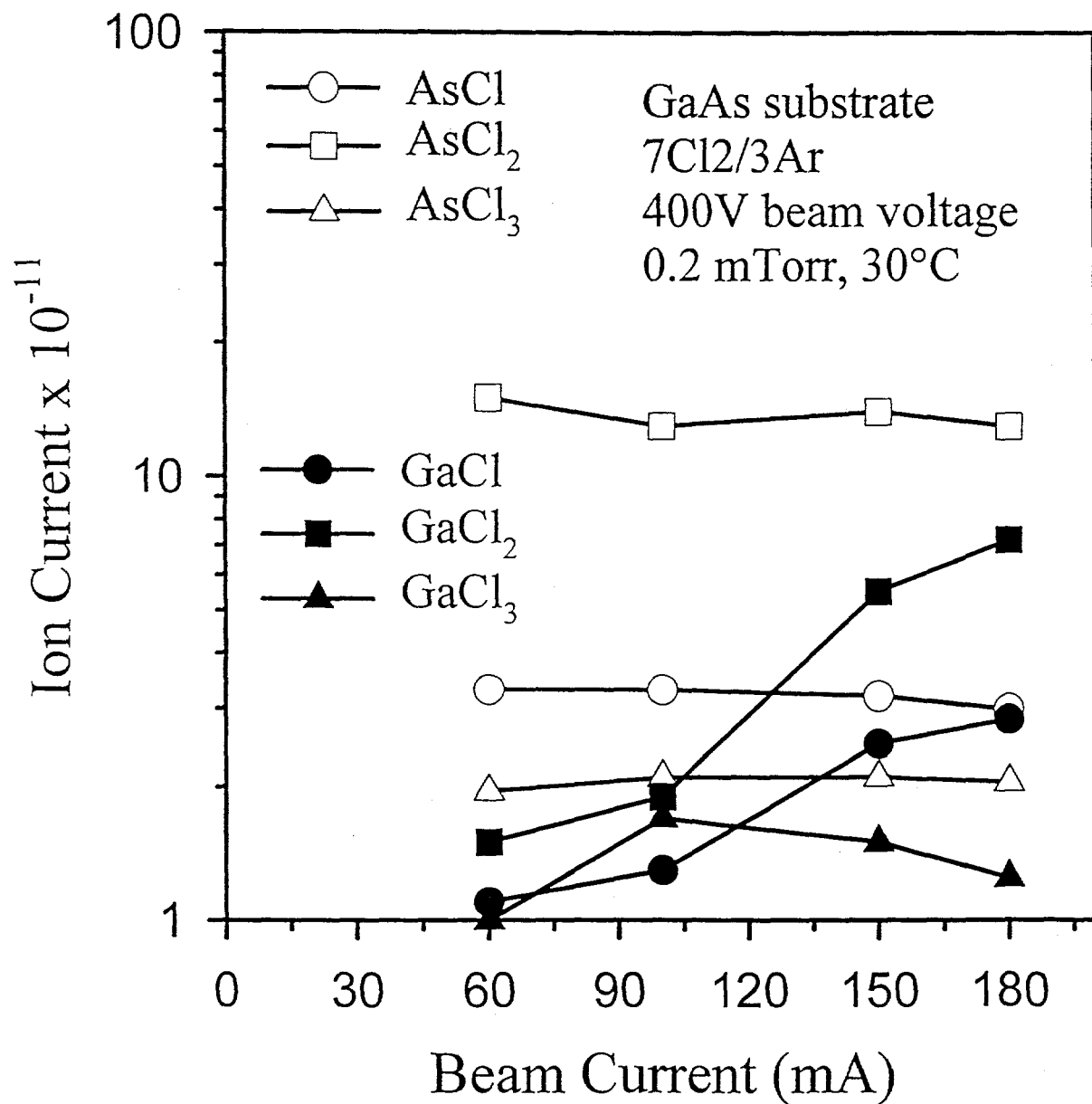


Fig 9. Y.B. Hahn et al.

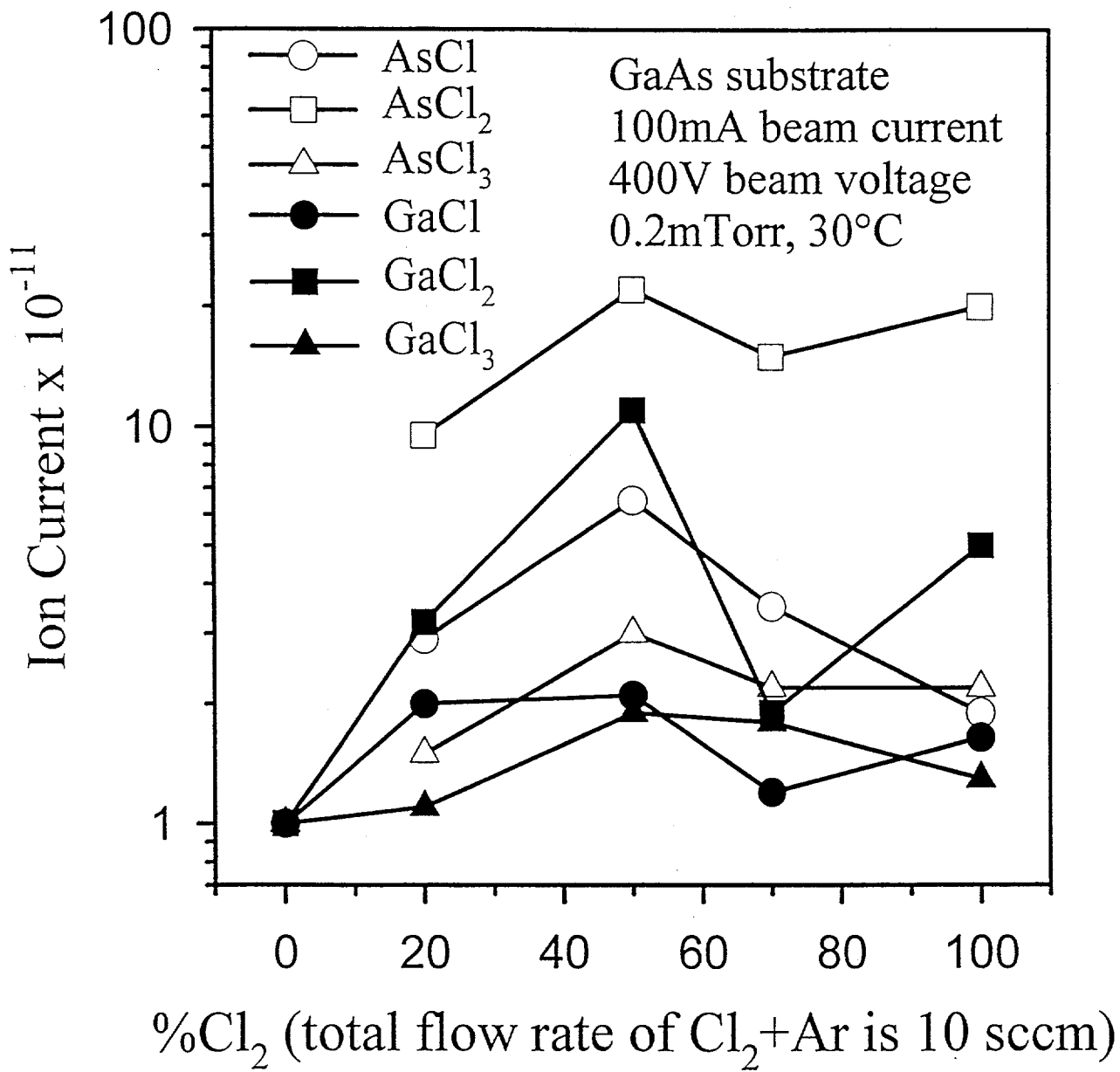


Fig 10. Y. B. Hahn et al.