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Chemical routes to GaAs etching with low-energy ion beams

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Abstract. The interaction of halogens on GaAs surfaces lies at the heart of a whole host of dry-etching methods. This paper considers the adsorption characteristics of chlorine on GaAs(100)(4×1) and the effect of low-energy ion bombardment on the chemisorbed states formed. The results are discussed in relation to ultra-low damage and low contamination chemically assisted ion beam etching (CAIBE) processes.

1. Introduction

'Dry' semiconductor etching involves, predominantly, the interaction of halogens or halogenated compounds (often in a fragmented form) with the semiconductor surface concerned. Volatile semiconductor halide species are then produced and subsequently removed. It is, therefore, of significant interest to consider the nature of the adsorbed phases formed when semiconductor surfaces are exposed to halogen gases. Recent studies have been performed on Si [1], InP [2] and GaAs [3]. A knowledge of such adsorbed states may allow a greater insight into a variety of dry etching methods, including an approach known as chemically assisted ion beam etching (CAIBE). In a CAIBE experiment, an inert gas ion beam (often argon) bombards a surface that is simultaneously exposed to a halogen vapour [4]. In this paper the implications of recent results obtained from the Cl₂/GaAs adsorption system for CAIBE are considered.

2. Experimental approach

All experiments described here were performed inside a stainless steel ultra-high vacuum (UHV) system consisting of an analytical chamber equipped with electron optics for LEED and AES measurements and a second chamber for adsorption/desorption experiments; this second region could be operated between UHV and several mtorr of reactant gas for simulation of real etching conditions. The system was equipped with a 1-300 amu quadrupole mass spectrometer (QMS), thus allowing thermal desorption spectroscopy (TDS) to be carried out in addition to residual gas analysis. The GaAs (100) sample received no treatment prior to insertion into the vacuum chamber and system bake-out. Before experiments commenced, the GaAs was argon-ion bombarded to remove

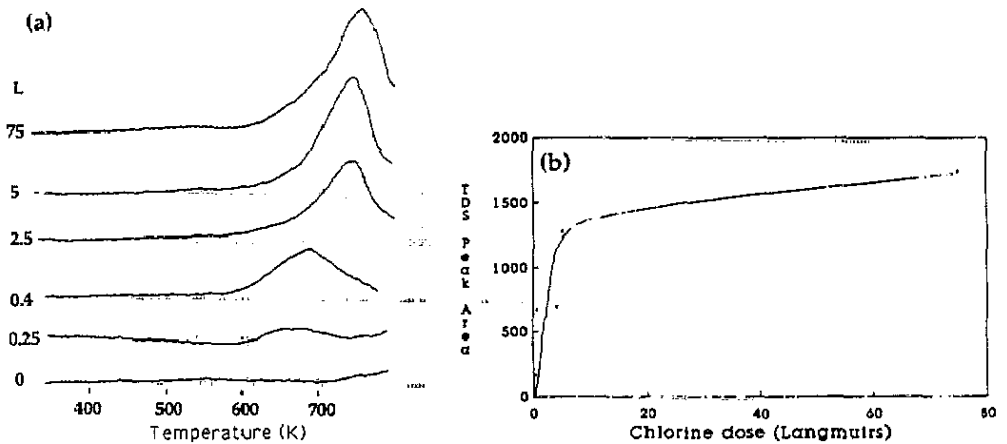


Figure 1. (a) Thermal desorption spectra for GaCl; (b) peak areas derived from (a) plotted as a function of increasing chlorine exposure.

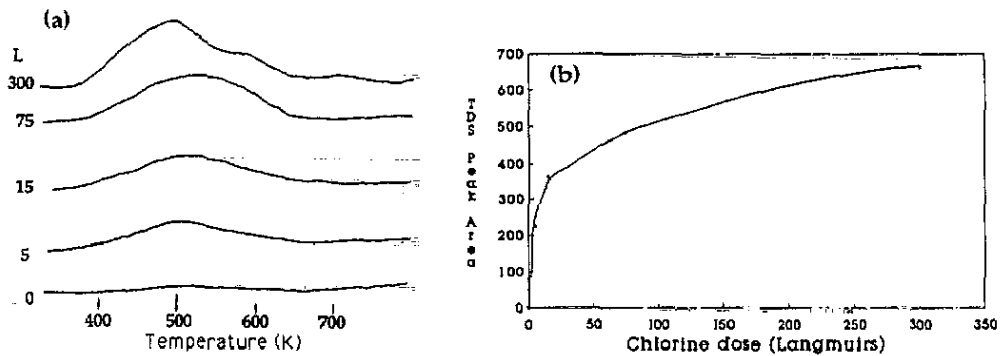


Figure 2. (a) Thermal desorption spectra for GaCl₂; (b) peak areas derived from (a) plotted as a function of increasing chlorine exposure.

oxides and residual surface contamination, and then annealed under UHV conditions using slow heating cycles to 780 K. Auger and LEED analysis showed this treatment to yield a contamination free, reconstructed GaAs(100)(4×1) surface. Chlorine gas was directly introduced through a directed dosing tube. Ion irradiation was by means of a simple hot-filament argon gun with ion fluxes of 2–3 $\mu\text{A cm}^{-2}$ at an energy of 550 V.

3. The adsorption of halogens on semiconductors: Cl₂/GaAs(100)

Clean GaAs(100)(4×1) surfaces were exposed to between 0.25 and 500 L of chlorine gas at a range of temperatures. Thermal desorption spectra were then recorded for fragments corresponding to Cl, Cl₂, As, As₂, AsCl_x and GaCl_x ($x = 1-3$). The plots shown in figures 1(a) and 2(a) represent typical spectra obtained for GaCl and GaCl₂ as a function of increasing exposure of GaAs to chlorine (expressed in Langmuirs) at 300 K.

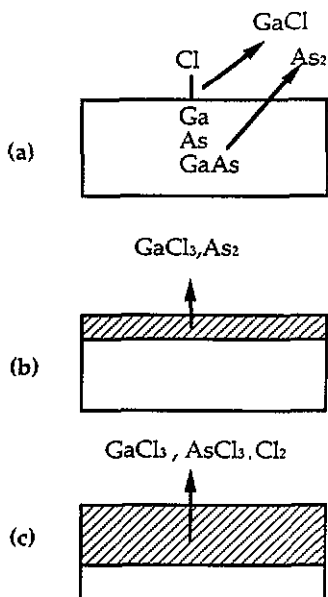


Figure 3. Schematic of mechanism for thermal etching of GaAs(001) with chlorine showing etch products at (a) low coverage (<1 monolayer); (b) medium coverage; and (c) high coverage ('corrosion' layer).

The intensities of the peaks observed are plotted as a function of chlorine exposure in figures 1(b) and 2(b). It is immediately apparent that whilst both sets of desorption spectra reveal the presence of only one major peak, the desorption temperature is relatively low (500 K) for GaCl_2 , but somewhat higher for GaCl (730 K). The former peak is also seen to continue to increase in intensity with increasing chlorine exposures, whilst the latter peak saturates after 8 L. This behaviour is indicative of the presence of two distinct surface states. The relative intensities of all observed GaCl_x species ($x = 1-3$) when compared with the cracking pattern of GaCl_3 allow the low-temperature peak to be assigned to predominantly desorbing GaCl_3 species (with GaCl_2 intensity arising through parent-ion fragmentation in the mass spectrometer), whilst the high temperature peak is attributed to gallium monochloride. All AsCl_x species were found to desorb at temperatures less than 300 K and corresponded to AsCl_3 .

When uptake characteristics, desorption energies and AES/LEED data are taken into account, a reaction sequence could be constructed for the coverage and temperature dependence of chlorine exposure to GaAs. A full analysis can be found elsewhere [3]; such a scheme is shown in figure 3. At low coverages, a strongly held chlorine monolayer phase is formed, which is bound to the terminating Ga species of the GaAs(100)(4×1) surface. Thermal desorption of this phase gives rise to gallium monochloride species. Figure 4 reveals (a) thermal desorption data and (b) uptake characteristics for desorbing As species. A single, high-temperature, peak is apparent; a comparison of As and As_2 data suggests that As_2 is the predominant desorbing species. Thus, surface stoichiometry appears to be maintained during desorption from a low-coverage surface by the loss of As_2 . At higher coverages, a mixed As/Ga/Cl corrosion layer forms, which desorbs at lower temperatures as GaCl_3 and As_2 . At higher coverages still, the penetration of further chlorine into the GaAs is hindered by this corrosion layer, which continues to thicken but now desorbs as GaCl_3 , AsCl_3 and Cl_2 as the supply of chlorine to the surface is effectively enriched. Ballooch *et al* [5] used modulated molecular beam techniques to

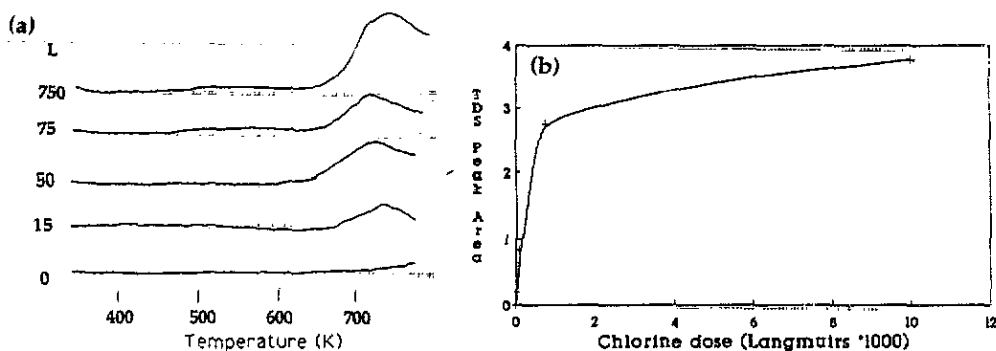


Figure 4. (a) Thermal desorption spectra for As; and (b) peak areas derived from (a), plotted as a function of increasing chlorine exposure.

study the thermal desorption products in this system. The dominant products were assigned as AsCl_3 and GaCl_3 at a temperature of 450 K, but monochlorides were observed at temperatures in excess of 550 K. These observations are in agreement with the model presented here.

The most obvious conclusion from the data presented above is the extent to which a chlorinated overlayer may be expected to exist on the GaAs surface if pure chlorine is used as an etching gas. In order to realise acceptable etching rates, reactions are usually carried out at considerably higher pressures than those used in this study. Thus, the presence of a corroded chlorine layer on the surface is highly likely if the surface is exposed to chlorine for even a short time after thermal/ion beam promotion of the etching reaction has ceased. If an interface of high quality (and hence purity) is to be fabricated in this region this is clearly undesirable. Furthermore, if a maskless etching reaction was to be undertaken (using a focused beam source), then considerable GaAs perturbation would exist *outside* the beam irradiated area. The observation of AsCl_3 desorption below room temperature also indicates some degree of etching is likely without additional energy being supplied; this may also limit the usefulness of chlorine as a precursor in maskless environments.

4. Ion beam bombardment of adsorbed states: $\text{Ar}^+/\text{Cl}_2/\text{GaAs}$

The effects of bombarding the adsorbed states formed when chlorine reacts with a GaAs surface have been identified. Figures 5(a) and 6(a) show thermal desorption spectra obtained for GaCl and GaCl_2 species for a single exposure of chlorine to the GaAs surface, plotted as a function of increasing bombardment by a 500 eV argon ion beam. No new peaks are evident after the ion bombardment; the major influence of the beam is upon the peak intensities. Figures 5(b) and 6(b) show this change in peak intensities, as monitored by the area under the curves from the desorption spectra. It is immediately apparent that whilst both species are seen to decrease in intensity after extended periods of bombardment, the GaCl signal actually *increases* in the first few seconds of bombardment. The GaCl peak intensity then gradually decreases over a period of several minutes, whilst the GaCl_2 peak disappears after the first few seconds. The relative cross sections for the total removal of each of these observed fragments are 0.1 \AA^2 and 125 \AA^2 .

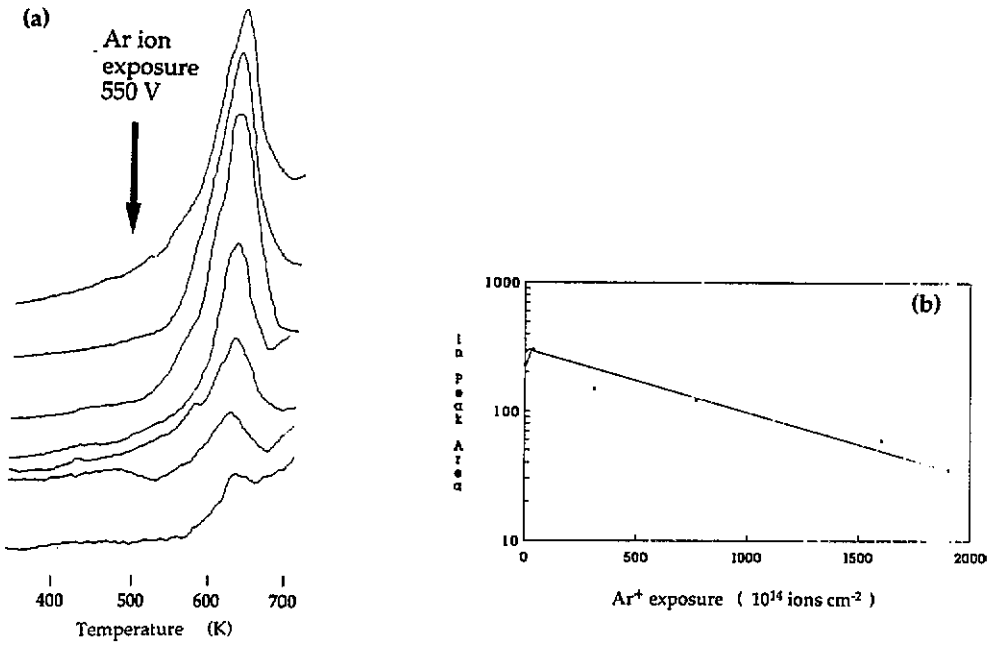


Figure 5. (a) Thermal desorption spectra for GaCl as a function of Ar⁺ irradiation; (b) semi-log plot of peak intensities as a function of Ar⁺ irradiation.

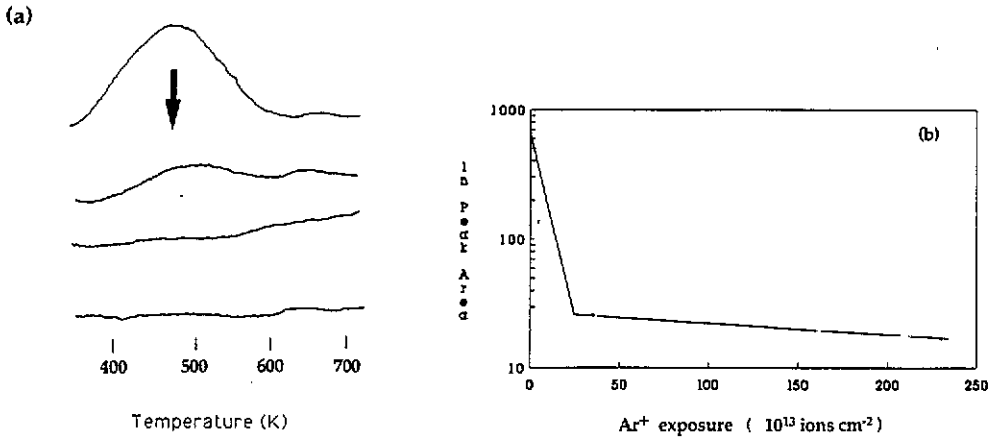
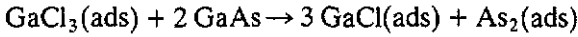


Figure 6. (a) Thermal desorption spectra for GaCl₂ as a function of Ar⁺ irradiation; (b) semi-log plot of peak intensities as a function of Ar⁺ irradiation.

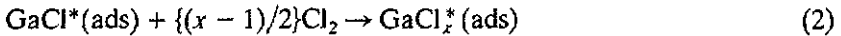
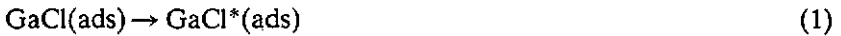
A full analysis of the effect of the beam on the thermal desorption yield of all observed species can be found elsewhere [3]. However, the information contained in figures 5 and 6 highlights the profound *chemical* effect that the beam has on the nature of desorbing gallium chloride fragments. The model described in section 2 ascribes the GaCl₃ desorption signal (represented in figure 6 by the GaCl₂ fragment) to the presence of a multilayer corrosion phase containing Ga, As and Cl. Thus the disappearance of this species from

the thermal desorption measurements concurrent to an increase in the GaCl phase is indicative of an ion mixing process where the Cl from the corrosion layer is dispersed throughout the sub-surface region by the beam. In this form, the thermodynamically favoured desorption product becomes GaCl. This mixed layer is then slowly sputter eroded by further ion beam bombardment. Thus, a reaction of the form:



is promoted by the ion beam, where the phase designation (ads) refers to a phase which desorbs as the species specified.

The bombardment of GaAs by argon ions alone can give rise to significant material removal. However, many studies have observed a significant enhancement in the etching rate achieved by ion beam bombardment following chlorine exposure to GaAs [5–8]. The observations made here indicate a beam-promoted reaction yielding a surface layer that is only slowly eroded by further beam exposure. Fast etching must therefore arise from ion-assisted adsorption and surface reaction with *impinging* chlorine, which was not present during ion irradiation in this work. A reaction scheme of the form:



would be consistent with the observations made here. The GaCl layer identified in this study is unreactive to chlorine adsorption, further uptake relying upon chlorine penetration to form a corrosion layer. Thus, a thickened GaCl layer (formed by ion irradiation) would require excitation by the ion beam (step (1) above), prior to reacting with fresh chlorine (step (2)). Step (3) could represent the spontaneous desorption of this form, or could correspond to desorption promoted by a second ion. The mechanism for such ion-assisted etching presented here shows agreement with models presented by other workers for Si, InP and GaAs [2, 5, 9], suggesting that the process in these differing systems follows a similar pathway. In the case of corrosion layers that are of the same thickness as the expected amorphization depth of the ion beam, the ion beam mixing process observed here would not be expected, and reactions (1) to (3) above would not apply. Mixing of species *within* this layer may then give rise to chemical change/sputtering directly. If the energy of the incoming ion beam is decreased then the amorphisation depth and corrosion layer thickness may be 'tailored' to give a fast etching process without considerably chemical perturbation of the semiconductor and the physical damage that is caused by beam provoked collisional cascades. Finally, it is worth noting that the observations made here suggest that the products of any ion-beam assisted chemical etch will depend upon the steady state surface concentration of the halogen overlayer; such an observation may explain the disagreements that are reported in the literature for the product distributions observed with differing ion flux/chlorine flux ratios [6, 7].

5. Implications for GaAs CAIBE

Chlorine is clearly highly reactive towards clean GaAs surfaces; an ideal CAIBE precursor may be one that is less reactive, displaying dissociative adsorption behaviour on the semiconductor concerned, then giving rise to a passivated surface layer. Such behaviour

would be particularly desirable in a maskless etching reaction, promoted with a focused beam. Low-energy inert gas ion irradiation may then effect this bound layer and hence provoke localized etching. However, unlike plasma or reactive ion beam etching (RIE) processes, prior fragmentation of the precursor does not occur in CAIBE. This may render many of the ultra-stable gases used in plasma etching (such as the family of freon gases) unsuitable since chemisorption of the intact species on GaAs may not be observed. Many of these species are also to be banned from use due to their inherent environmental toxicity [10].

Adsorption studies of CCl_4 on silicon surfaces have revealed potentially useful characteristics [11]. When this molecule interacts with a clean Si(100) surface, dissociative chemisorption is observed, giving rise to around two atom layers of fragmented species. The desorption characteristics of the chlorine in this layer were similar to those observed for the adsorption of pure chlorine on such a surface [12]. Further adsorption was molecular in form, with no further perturbation to the Si lattice occurring unless energy was provided (thermal or beam) to drive interfacial reactions and etching. However, the degrading CCl_4 molecule gave rise to carbon deposits that were not readily desorbed. Thus, a more suitable etching precursor should decompose giving rise to a carbon-containing fragment, which may in turn be desorbed *intact* during etching. The ability of short-chain alkanes, when chemisorbed to GaAs surfaces to undergo β -hydride elimination and desorb as alkenes has been observed in recent adsorption studies of gallium alkyls [13]. The adsorption of a molecule such as dichloroethane onto GaAs may, therefore, be of interest for etching.

A major effect of the impinging ion beam during a CAIBE experiment appears to be mixing the adlayer with the sub-surface region. The surface then becomes more reactive to further adsorbing species. This reliance upon *physical perturbation* of the host lattice will have serious implications for the extent of damage inflicted upon the host lattice through collisional cascade and thermal spike effects [14]. If the ion-beam energy is reduced to below the sputter threshold for the GaAs (around 10 eV), the beam should only perturb the adlayer present. From the results discussed above it is clear that, provided that a multilayer corrosion phase exists on the surface, the lattice of the GaAs will be perturbed by *purely chemical action*. This should allow an etching reaction to proceed with virtually no bulk material damage. A prototype source for such an application has recently been developed by Ion Tech Ltd and early results with beam energies as low as 6 eV are very promising [15].

Acknowledgments

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References

- [1] Tyrrell G C, Boyd I W and Jackman R B 1989 *Appl. Surf. Sci.* **43** 439
- [2] Murrell A J, Price R J, Jackman R B and Foord J S 1990 *Surf. Sci.* **227** 197
- [3] Jackman R B, Tyrrell G C, French C L and Foord J S 1991 *Surf. Sci.* at press
- [4] Dieleman J, Sanders F H M, Kolfshoten A W, Zalm P C, deVries A E and Haring A 1985 *J. Vac. Sci. Technol* **B3** 1884

- [5] Balooch M, Olander D R and Seikhaus W J 1986 *J. Vac. Sci. Technol.* B4 794
- [6] McNevin S C and Becker G E 1985 *J. Appl. Phys.* 58 4670
- [7] O'Brien W L, Paulsen-Boaz C M, Rhodin T N and Rathbun L C 1988 *J. Appl. Phys.* 64 6523
- [8] Orrmann-Rossiter K G and Armour D G 1989 *Nucl. Instr. and Meths. Phys. Res B* 42 334
- [9] Ameen M S and Mayer T M 1988 *J. Appl. Phys.* 63 1152
- [10] Stevenson R 1990 *Chem. in Britain* 26 731
- [11] French C L, Price R J, Jackman R B and Foord J S 1991 *Surf. Sci.* at press
- [12] Jackman R B, Ebert H and Foord J S *Surf. Sci.* 176 207
- [13] Foord J S, Murrell A J, O'Hare D, Singh N K, Wee A T S and Whitaker T J 1989 *Chemitronics* 4 262
- [14] Sigmund P 1989 *J. Vac. Sci. Technol.* A7 585
- [15] Jackman R B and Beckman J 1991 unpublished results