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Investigations of the thermal reactions of chlorine on the GaAs(100) surface

C L French, W S Balch and J S Foord

Physical Chemistry Laboratory, University of Oxford, South Parks Rd, Oxford OX1 3QZ, UK

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Abstract. The thermal reactions of Cl_2 with the GaAs(100) surface were studied using XPS, LEED and thermal desorption spectroscopy. Chlorine uptake at 175 K is initially very rapid, but an extensive corrosion phase is not formed. Five thermal desorption features are seen, with cracking patterns corresponding to GaCl, As_2 , GaCl_3 , Cl_2 , and AsCl_3 . The implications for the thermal etching of gallium arsenide are discussed.

1. Introduction

The interaction of chlorine with the gallium arsenide surface is important from both scientific and technological points of view. The adsorption of halogens on transition metal surfaces has been extensively investigated [1, 2] so it is of interest to extend these studies to compound semiconductor surfaces. Because gallium and arsenic halides are quite volatile, chlorine-containing compounds are used in the microelectronics industry for the dry etching of gallium arsenide, either thermally or in conjunction with ion, photon or electron beams, or in reactive plasmas. In this work the reactions of Cl_2 with the GaAs(100) surface are investigated and the relevance of the results to the thermal etching of GaAs is discussed.

2. Experimental details

All experiments were performed in a stainless steel ultra-high vacuum system equipped with facilities for XPS ($\text{Mg K}\alpha$), LEED and thermal desorption spectroscopy. Controlled doses of chlorine were obtained from a Cd-doped AgCl electrochemical cell [3]. The GaAs sample was cleaned by cycles of argon bombarding and annealing at 825 K until no carbon or oxygen could be detected on the surface by XPS, and LEED showed the Ga-stabilized (4×1) reconstruction.

3. Results and discussion

The Cl 2p, Ga 2p, Ga 3d, As 3d, and x-ray excited Cl Auger peaks were monitored by XPS as a function of chlorine exposure at 175 K. XPS shows that the initial uptake of

chlorine on the GaAs(100) (4×1) surface at 175 K is rapid, reaching a Cl coverage of 0.6 ± 0.1 monolayers following an exposure of 2 L. Chlorine uptake continues at higher exposures but is two orders of magnitude slower, suggesting that there is a barrier to the adsorption of chlorine after the formation of the initial layer, and any diffusion of chlorine into the substrate is slow.

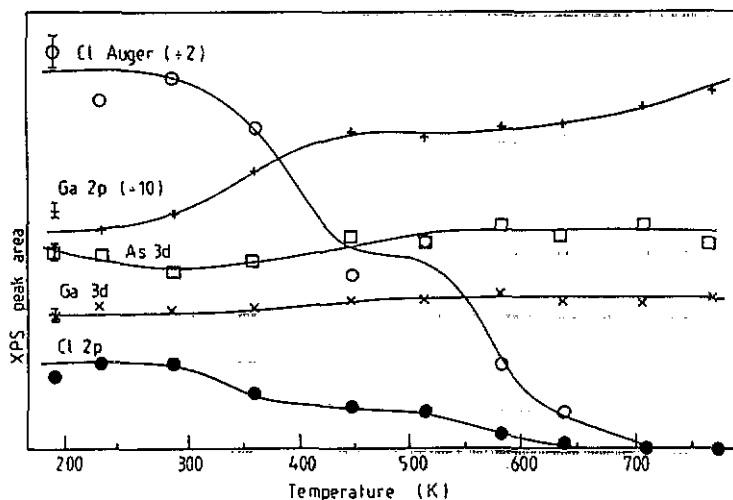


Figure 1. Variation of peak areas measured by XPS with increasing temperature, following exposure of the GaAs(100) (4×1) surface to 5.5 L chlorine.

Figure 1 shows the change in the XPS peak area for the Cl 2p, Ga 2p, Ga 3d, As 3d and x-ray excited Cl Auger transitions with increasing substrate temperature following exposure of the GaAs(100) (4×1) surface to 5.5 L chlorine at 175 K. Most of the chlorine is lost in two stages, between 300 and 450 K, and between 500 and 600 K. The Ga-rich stoichiometry of the initial surface returns on heating to 775 K.

The surface structure was monitored by LEED as a function of chlorine dose and substrate temperature. Adsorption of chlorine at 175 K leads to the lifting of the (4×1) reconstruction of the clean ordered surface to form a (1×1) LEED pattern. Additional chlorine adsorption increases the background intensity; heating the chlorine-dosed surface to 300 K produces a further increase in background intensity. A weak (4×1) reconstruction returns at 700 K, where the XPS shows all chlorine has been lost from the surface, and sharpens up on heating to 800 K.

Figure 2 shows thermal desorption spectra recorded with the mass spectrometer tuned to the indicated ion fragments, following exposure of the GaAs surface to 12 L chlorine at 175 K. Five desorption features are seen, with cracking patterns corresponding to As_2 , GaCl , Cl_2 , GaCl_3 , and AsCl_3 .

Figure 3 shows the desorption yields of Cl_2^+ , As^+ , GaCl^+ , GaCl_2^+ and AsCl_3^+ , corresponding to the desorption of Cl_2 , As_2 , GaCl , GaCl_3 and AsCl_3 respectively, as a function of chlorine exposure at 175 K. At the smallest chlorine exposures only the GaCl and As_2 thermal desorption peaks are seen, with the GaCl_3 starting to appear after 1 L exposure. Thermal desorption of GaCl_3 , GaCl and As_2 has saturated by 5 L exposure, again suggesting that an extensive corrosion phase does not form. The formation of As_2 rather than arsenic chlorides is consistent with thermodynamic calculations on chlorine/GaAs systems [4, 5], which predict that in the presence of

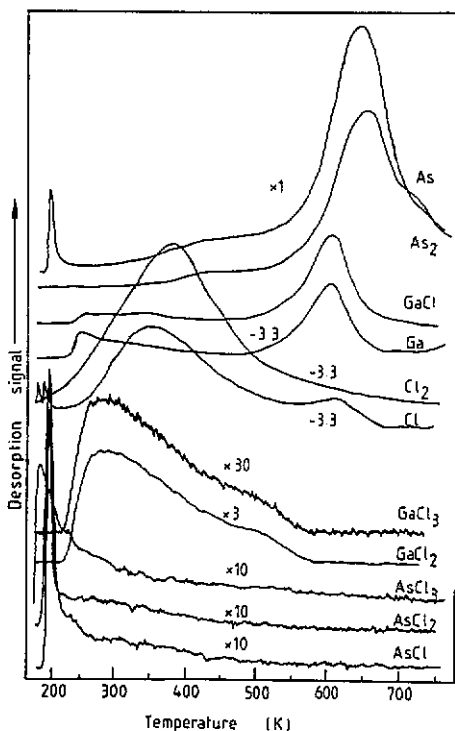


Figure 2. Thermal desorption spectra recorded following exposure of GaAs(100) (4×1) at 175 K to 12 L chlorine.

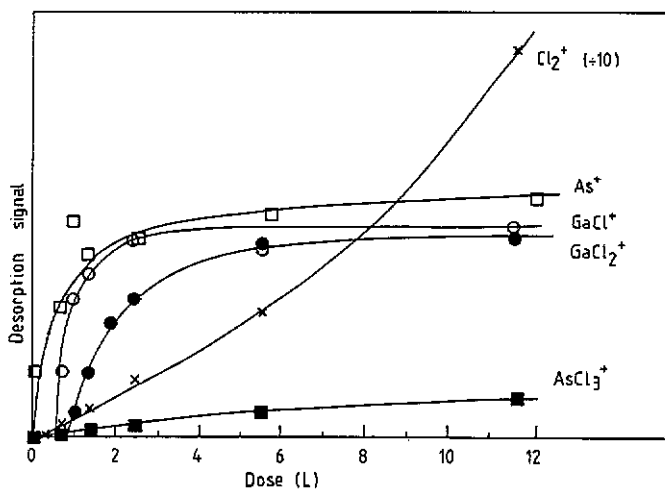


Figure 3. Thermal desorption yields of Cl_2^+ , As^+ , GaCl^+ , GaCl_2^+ , and AsCl_3^+ , corresponding to the desorption of Cl_2 , As_2 , GaCl , GaCl_3 and AsCl_3 respectively, as a function of chlorine exposure at 175 K.

excess GaAs, gallium chlorides and arsenic are the most stable products.

The less thermodynamically favoured product, AsCl_3 , is seen in the thermal desorption spectra following high chlorine exposure. The low desorption temperature

is consistent with the relatively high volatility of AsCl_3 (vapour pressure 10 torr at 23.5°C [6]).

Thermal desorption of Cl_2 is also seen following high chlorine exposure, suggesting associative desorption of Cl_2 competes with AsCl_3 formation on the Cl-saturated surface.

The results suggest the following scheme for the thermal reactions of chlorine on the GaAs(100) (4×1) surface:

(i) At small chlorine exposures, Cl_2 dissociatively adsorbs on the GaAs surface to form chemisorbed Cl. No chemical shifts were seen in the Ga or As XPS signals after chlorine exposure, so the chlorine adsorption site cannot be specified. However, since this initial chemisorbed phase desorbs as GaCl at 600 K, it is possible that initial chlorine chemisorption is on Ga atoms. Following GaCl desorption, the leftover arsenic is probably adsorbed as As_2 , giving rise to the first order As_2 desorption peak at 640 K.

(ii) At slightly larger chlorine exposures a small corrosion phase forms which desorbs as GaCl_3 at 300 K, leaving the chemisorbed phase on the surface.

(iii) Chlorine uptake is very slow at higher chlorine exposure and leads to a higher chlorine concentration near the surface, rather than diffusion into the lattice to form additional gallium chlorides. The extra chlorine desorbs as AsCl_3 and Cl_2 .

4. Implications for etching

The thermal etching of GaAs by Cl_2 has been studied by modulated molecular beam spectroscopy by several authors [7–9]. Hou *et al* [7] and Houle [8] report GaCl, As_2 and As_4 as the major etch products above 600 K, while Balooch *et al* [9] suggest AsCl is the arsenic species desorbing in this temperature region. Below 600 K the etch rate is much slower and AsCl_3 and GaCl_3 are the principal desorbing species [7–9]. Houle suggests gallium and arsenic dichlorides are important additional desorption products [8] at low temperatures. Although caution must be used in comparing adsorption processes at 175 K to continuous etching taking place at high temperature, some insights into thermal etching can be obtained from our results:

(i) GaCl and As_2 are the first thermal desorption products obtained on adsorption of Cl_2 on GaAs at 175 K. Both desorb below 650 K, so the predominance of these species when etching at high temperatures is consistent with our results.

(ii) The activation energy for desorption of GaCl and As_2 are 155 and 170 kJ mol^{-1} respectively (assuming a pre-exponential of 10^{13}). At moderate temperatures the GaCl and As_2 desorption steps would be expected to limit the etch rate, and below 600 K their desorption rate would be very slow.

(iii) GaCl_3 formation occurs easily at surface chlorine concentrations slightly higher than those needed to produce GaCl, and the GaCl_3 desorption energy (75 kJ mol^{-1}) is much lower than for GaCl. This explains why GaCl_3 rather than GaCl desorption is seen at lower etch temperatures.

(iv) At temperatures too low for rapid As_2 desorption a build-up of arsenic on the surface would be expected as GaCl_3 desorbs. We have shown that arsenic can desorb as AsCl_3 given a sufficient surface concentration of chlorine. The rate-limiting step would be the formation of AsCl_3 rather than its desorption, since AsCl_3 has a very low desorption energy ($< 44 \text{ kJ mol}^{-1}$).

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