Halogen etching of group 13–15 (3–5) semiconductors and its relevance to chemical–mechanical polishing. The reactions of dibromine, dichlorine and sodium hypochlorite with gallium arsenide and related materials

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Room-temperature etching of gallium arsenide, gallium antimonide, indium phosphide, indium arsenide and indium antimonide by dibromine or dichlorine has been studied under anhydrous conditions using Raman spectroscopy to identify the primary products and radiotracers, [^{82}Br] or [^{36}Cl], to probe interactions among the species formed. Comparisons are drawn with etching behaviour in solution particularly with sodium hypochlorite towards GaAs for which the reactive species at $\mathrm{pH} < 8.0$ is shown to be Cl_2. Under anhydrous conditions the GaAs surface is passivated rapidly owing to the formation of an involatile liquid layer, believed to be a solution of Ga_2Cl_6 in $AsCl_3$. Above $\mathrm{pH} = 8.0$, where the dominant etchant is believed to be $[OCl]^-$, an active surface, in which considerable reconstruction has occurred, is formed. The etching behaviour has enabled the chemomechanical polishing of 13–15 semiconductors by Br_2 and NaOCl based reagents to be rationalised. In particular, it is shown that the alumina component of a NaOCl-based polishing reagent has a minimal chemical role.

Although halogens and their compounds have been used for the etching of semiconductor materials for many years,[1] it is only relatively recently that significant progress has been made in understanding the fundamental surface processes involved. Molecular beam surface science and theoretical techniques have been applied, particularly to the etching of gallium arsenide by dichlorine.[2–11] Formation of surface Ga—Cl (ref. 2–6, 8–10) and As—Cl (ref. 4,5,8–10) is followed by desorption of $GaCl_n$ ($n = 1$–3), As_2, As_4 and $AsCl_3$ depending on the experimental conditions used.[2,3,5–7] In some cases a Ga—Cl surface layer can passivate the surface to further reaction.[2,11]

In contrast, far less is known regarding the events occurring during solution etching reactions, since much of the available information has resulted from studies of chemical–mechanical polishing[1,12] where the main emphasis has been on determining the nature of the wafer surface produced. To understand fully the nature of the polishing process requires detailed knowledge of the chemical events involved in solution etching and this has been the main reason for undertaking the present study. Attention has been concentrated on dibromine, since its solution in methanol has been used widely for both gallium arsenide[13–15] and indium phosphide,[13,16–19] and on dichlorine, since we have shown previously that aqueous NaOCl, also used as a reagent,[20–22] is superior to Br_2–MeOH for GaAs polishing.[23] The pH-dependent behaviour observed suggested the possibility that the active etchant was $[OCl]^-$ anion or Cl_2 depending on the conditions and the involvement of Cl_2 at low pH has been confirmed in the present work. Primary products from the etching of GaAs and related semiconductor materials have been identified in most cases and evidence for GaAs surface passivation during Cl_2 vapour etching through the formation of an involatile solution of Ga_2Cl_6 in $AsCl_3$ is presented.

α-Alumina is often used as an abrasive in polishing situations to improve stock removal, although it can lead to sub-surface damage.[24] We have investigated the possibility that halogenation of aluminas, a process that is well documented for γ-alumina,[25] may be a factor, for example in delivering reagent Cl_2 or Br_2 to the surface.

Finally, the observations made on these 'massive' etching reactions have enabled the different polishing behaviour of these reagents towards group 13–15 semiconducting materials to be rationalised.

Experimental

The wafers used in this work, GaAs(100), GaSb(111), InP, InAs and InSb, all (100), were commercial samples (MCP Wafer Technology) and were used as received. Sections for individual experiments were cut with a diamond saw.

Radiotracer experiments

***(a)* Preparation of radiolabelled reagents.** [^{36}Cl]-Labelled dichlorine was produced from [^{36}Cl]-labelled aqueous sodium chloride (2.4 cm^3, 60 μCi Amersham) in 35% hydrochloric acid (30 cm^3, Fisons Analytical Grade) by oxidation of an aliquot (2 μCi) using a saturated solution of potassium permanganate. The dichlorine was generated in a round-bottom flask reaction vessel to which a series of traps, cooled to 193 K in dichloromethane/solid carbon dioxide, and a collection vessel, was attached. The first two traps contained solid $KMnO_4$ (*ca.* 5 g) to remove hydrogen chloride and a further two contained small quantities of phosphorus(v) oxide (*ca.* 1 g) to remove moisture. The operation was carried out in dry air at reduced pressure by attachment to a vacuum line. The collection vessel was equipped with high-vacuum PTFE stop-cocks so that it could be isolated from the rest of the apparatus. The Cl_2 liberated was distilled through the traps and collected before degassing at 77 K and was stored over P_2O_5 in a Monel pressure vessel.

[^{36}Cl]-Labelled Cl_2 was also liberated directly from NaOCl solution, by addition of [^{36}Cl]-labelled sodium chloride in HCl (1 cm^3, 2 μCi, Amersham). The NaOCl solution (Spectrosol, BDH, 12% m/m, 40 cm^3) was placed in a reaction vessel equipped with a sealed rubber septum cap and attached to a Pyrex glass vacuum line (10^{-4} Torr). The pressure in the vessel was reduced slowly until the NaOCl solution began to bubble, at which point the vessel was isolated from the vacuum manifold. The [^{36}Cl]-labelled sodium chloride solution in HCl was injected into the vessel *via* the septum cap and the vessel opened to the vacuum manifold, which was isolated from the

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vacuum pump. [^{36}Cl]-Labelled Cl_2 evolved in this way was usually not collected, but used directly in adsorption experiments to confirm Cl_2 evolution from NaOCl at pH <8.

[^{82}Br]-Labelled dibromine was produced from [^{82}Br]-labelled ammonium bromide by reaction with H_2SO_4 *in vacuo*. Neutron irradiations, ^{81}Br (n, γ) ^{82}Br, were carried out in the Scottish Universities Reactor Research Centre, East Kilbride, with a neutron flux of 3.6×10^{12} neutron cm^{-2} s^{-1} for 3 h. The activity of the [^{82}Br]-labelled NH_4Br so produced was *ca.* 100 mCi. Labelled solids were transferred to Glasgow *ca.* 24 h after irradiation to ensure complete decay of short-lived isotopes. The specific activity of the [^{82}Br]-labelled Br_2 was determined by counting a measured aliquot of Br_2 in AnalaR chloroform (1 cm^3).

To prepare [^{82}Br]-labelled dibromine, solid NH_4Br (0.5 g) and [^{82}Br]-labelled NH_4Br (2 mg) were placed in a pressure equilibrated vessel and 98% H_2SO_4 (5 cm^3) was allowed to drip slowly onto the mixture. The vessel was connected to a vacuum system (0.01 Torr) and two storage vessels attached. The [^{82}Br]-labelled dibromine which was liberated, was vacuum distilled into the first storage vessel using liquid nitrogen (77 K) and was then allowed to reach 263 K. The storage vessel was degassed to remove any hydrogen bromide or sulfur dioxide impurities. Dibromine was distilled into the second storage vessel over P_2O_5 and was stored at 77 K.

A similar method was used to produce [^{82}Br]-labelled hydrogen bromide from [^{82}Br]-labelled NH_4Br. Sulfuric acid was not suitable in this case, since it readily oxidises HBr. Syrupy phosphoric acid gave a good yield but its high viscosity was a disadvantage and the mixture required heating to initiate the reaction. Triflic acid, CF_3SO_3H, was the most satisfactory since the reaction was rapid at room temperature.

(*b*) Adsorption/reaction of [^{82}Br]-labelled dibromine and [^{36}Cl]-labelled dichlorine on 13–15 semiconductors. [^{82}Br] Count rates were determined using a sodium iodide scintillation counter with a scaler ratemeter (NE Technology). The usual background and decay corrections were made and radiochemical purity was determined by half-life measurement ($t_{1/2} = 35.3$ h). [^{36}Cl] Count rates were determined using Geiger–Müller detectors (Centronic) with scaler ratemeters (NE Technology). Etching and adsorption experiments using radioactive Cl_2 previously dried over P_2O_5 *in vacuo*, were carried out in a specially designed counting cell which allowed direct monitoring of the reaction.[26] The counting cell contained two GM tubes and was an integral part of a Pyrex glass vacuum line.

Gas + solid counts were recorded from one GM tube and gas only counts recorded from the other, allowing independent determination of count rates from the solid and the vapour. All counts were corrected for background radiation and were intercalibrated where two Geiger Müller tubes were used.

[^{36}Cl]-Labelled Cl_2 was used to determine the adsorption of Cl_2 onto a GaAs wafer surface and to follow the outcome of the adsorption process. Uptake experiments were undertaken in the counting vessel described above. The apparatus was modified to include a 'reaction boat' that contained any liquid product from the reaction. This was necessary to avoid influencing the gas-only count with stray counts from liquid product. A section of GaAs wafer (0.3371 g, 2.33 mmol) was cut and placed in the reaction boat under one GM tube. Initially, a small pressure (10 Torr) was added over the wafer; aliquots of ^{36}ClCl were added to increase the pressure to 30, 45 and 50 Torr subsequently at *ca.* 30 min intervals. Counts were accumulated over 30 min, to ensure statistical reliability. For pressures of 50 Torr and above, the total counts accumulated was at least 12500, before correction for background.

This procedure resulted in progressive increases in the [^{36}Cl] count originating from the surface of the wafer with concomitant decrease in count from ^{36}ClCl in the gas phase. When no further increase in surface count could be detected, volatile material and weakly adsorbed species were removed by pumping. The count from the surface however was essentially unaffected, indicating that any products formed were involatile.

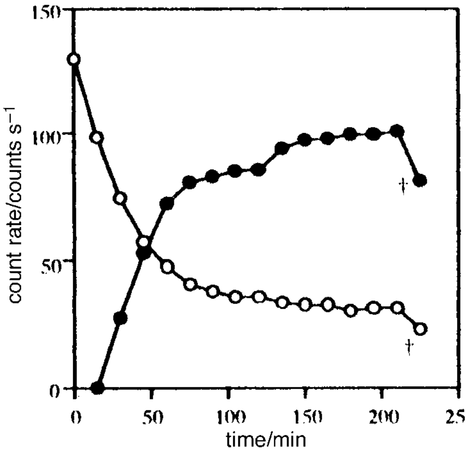

Fig. 1 [^{36}Cl] Count rates *vs* time for GaAs + ^{36}ClCl; † = count rates after removal of volatile material; (○) gas only, (●) solid only

This experiment was repeated using [^{36}Cl]-labelled Cl_2 evolved from NaOCl solution. Gas was added to build up to a pressure of *ca.* 400 Torr (8.0 mmol) in the vacuum manifold before opening to the counting cell, containing a GaAs wafer section (0.3697 g, 2.5 mmol). Counts were recorded from the gas phase and from the gas + solid, for counting periods of 300 s at intervals of 15 min.

[^{36}Cl] Radioactivity was detected from the surface after *ca.* 20 min; the count rate increased thereafter with a parallel decrease in the [^{36}Cl] count rate for the gas phase. Removal of volatile material after 200 min reduced the gas phase count rate to background but had a very small effect on the count rate from the GaAs surface. The observed behaviour is summarised in Fig. 1.

[^{82}Br]-Labelled Br_2 was used to determine the uptake of dibromine by InP, InSb, InAs, and GaSb wafers at room temperature, using the method developed for GaAs.[23] A Pyrex counting vessel (40 cm^3) with a central stopcock, allowing isolation of one limb from the other, was degassed after inserting a wafer segment (1 cm^2). [^{82}Br]-Labelled Br_2 was introduced into one limb and counted, before opening the central stopcock and measuring uptake on the wafer section in the other limb. Both limbs were counted alternately to determine changes in solid and gas phase count rates with time. After uptake appeared complete, all volatile and weakly adsorbed species were removed by pumping at room temperature and [^{82}Br]-activity retained on the wafer was determined.

Exposure to [^{82}Br]-labelled Br_2 at room temperature led to the immediate detection of [^{82}Br] activity from the wafer. Thereafter there was a slow, continuous increase in [^{82}Br] count rate from the solid, with a concomitant decrease in the count rate for the vapour. This type of behaviour was illustrated in previous work from the GaAs system.[23] After 2–3 h exposure and the removal of all volatile and weakly adsorbed materials by pumping, the count rate from GaAs decreased to 58% of its maximum value, consistent with the reaction reported above. The behaviour of InAs towards^{82}BrBr was similar but labelled volatile products were not observed from InP, InSb or GaSb. The results are summarised in Table 1. In all cases the radioactive species formed on the surface were removed entirely by washing the products with acetonitrile under anhydrous conditions.

(*c*) Adsorption of [^{82}Br]-labelled dibromine and [^{36}Cl]-labelled dichlorine onto α-alumina and γ-alumina. [^{82}Br]-Labelled Br_2 uptakes were determined using the procedure

Table 1 Interaction between ^{82}BrBr and group 13–15 wafers at room temperature

wafer	Br uptake/ mg atom mmol^{-1}	[^{82}Br] activity removed on pumping (%)	volatile product
GaAs	—[a]	42	$AsBr_3$
InAs	0.52	53	$AsBr_3$
InP	0.15	0	none
InSb	4.3	0	none
GaSb	—[a]	0	none

[a]Uptake not determined.

Table 2 Dip-etching of group 13–15 wafers by Br_2 in MeOH at room temperature for 15 min

wafer	[Br_2]/mol dm^{-3}	mass decrease (%)
GaSb	0.10	0.25
	0.23	2.8
	0.37	17.3
InP	0.20	14.1
	0.25	10.4
	0.45	17.6
InAs	0.19	3.0
	0.25	13.1
	0.41	23.2
InSb	0.20	10.1
	0.25	4.4
	0.53	11.9

described in (*b*) and alumina samples that had been calcined *in vacuo* at *ca.* 500 K for 3 h. [^{36}Cl]-Labelled Cl_2 uptake experiments used labelled dichlorine evolved from NaOCl solution, part (*a*), and a procedure identical to that employed to measure uptake on GaAs, replacing the wafer segment with α-alumina (1.09 g) or γ-alumina (0.64 g).

Addition of either α- or γ-alumina (0.5 g) to aqueous NaOCl (25 cm^3) at pH = 8.5 led to small but measurable increases in its decomposition as determined by monitoring change in absorbance of 100 μl aliquots at $\lambda = 292$ nm,[27] using a P.E. Lambda 9 instrument. γ-Alumina was slightly more effective than α-alumina. More significantly, there was no evidence for adsorption of ^{36}ClCl, generated from aqueous NaO^{36}Cl decomposition, on α-alumina and its interaction with γ-alumina was small. Similarly ^{82}BrBr did not interact with α-alumina at room temperature but exposure of γ-alumina to ^{82}BrBr led to a gradual increase in the count rate determined from the solid over 120 h. This corresponded to an uptake of Br_2 by γ-alumina of 8.5 mmol (g γ-alumina)$^{-1}$. From those observations it is concluded that the effects of refractory oxides on polishing were purely mechanical.

Etching experiments

(*a*) In solution. Etchant solutions were freshly prepared prior to each experiment from analytical grade materials. Decomposition data for dibromine in methanol and sodium hypochlorite at room temperature have been reported previously.[23] Mixtures of Br_2–MeOH (0.2–0.45 mol dm^{-3}) were prepared from Br_2 and MeOH (AnalaR, BDH) and the concentration determined by iodometric titration using 0.100 mol dm^{-3} thiosulfate (Volucon, M&B). Aqueous NaOCl (14% m/m, BDH) was brought to the desired pH (13, 8.5 or 7) by dropwise addition of glacial acetic acid (Pronalys, M&B). Provided solutions were prepared immediately prior to etching, no significant change in pH occurred over the 0.5 h duration of an experiment, as shown by control experiments. The acidities of solutions were determined using a standard pH electrode (Russell pH Ltd.) with an EIL 7050 meter.

Material lost to etch solutions was determined by mass change and/or determination of soluble product by atomic absorption spectroscopy. A P.E. 1100B spectrophotometer was used in conjunction with an MHS-10 hydride generator (to detect soluble As or Sb). Indium was detected using the flame method. No attempt was made to determine Ga or P using AAS since their sensitivities to detection are low. Spectrosol standard solutions, matrix-matched to the analytes, were employed throughout and sample solutions required no pretreatment other than dilution. Replicate analyses (minimum two) were performed in all cases.

Wafer sections (2.5 cm × 2.0 cm GaAs, 1.0 cm^2 for all other materials) of GaAs, InP, InSb, InAs, all (100) and GaSb (111) were etched in solutions which were stirred continuously. The wafer sections were supported in a Pyrex glass holder inside a Pyrex reaction vessel. Etching of GaAs in NaOCl (pH 12.9 ± 0.1, 60 cm^3) employed etch periods ranging from 1 to 3 h to examine differences in surface product density/thickness. Other materials were etched in solutions (50 cm^3) of Br_2–MeOH for 15 min, or NaOCl for 30 min.

Apart from GaAs, none of these materials appeared to be etched by NaOCl at high pH. Mild etching (<0.2% mass decreases after 0.5 h) was observed on the indium compounds in the pH range 6–8 but there was no observable reaction with GaSb. In contrast, room-temperature etching by Br_2 in methanol was observed in all cases. Typical results, comparable to those reported previously for GaAs under identical conditions,[23] are given in Table 2 and the behaviour was confirmed in many cases by AAS analysis.

(*b*) Under anhydrous conditions. These experiments were undertaken on all five materials using dried (P_2O_5) dibromine and dichlorine. These experiments used flamed out Pyrex vacuum vessels (*ca.* 100 cm^3) incorporating side arms to allow isolation of one product from the other by vacuum distillation; vessels were attached to a Pyrex vacuum line (10^{-4} Torr). NMR spectra of the InP products were obtained using a Bruker WP200 instrument. Infrared spectra of the products were recorded using P.E. 983 and PC16 FTIR spectrometers, samples being contained between silicon plates. Raman spectra were determined using a Spex Ramalog spectrometer (514.6 nm excitation), from reaction products sealed *in vacuo* into thin glass capillaries. For most reactions Raman spectroscopy was more useful, particularly where the products could be separated *in vacuo*. Generally, sufficient bands were observed to make a positive identification (Table 3). Halogen vapours were normally used as reactants but when reactions were slow at room temperature, liquid X_2, X = Cl or Br, was used to obtain macroscopic samples for investigation.

Reactions between Br_2 vapour and the wafer samples were generally rapid and product identification unambiguous, Table 3. Additional characterization for the single product obtained from InP + Br_2 was provided by its analysis (Found: Br, 81.1; In, 14.35; P, 4.0: Br_8InP requires Br, 81.4; In, 14.6; P, 3.95%) and NMR spectrum. The ^{31}P NMR spectrum in CD_3CN consisted of two major singlets, δ 235 (br) and −94 (85% H_3PO_4). The former signal sharpened on cooling and was assigned to exchange-broadened PBr_3 (δ 222–227[28]). The higher field signal was tentatively assigned to the $[PBr_4]^+$ cation. A colourless solid isolated from the reaction between PBr_3, $InBr_3$ and Br_2 (1 : 1 : 1 mole ratio) resulted in a very similar Raman spectrum and a ^{31}P NMR singlet δ −99. The ^{31}P chemical shift value for $[PBr_4]^+$ has been reported to be at δ −85 in oleum [29] and −76.5 in liquid Br_2.[30]

The exothermic reaction between GaSb and Cl_2 vapour was complete within 1 h and produced Ga_2Cl_6 and $SbCl_5$, Table 3, which were easily separated. In contrast Cl_2, reacted with GaAs overnight, gave a yellow viscous liquid. If any of the wafer remained this liquid was difficult to separate into individual components by fractional distillation *in vacuo* but in its

Table 3 Species identified by Raman spectroscopy[a] from reactions of group 13–15 wafers with Br_2 or Cl_2

reaction	product	mp[b]/K	observed Raman bands/cm^{-1}	ref.
$GaAs+Br_2$	Ga_2Br_6		340, 288, 240, 200, 158, 119	*c*
$GaSb+Br_2$				
$GaAs+Br_2$	$AsBr_3$	306	285, 269, 137, 102	*d*
$InAs+Br_2$				
$GaSb+Br_2$	$SbBr_3$	369	248, 236, 107, 85	*e*
$InSb+Br_2$				
$InP+Br_2$	$[PBr_4][InBr_4]$		504, 495, 258, 245, 196, 152	*f, g*
$InAs+Br_2$	$InBr_3$		172, 77	*h*
$InSb+Br_2$				
$GaSb+Cl_2$	Ga_2Cl_6		404, 328, 240, 214, 164, 146, 112	*i*
$GaAs+Cl_2$			(IR: ν_{max} 608m, 468s, 395s, 304m)	
$GaSb+Cl_2$	$SbCl_5$		353, 308, 180, 157	*j*
$InAs+Cl_2$	$InCl_3$		406, 359, 116	*k*
$InAs+Cl_2$	$AsCl_3$		414(sh), 406, 370 (br), 191, 164(sh),156	*l*
$GaAs+Cl_2$			(IR: ν_{max} 412s, 371s)	

[a] Additionally IR spectra for the products from $GaAs+Cl_2$. [b] In good agreement with data from *Handbook of Chemistry and Physics*, 76th edn., C.R.C. Press Inc., Baton Rouge, FL. [c] I. R. Beattie, T. Gilson and G. A. Ozin, *J. Chem. Soc. A*, 1968, 813. [d] F. A. Miller and W. K. Baer, *Spectrochim. Acta*, 1961, **17**, 112. [e] J. C. Evans, *J. Mol. Spectrosc.*, 1960, **4**, 435. [f] $[PBr_4]^+$, W. Gabes and H. Gerding, *Rec. Trav. Chim. Pays-Bas*, 1971, **90**, 157. [g] $[InBr_4]^-$, L. A. Woodward and P. T. Bill, *J. Chem. Soc.*, 1955, 1699. [h] N. N. Greenwood, D. J. Prince and B. P. Straughan, *J. Chem. Soc. A*, 1968, 1694; I. R. Beattie and J. R. Horder, *J. Chem. Soc. A*, 1969, 2655. [i] A. Balls, A. J. Downs, N. N. Greenwood and B. P. Straughan, *Trans. Faraday Soc.*, 1966, **62**, 521; I. R. Beattie, T. Gilson and P. Cocking, 1967, 702; P. Klaeboe, E. Rytter and C. E. Sjoegren, *J. Mol. Struct.*, 1984, **113**, 213; C. E. Sjoegren, P. Klaeboe and E. Rytter, *Spectrochim. Acta, Part A,* 1984, **40**, 457. The only ambiguity concerns the observation in the present work of an IR band, ν_{max} 608 cm^{-1}; this could be a combination band but its origin from trace hydrolysis cannot be discounted. [j] I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett and G. A. Ozin, *J. Chem. Soc. A,* 1967, 712; J. A. Creighton and J. H. S. Green, *J. Chem. Soc. A,* 1968, 808. [k] Spectrum resembles that reported for monomeric $InCl_3$, I. R. Beattie, H. E. Blaydon, S. M. Hall, S. N. Jenny and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1976, 666, rather than that of solid $InCl_3$, ref. *h*. [l] P. W. Davis and R. A. Oetjen, *J. Mol. Spectrosc.*, 1958, **2**, 253; B. Lunelli, G. Cazzoli and F. Lattanzi, *J. Mol. Spectrosc.*, 1983, **100**, 174.

absence, substantial separation into its components, a colourless liquid identified (Table 3) as $AsCl_3$ from its Raman and IR spectra and a colourless crystalline solid identified from its IR spectrum as Ga_2Cl_6, was possible. On this basis the primary product from the reaction was formulated as a solution of Ga_2Cl_6 in $AsCl_3$, in which the volatility of the latter is decreased significantly as a result of the intermolecular interaction. What appears to be a similar situation, has been reported previously for gallium(III) chloride in PCl_3.[31]

Less definitive results were obtained from reactions of InP, InAs and InSb with Cl_2 even using liquid Cl_2. The InP reaction appeared to be similar to the Br_2 analogue but the colourless solid isolated (Found Cl, 58.4; In, 33.5; P 6.1%) was not pure since Cl_8InP requires Cl, 66.1, In, 26.7; P, 7.2%. Its ^{31}P NMR spectrum in CD_3CN comprised two singlets, δ 88.2 (br), assigned to $[PCl_4]^+$ by comparison with $[PCl_4]^+$ in oleum (δ 88),[29] and δ 5.1, possibly due to $[PO_4]^{3-}$. No Raman spectrum could be obtained. Products from Cl_2 and InAs were $AsCl_3$ and a solid that appeared from its Raman spectrum to be molecular $InCl_3$, Table 3. No products were isolated from liquid Cl_2 and InSb, although there was evidence, on hydrolysis, for a surface Cl-containing layer.

Surface analyses of GaAs etched by aqueous NaOCl at high pH

Wafers etched in NaOCl at pH 12.9 decreased in mass ranging from 24.9% after 1.0 h to 60.4% after 3.0 h. A black glassy, non-conducting layer was formed, the other product being NaCl. The layer was examined using several methods, sample preparation being limited to rinsing in de-ionised water and cleaning the surface with 1,1,1-trichloroethane (Genklene, ICI) to remove most of the surface organic contamination. FTIR spectroscopy was carried out at Paisley University Chemistry Department on a BIORAD FTS 40 infrared spectrometer. Spectra were recorded in the range 4000–400 cm^{-1} and 60 scans were used to analyse any given point on the wafer surface. Auger, ESCA and LIMA/SIMS analyses were carried out at Pilkington plc, Group Analytical Services. Auger and ESCA analyses used Al-Kα X-ray excitation (1486.6 eV) on a Kratos XM 800 instrument. Auger work was undertaken at a take-off angle of 90°. The base operating pressure, after loading samples and pumping down, was *ca.* 9×10^{-10} Torr, previous to Ar^+ sputter etching (4 kV). The proportions of elements detected by Auger and ESCA were quantified using standard Scofield sensitivity factors.[32]

SEM examination indicated the formation of a distinct product layer with numerous etch pits, Fig. 2(*a*). XPS and Auger analyses indicated surface contamination by C which was easily removed by mild (2 min) Ar^+ bombardment. Species identified were elemental As, Ga and arsenic(III) oxide but gallium(III) oxide was not detected. Atomic ratios determined from the Auger spectra prior to Ar^+ bombardment are given in Table 4.

Auger depth profiling through the surface layer on the section etched for 3.0 h indicated a rapid decrease in carbon and the presence of a discontinuous oxide layer, thickness 300–600 Å. LIMA/SIMS analyses indicated a high proportion of gallium oxide on the surface. Below this was an amorphous GaAs layer and finally crystalline GaAs. FTIR spectroscopy indicated very few surface hydroxy groups except directly above the etch pits, where a degree of surface hydration was apparent.

Examination by SEM of a GaAs wafer surface that had been etched by Cl_2 at room temperature for 18 h revealed a very different situation. The striations visible [Fig. 2(*b*)] appeared to be the result of the inhibition of reaction between Cl_2 and GaAs due to the formation of the solution of Ga_2Cl_6 in $AsCl_3$ described above.

Results and Discussion

Although dibromine is, from a thermodynamic standpoint, an inferior oxidizing agent than dichlorine, its reactions with gallium arsenide, gallium antimonide, indium phosphide, indium arsenide and indium antimonide are more rapid than those that involve Cl_2. The products, mixtures of binary bromides of the elements in their +III oxidation state, are those expected, Table 3; the formation of $[PBr_4][InBr_4]$ from the InP reaction can be rationalised on the basis of a

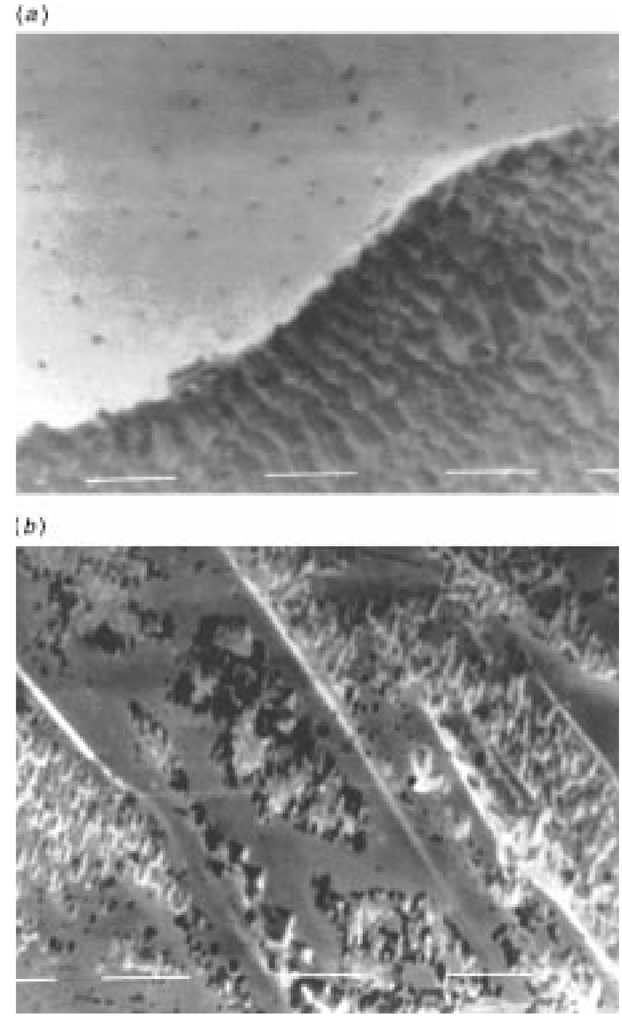

Fig. 2 Scanning electron micrographs of GaAs after (*a*) etching in aqueous NaOCl, pH = 13 and (*b*) etching with Cl_2 at room temperature for 18 h; scale bar = 10 mm

Table 4 Auger analysis, prior to surface cleaning, of GaAs wafer sections after etching with aqueous NaOCl at pH = 13

	atomic ratio (atom%)					
	Ga	As	As^{III} oxide	O	C	Na
1.0	4.5	3.1	1.3	25.3	65.8	0
3.0	23.1	6.2	8.1	34.2	26.7	1.7

[a] Corresponding mass losses were 24.9 and 60.4%, respectively.

subsequent reaction of Br_2 with PBr_3 and $InBr_3$. The results of the [^{82}Br] radiotracer experiments, Table 1, confirm the expected adsorption of ^{82}BrBr as the primary event in the reaction sequence, and confirm, in contrast to the corresponding chlorine reaction described below, the lack of any significant interaction between Ga_2Br_6 and $AsBr_3$ following the reaction between GaAs and Br_2. The [^{82}Br] experiments demonstrated also that the involatile Br-containing products are soluble in polar organic solvents such as acetonitrile. The substantial etching that was observed using Br_2 in methanol is therefore readily understood and is the main reason for the widespread use of this reagent.[1,13–19] However the quality of the surface finishes obtained from wafers that have been chemo-mechanically polished using the Br_2, MeOH reagent is not high and it is considered that this is the result of the absence of any mechanism for chemical control of the etching reaction that is an integral part of the polishing process.

Etching of 13–15 wafers by Cl_2 under anhydrous conditions follows a similar pattern to the Br_2 reactions, oxidation of GaSb to Sb^V being a reflection of the greater oxidizing power of Cl_2 compared with Br_2, Table 3. The formation of Ga_2Cl_6 and $AsCl_3$ would have been expected from previous surface science studies of the GaAs, Cl_2 system,[2–10] but the interaction between the two products, clearly indicated by the [^{36}Cl] radiotracer experiments, *cf.* Fig. 1, and the appearance of the wafer surface when examined by SEM, Fig. 2(*b*), after extensive treatment with Cl_2, could not have been predicted. These observations, described in detail in the Experimental section, illustrate the effect which the structures of the etching products have on the outcome of an etching reaction. Thus etching of GaAs by Br_2 is rapid due to the absence of any interaction between Ga_2Br_6 and $AsBr_3$ (Table 1) whereas it is slow by Cl_2 due to an, albeit weak, interaction between Ga_2Cl_6 and $AsCl_3$ (Fig. 1). Etching of the indium-containing wafers by Cl_2 is also slow and it is suggested tentatively that this may be the result of the layer lattice structure of solid $InCl_3$.[33] Unfortunately, the Raman data obtained here (Table 3) provide no definitive information.

There are two important conclusions to be drawn from a comparison of the results obtained from the etching of GaAs by anhydrous Cl_2 or by aqueous NaOCl. First, although we have reported that etching of GaAs by aqueous NaOCl was negligible below pH 8,[23] the [^{36}Cl] experiment using ^{36}ClCl generated from aqueous NaOCl *in situ* (Fig. 1) established that reaction did occur and the identical behaviour to that observed when anhydrous ^{36}ClCl was used directly, indicates that the active etching species is Cl_2. The superior quality of the GaAs surface finish achieved by chemical–mechanical polishing using aqueous NaOCl at pH 8.0–8.5 compared with Br_2 in MeOH[23] is considered to be the result of the kinetic control that is possible. There are four important elements in the control process, the rate at which the active etchant Cl_2 is generated, the interaction between the primary products $AsCl_3$ and Ga_2Cl_6, the rapid hydrolysis of $AsCl_3$, Ga_2Cl_6 to give a mixture of oxo-species and the controlled removal of the latter from the surface by mechanical wiping.

The second conclusion is that the GaAs surfaces produced from etching with NaOCl at pH 13 or with anhydrous Cl_2 are very different as shown by SEM, Fig. 2. At high pH the active etchant appears to be the $[OCl]^-$ anion and the considerable degree of surface reconstruction observed following the reaction between GaAs and $[OCl]^-$ indicates a situation where kinetic control of the reactions is difficult. The surface analyses, Table 4, are generally consistent with previous work,[20,22] although in the present case, in contrast with one previous report,[22] the Na content was very small. Although polishing of GaAs is more rapid at pH = 13 than at 8.0–8.5, the changes in the surface that occur make it unsuitable for most applications.

The extent of reactions between NaOCl at low pH and other 13–15 materials is minimal and this is surprising in the case of GaSb in view of its behaviour towards Cl_2. The different behaviour of GaSb towards Cl_2, where reaction is rapid (Table 3) compared with aqueous NaOCl is possibly due to the rapid hydrolysis of $SbCl_5$ to give Sb_2O_5 which appears to be removed from the surface only with difficulty.

In conclusion, the observations made in this paper provide an experimental basis for rationalising the difference between the behaviour of Br_2, MeOH and aqueous NaOCl as reagents for chemical–mechanical polishing of GaAs and other 13–15 compound semiconducting materials. The Br_2, MeOH reagent can be used for all materials but since interactions among the products are minimal and hydrolyses are unimportant, there is no mechanism to control product removal and so control the nature of the surface produced. It has been suggested that the formation of relatively insoluble oxidic species when silica and lithium niobate wafers are chemomechanically polished using hydrogen difluoride modified ceria and alkaline silica sol respectively is one reason for the rapid polishing of these materials without loss of surface finish quality.[34] The $LiNbO_3$ case in which $LiNbOF_4$, formed as a primary etching product, undergoes rapid hydrolysis to give Nb_2O_5,[34b] is similar to the proposal made here for GaAs polishing by NaOCl at low pH. The disadvantage of NaOCl as a reagent however is that the compounds formed as reaction intermediates or products may be too efficient in passivating the surface and thus prevent further reaction.

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