

An investigation of the Ar⁺ ion-enhanced reaction of CCl₄ on Si(1 0 0) by secondary ion mass spectrometry

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The Ar⁺ ion-enhanced reaction of carbon tetrachloride (CCl₄) on Si(1 0 0) at room temperature is investigated at primary ion energies of 2 and 9 keV using the secondary ion mass spectrometry (SIMS) technique. Static SIMS shows that CCl₄ reacts with Si at room temperature. This surface reaction is enhanced by simultaneous sputtering with an Ar⁺ ion beam, the reaction rate being higher at 9 keV than at 2 keV. Possible products of surface reaction are discussed.

1. Introduction

The fundamental mechanisms in plasma and ion-enhanced etching have been the subject of intensive research [1]. In particular, spatially selective ion-beam etching is becoming an important method for mask restructuring in photolithography and in integrated circuit diagnosis. Higher etch rates have been observed in ion-enhanced etching, where reactive gas molecules such as chlorine are introduced simultaneously with ion beam irradiation [2]. This is to be expected, since the energy deposited by the ion beam enhances the chemical reaction between the reactive gas molecules and the substrate atoms, forming volatile products.

The CCl₄-Si adsorbate-substrate system is chosen as our model system since it has been previously studied by the surface-sensitive techniques of X-ray photoelectron spectroscopy and thermal desorption spectrometry [3]. In the absence of an ion beam, initial CCl₄ adsorption is dissociative at temperatures as low as 175 K with silicon chlorides (SiCl_x, $x \leq 4$) being the only observed desorption products above 300 K. In this study, we investigate the surface reactions of Ar⁺ ion-enhanced etching of Si with CCl₄ as a function of CCl₄ partial pressure at two primary ion energies. The ion-energy dependence of the etching mechanism is examined by monitoring the secondary ion species formed.

2. Experimental procedure

Experiments were conducted in a VG SIMSLAB with a base pressure after system bake-out of $\sim 2 \times 10^{-10}$ mbar. Such an ultra-high vacuum (UHV) environment enables the starting surface studied to be cleaned to $< 1\%$ coverage of surface contaminants. Furthermore, surface reactions at low gas exposures can be monitored reproducibly. Fig. 1 shows the experimental conditions involving the *in situ* analysis of

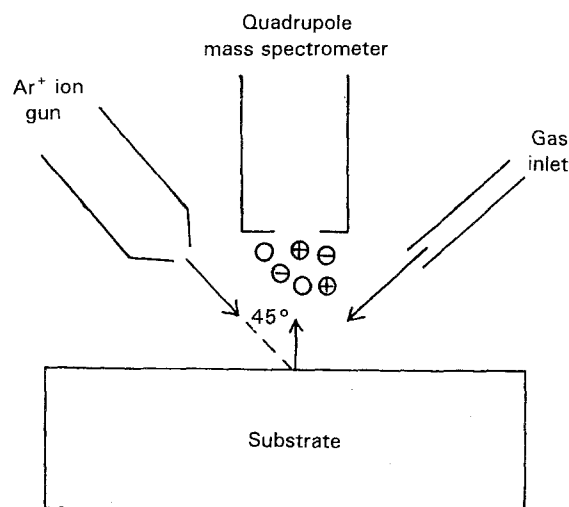


Figure 1 Schematic diagram of experimental conditions used, showing the *in situ* analysis of reaction products formed under dynamic dosing of CCl₄ and simultaneous Ar⁺ sputtering.

reaction products formed when the Si(1 0 0) surface is exposed to a flux of CCl₄ molecules. The surface etching reaction is enhanced by the simultaneous bombardment with an Ar⁺ ion beam, which also results in the emission of ions (positive and negative) and neutrals. In this study, we use secondary ion mass spectrometry (SIMS) to study the positive and negative secondary ions, the intensity and distribution of which are determined by the formation and sputter rate of the species. At each condition of ion beam energy and CCl₄ partial pressure, a steady state is reached with respect to the formation and removal of the respective secondary ions.

The Si(1 0 0) (B-doped, 0.04 p.p.m) surface at room temperature was sputtered using mass-filtered 2 or 9 keV Ar⁺ ions from a VG DP50B duoplasmatron ion gun. Beam currents of 52.5 and 5.0 nA were used at 2 and 9 keV, respectively, corresponding to a constant

ion current density of $0.82 \mu\text{A cm}^{-2}$. The secondary ions emitted were detected using a VG M12-12 quadrupole mass spectrometer (QMS), which was set up to give unit mass resolution at $< 10\%$ valley over the mass range used. The sample bias was adjusted so that the kinetic energy peak (5–10 eV) of the secondary ions was selected by the energy pre-filter of the QMS. Since cluster ions have a narrower kinetic energy profile and the position of the kinetic energy maximum does not change much for Si cluster ions [4], the signal was maximized at higher mass cluster ions.

Prior to each experiment, the surface was cleaned by sputtering with Ar^+ ions and monitoring the SIMS yields of Si ion species. The Si surface was judged clean only when the SiO^+ yield fell to below 0.1% of the Si^+ yield in the positive SIMS spectra. CCl_4 vapour (research grade, $\geq 99.9\%$ purity) was introduced via a leak valve at various partial pressures and the steady-state secondary ion intensities were recorded. Fig. 2 shows a typical experimental run where the intensities of secondary ions with ten different m/z values were recorded (dwell time = 10 s) at increasing partial pressures of CCl_4 . Care was taken to ensure that a steady state was reached before readings were taken, and the average of at least three consistent readings was used to minimize error.

A few experiments were conducted under static SIMS conditions in order to determine the surface species whilst minimizing ion-beam damage. An Ar^+ ion beam at 2 keV, 1 nA cm^{-2} was used here so that the total dose during the acquisition of a spectrum was $< 5 \times 10^{12} \text{ ions cm}^{-2}$, the generally accepted limit for static SIMS [5].

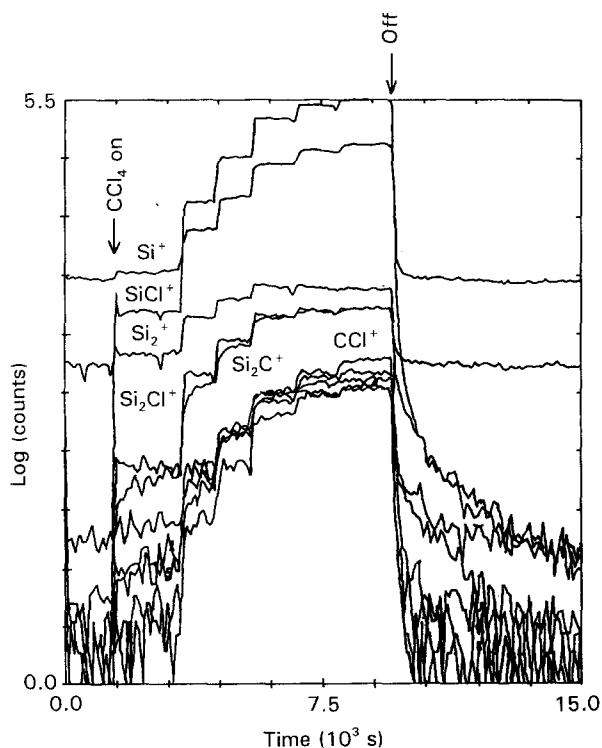


Figure 2 Typical experimental run at 9 kV, showing the secondary ion intensities of ten different ion species at increasing partial pressures of CCl_4 . The steady state was attained before the CCl_4 partial pressure was increased, giving rise to the stepped profile.

3. Results

Fig. 3a and b shows the positive secondary ion yields when the Si surface was exposed to increasing partial pressures of CCl_4 and simultaneously sputtered with 2 keV, 52.5 nA and 9 keV, 5.0 nA Ar^+ ions, respectively. Before CCl_4 was introduced, the main positive ion species detected were Si^+ and Si_2^+ due to sputtering of the clean Si substrate. If the counts for Si^+ are normalized for the same beam current, the intensity at 9 keV relative to that at 2 keV (~ 10) is in agreement with the result obtained by Wittmaack [4]. The intensities of chlorine-containing ion species are low and are due to the adsorption of residual CCl_4 from previous experimental runs, the estimated partial

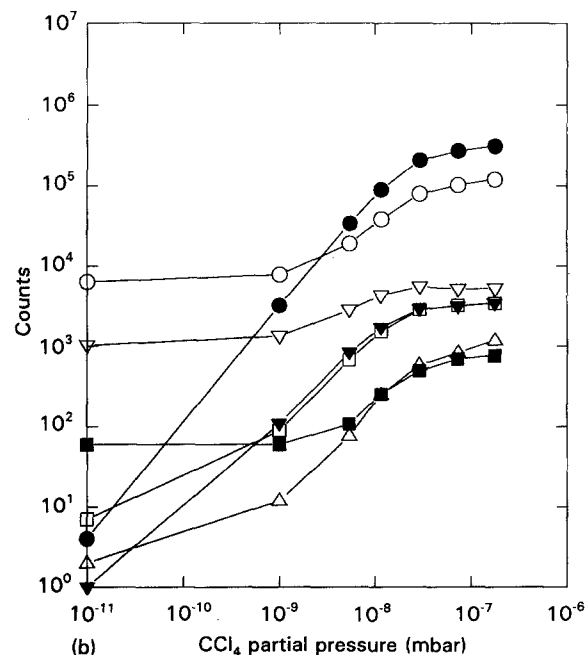
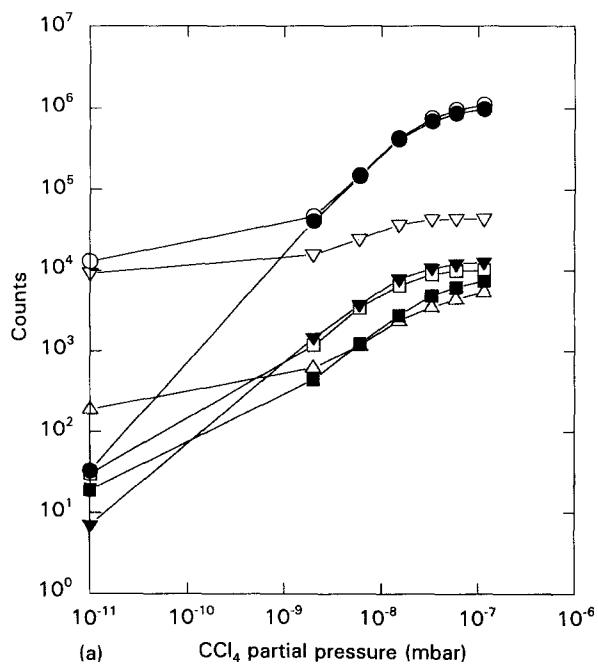


Figure 3 Positive secondary ion yields upon exposure of Si to increasing CCl_4 partial pressures under simultaneous (a) 2 kV, 52.5 nA and (b) 9 kV, 5.0 nA Ar^+ sputtering. (\circ) Si^+ , (\bullet) SiCl^+ , (∇) Si_2^+ , (\triangledown) Si_2Cl^+ , (\square) Si_2C^+ , (\blacksquare) SiC^+ , (\triangle) CCl^+ .

pressure being $\leq 10^{-11}$ mbar (since CCl_4 is not pumped away completely overnight).

Upon exposure to CCl_4 , many Cl- and C-containing species were detected with intensities which increased with increasing partial pressures of CCl_4 . In particular, many species contain both Si and Cl, suggesting that a surface chemical reaction has occurred. The most intense product ion is SiCl^+ , which has a count similar to that of Si^+ at 2 keV but greater than that of Si^+ at 9 keV above 10^{-9} mbar exposure. The intensities of the product ions begin to saturate above 10^{-7} mbar, indicating a surface coverage-dependent sticking probability for the impinging CCl_4 molecules. The Si_2^+ yield does not increase as much and saturates at lower CCl_4 pressures. This phenomenon has been

observed for Si exposed to O_2 [6] and is due to the decreasing probability of Si_2^+ formation with higher CCl_4 coverage. Other less intense species monitored but not shown in Fig. 3 are SiCl_2^+ , SiCCl^+ and Si_2CCl^+ [7].

Fig. 4a and b show the corresponding negative secondary ion yields when the Si surface was exposed to increasing partial pressures of CCl_4 and simultaneously sputtered with 2 keV, 52.5 nA and 9 keV, 5.0 nA Ar^+ ion beams, respectively. Since the transmission for our QMS is smaller for negative ions, the overall counts are observed to be significantly lower than the positive ion yields. Before Si was exposed to CCl_4 , the main secondary ion species observed are Cl^- and Si^- . Although the residual CCl_4 partial pressure was estimated to be $\leq 10^{-11}$ mbar between each day's experiments and the surface coverage of Cl-containing species to be $< 1\%$, the relatively large Cl^- signal is due to the higher electron affinity of Cl. This is confirmed by the three orders of magnitude increase in Cl^- counts when 2×10^{-10} mbar CCl_4 was admitted (Fig. 4a). Whilst the Si^- counts remain fairly constant, the intensities of the other product ions increase with increasing CCl_4 partial pressure, saturating at lower pressures at 2 keV than at 9 keV. Other less intense species monitored but not shown in Fig. 4 are SiC^- , SiCCl^- , SiCCl_2^- , CCl_2^- , C_2Cl^- , Si_2^- , Si_2Cl^- and SiCl_3^- [7].

A few experiments were also conducted under static SIMS conditions (2 keV, 1 nA cm^{-2}) to ascertain the nature of the surface species when ion beam effects are minimized. It was found that after a saturation dose of CCl_4 at room temperature, the SiCl^+ and SiCl^- yields were observed to increase although the intensities of other product ions were below the detection limit of the mass spectrometer. This indicates that CCl_4 does indeed react with Si at room temperature in the absence of ion-beam effects, although the surface coverage of the reaction products is small.

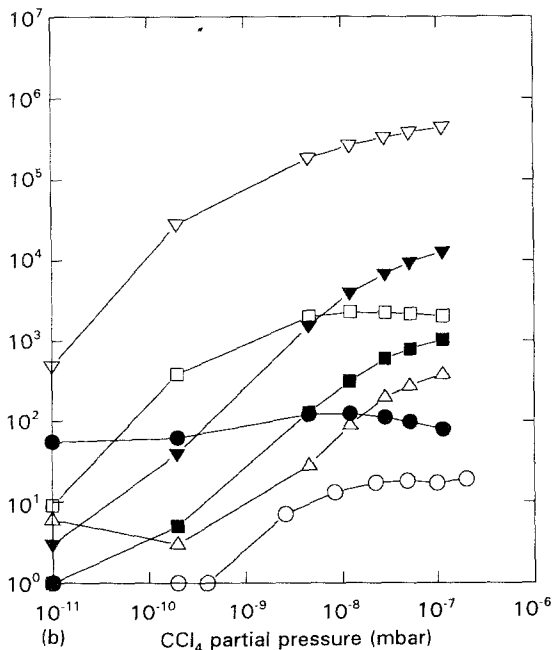
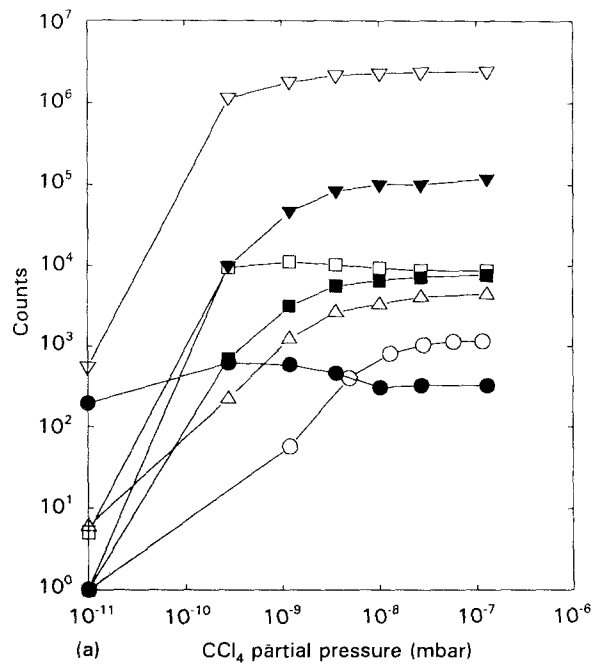


Figure 4 Negative secondary ion yields upon exposure of Si to increasing CCl_4 partial pressures under simultaneous (a) 2 keV, 52.5 nA and (b) 9 keV, 5.0 nA Ar^+ sputtering. (∇) Cl^- (\blacktriangledown) Cl_2^- , (\square) SiCl^- , (\blacksquare) CCl_2^- , (\triangle) C_2^- , (\bullet) Si^- , (\circ) SiCl_3^- .

4. Discussion

The basic equation for the secondary ion yield is

$$i_s^M = i_p S_M R^\pm \theta_M \eta$$

where i_s^M is the secondary ion current of species M, i_p the primary ion current, S_M the sputter yield for M per incident primary ion, R^\pm the ionization probability for the formation positive/negative ions, θ_M the fractional surface coverage of M and η the transmission of the system [8]. Since i_p is fixed in our experiments and the transmission of our system η can be assumed to be constant for all species, the secondary ion yield i_s^M is primarily controlled by S_M , R^\pm and θ_M . The coverage θ_M is directly related to the CCl_4 partial pressure. The sputtering yield S is believed to be enhanced by the presence of CCl_4 . This is supported by a previous investigation of Ga^+ ion beam-enhanced etching of Si in chlorine gas which showed that the etch yield (Si atoms/primary ions per second) increases with Cl_2 gas flux until saturation is reached at higher fluxes [2]. Apart from the sputter yield S_M , the secondary ion yield also depends on R^\pm which has been found to be

very sensitive to sub-monolayer surface coverages of electronegative gases, of which oxygen has been the most extensively studied [6].

The mechanism of secondary ion emission in the presence of reactive species is in general not well understood. This is due to the fact that in principle a variety of processes can lead to ionization [9]. There are many models which have been advanced in attempts to rationalize the effects of reactive species on sputtered ion yields. The molecular model proposed by Thomas [10] argues that because electronic transition rates are so rapid (10^{14} – 10^{16} s $^{-1}$) it should really be expected that no excited or ionized species formed at the surface can escape without de-excitation or neutralization in the 10^{-13} s required to move outside the range of electronic interaction. Hence he suggested that excited or ionized species can survive only if they are formed some distance away from the surface. A variant of this model involves the production of “ion pairs” in which neutrally emitted molecules dissociate into ion pairs above the surface [11].

Ion pair production was proposed by Plog *et al.* [12] who studied the secondary ion emission from silicon exposed to oxygen at different partial pressures. The model would allow for an equal number of positive and negative ions in the dissociation process, thereby involving charge conservation. When the CCl₄ partial pressure increases from $\sim 10^{-11}$ mbar to $\sim 10^{-7}$ mbar, the total positive secondary ion yield increases by a factor of ~ 100 , whilst the total negative secondary ion yield increases by a factor of ~ 1000 . Thus ion pair production cannot account for the excess negative secondary ions (especially Cl $^{-}$) and some other mechanism for the ionization of negative ion species must also be invoked, for example the surface excitation model [9].

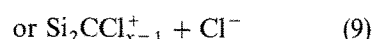
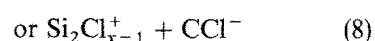
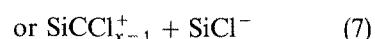
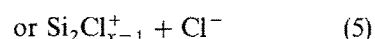
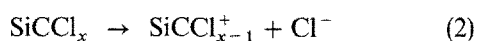
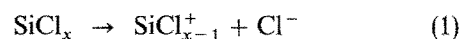
A comparison of the positive and negative secondary ion yields (especially Si $^{+}$, SiCl $^{+}$ and Cl $^{-}$) as a function of CCl₄ partial pressure shows different profiles. One possible reason for the lack of ion-pair partners is the instability of the partner ion leading to further fragmentation [13]. This idea is utilized in another similar model known as the “desorption ionization model” which attempts to explain the emission of large cluster fragments [14]. After desorption in the free vacuum, unimolecular dissociations or metastable transitions occur, governed by the internal energy of the parent ions giving rise to fragment ions. This process is analogous to mass spectrometry, and the identity of surface intermediates can be unravelled by looking at the “cracking pattern” of the fragment ions. We therefore use the ion pair production and desorption ionization models in an attempt to classify the major observed ion fragments into groups which have similar intensity profiles as a function of CCl₄ partial pressure (Table I).

We note that the classification of Table I is also complicated by the fact that some groups may also be ion fragments of another. For example, group B ions are also fragments of the parent molecule of group C, and the group E ions are also fragments of the parent molecule of group F. Ions like Si $^{+}$ and Cl $^{-}$ are not classified as they are fragments of many parent mole-

TABLE I Classification of ion fragments

Group	Ion fragments detected	Parent molecule
A	SiCl $^{+}$, SiCl $_2^{+}$	SiCl $_x$ ($x = 1-4$)
B	SiC $^{+}$, SiCCl $^{+}$	SiCCl $_x$ ($x = 0-4$)
C	Si $_2$ C $^{+}$, Si $_2$ Cl $^{+}$, Si $_2$ CCl $^{+}$	Si $_2$ CCl $_x$ ($x = 0-4$)
D	SiCl $^{-}$, SiCl $_2^{-}$, SiCl $_3^{-}$	Si $_2$ Cl $_x$ ($x = 1-4$)
E	CCl $^{-}$, CCl $_2^{-}$	SiCCl $_x$ ($x = 1-4$)
F	SiCCl $^{-}$, SiCCl $_2^{-}$	Si $_2$ CCl $_x$ ($x = 1-4$)

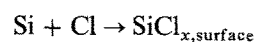
cules. A few ion-pair production processes for the above parent molecules are listed below:



Some of the larger ions thus formed are probably unstable and undergo further dissociations.

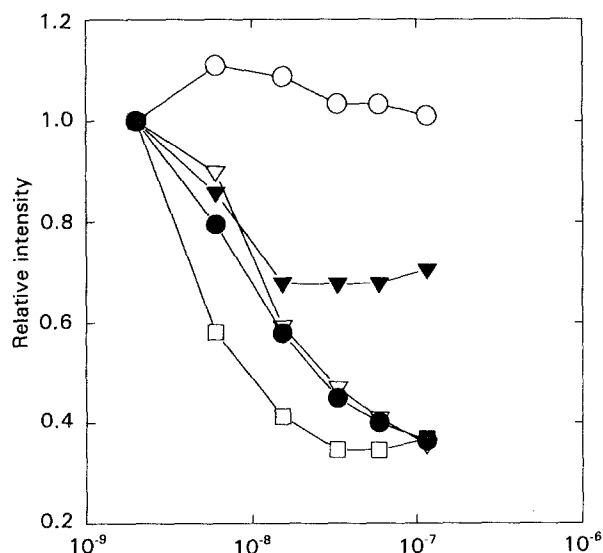
In order to differentiate the profiles of the various product ions as a function of CCl₄ partial pressure, they are plotted relative to Si $^{+}$ in Fig. 5a and b (for positive ions). The Si $^{+}$ ion originates both from the substrate and as a fragmentation ion of Si-containing product species. Nevertheless, this ratio gives the relative changes in the intensity of the product ions as a function of incident ion energy and CCl₄ partial pressure. The counts are normalized to the smallest CCl₄ partial pressure ($\sim 10^{-9}$ mbar) so as to neglect the effect of residual CCl₄ before exposure.

It is immediately apparent that the intensities of the product ions generally increase relative to Si $^{+}$ at 9 keV but decrease at 2 keV. This can be explained in terms of the increase in sputter rate S_M , surface concentration θ_M and ionization probability R^{+} of the product species relative to Si $^{+}$. We are not able to determine the ionization probabilities R^{+} of the various surface species, but if we assume that they remain approximately constant relative to that of Si $^{+}$ for both primary ion energy and CCl₄ partial pressure, then it follows that the sputter rate S_M of the product species is higher at 9 keV. This is a reasonable conclusion since we expect higher-energy incident ions to transfer more energy to the substrate, increasing the sputter rate. Flamm [1] explains this synergism between surface chemical reactions and physical sputtering by the conversion of slow-sputtering surface matter into faster-sputtering products:

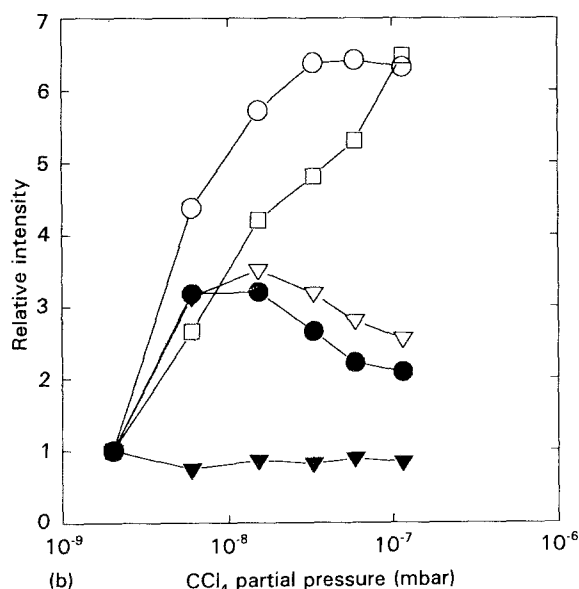


He postulates that the chemisorbed product (SiCl $_{x,\text{surface}}$) is sputtered faster than Si.

As regards the nature of the surface reaction products, the groupings of the positive ion species (groups



(a)

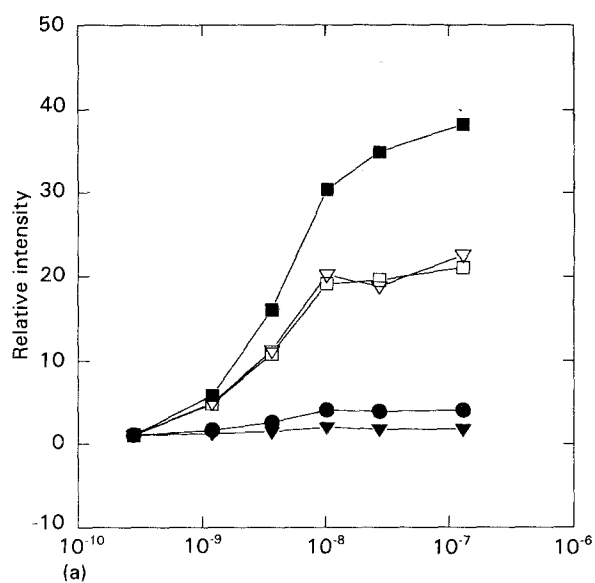


(b)

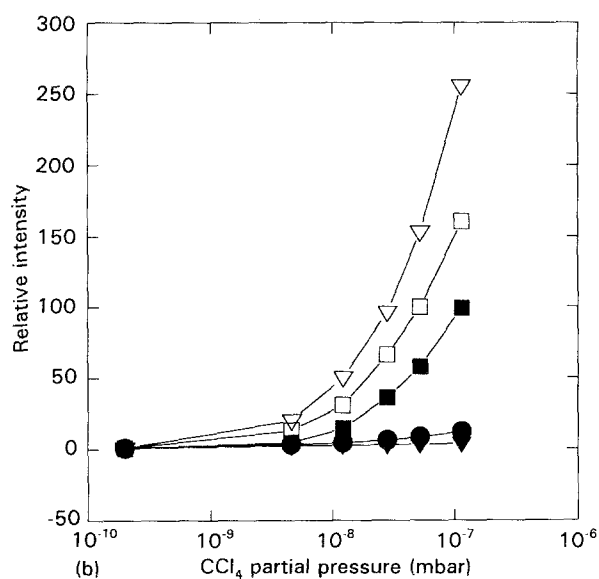
Figure 5 Positive secondary ion yields relative to Si^+ as a function of CCl_4 partial pressure, normalized to the smallest CCl_4 partial pressure admitted: (a) 2 kV, (b) 9 kV. (\circ) $\text{SiCl}^+/\text{Si}^+$, (\blacktriangledown) SiC^+/Si^+ , (\bullet) $\text{Si}_2\text{Cl}^+/\text{Si}^+$, (∇) $\text{Si}_2\text{C}^+/\text{Si}^+$, (\square) CCl^+/Si^+ .

A–C) indicate that at least three surface reaction products are formed: SiCl_x ($x = 1-4$), SiCCl_x ($x = 0-4$) and Si_2CCl_x ($x = 0-4$). SiCl_x is the dominant reaction product and has been reported in several studies using Cl-containing adsorbates [13, 15, 16]. SiCCl_x is probably a reaction product between Si and CCl_x , the C–Cl bond of the original adsorbate molecule remaining intact. From Fig. 5, we deduce that the Si_2CCl_x surface concentration falls relative to that of SiCl_x or SiCCl_x at higher CCl_4 partial pressures. This is not surprising since bridge-bonded CCl_x (which forms Si_2CCl_x) would be more likely to form at lower CCl_4 coverages.

Fig. 6a and b show the corresponding profiles of the major negative product ions as a function of CCl_4 partial pressure, plotted relative to Si^- and normalized to the smallest CCl_4 partial pressure admitted. The intensities of C_2^- , Cl_2^- and CCl^- relative to Si^{-1} appear to saturate by $\sim 5 \times 10^{-8}$ mbar at 2 keV whilst continuing to increase above 10^{-7} mbar at 9 keV. C_2^- and Cl_2^- are likely to originate from the



(a)



(b)

Figure 6 Negative secondary ion yields relative to Si^- as a function of CCl_4 partial pressure, normalized to the smallest CCl_4 partial pressure admitted: (a) 2 kV, (b) 9 kV. (\blacksquare) C_2^-/Si^- , (∇) $\text{Cl}_2^-/\text{Si}^-$, (\square) CCl^-/Si^- , (\bullet) Cl^-/Si^- , (\blacktriangledown) $\text{SiCl}^-/\text{Si}^-$.

reaction between the CCl_x species on the surface, and this reaction appears to be enhanced at 9 keV. The groupings of the negative ion species (groups D–F) suggest similar surface reaction products as previously discussed, and the detection of SiCl_3^- gives evidence for the presence of higher silicon chlorides such as SiCl_3 .

5. Conclusions

The Ar^+ ion-enhanced reaction of CCl_4 on Si(1 0 0) at 320 K has been investigated at primary ion energies of 2 and 9 keV. Static SIMS shows that CCl_4 reacts with Si even at room temperature. This surface reaction is enhanced by simultaneous sputtering with an Ar^+ ion beam during adsorption, the reaction rate being higher at 9 keV than at 2 keV. The secondary ion species detected during simultaneous sputtering with an ion beam indicate that at least four types of surface reaction product are formed: SiCl_x ($x = 1-4$), SiCCl_x

($x = 0-4$), Si_2Cl_x ($x = 1-4$) and SiCCl_x ($x = 0-4$). The enhancement of the surface reactions by a higher-energy beam can be explained by a synergism between surface chemical reactions and physical sputtering, resulting in the conversion of slow-sputtering surface matter into faster-sputtering products.

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