IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Semiempirical calculations of the chemisorption of chlorine on the Si(111)7*7 surface

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 7125

(http://iopscience.iop.org/0953-8984/7/36/003)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.151
The article was downloaded on 12/05/2010 at 22:04

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 7 (1995) 7125–7139. Printed in the UK

Semiempirical calculations of the chemisorption of chlorine on the Si(111)7 × 7 surface

P V Smith† and Pei-Lin Cao‡

† Physics Department, The University of Newcastle, Callaghan, NSW, Australia 2308
‡ Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 23 May 1995

Abstract. The chemisorption of chlorine on the Si(111)7 × 7 surface has been studied using clusters and the well known AM1 semiempirical molecular orbital method. Both the equilibrium structures corresponding to n Cl atoms ($1 \leqslant n \leqslant 7$) chemisorbing onto the adatom and rest atom positions of the Si(111)7 × 7 reconstructed surface, and the etching energies for an adatom or rest atom bonded to x Cl atoms ($0 \leqslant x \leqslant 4$), have been obtained. We find that as successively more chlorine is chemisorbed, an adatom moves from its original threefold site (one chlorine) to an adjacent bridge site (two and three chlorines), and then to a neighbouring on top site (four or more chlorines). A rest atom bonded to up to four chlorine atoms, on the other hand, remains close to its threefold clean surface position. Our results also predict, in agreement with experiment, that all of the $SiCl_x$ species ($1 \leqslant x \leqslant 4$) will occur on an Si(111)7 × 7 surface exposed to atomic chlorine at low temperature. Increasing the temperature will first result in all of the $SiCl_3$ and $SiCl_4$, and most of the $SiCl_2$, desorbing from the surface. This will be followed by the desorption of the remaining $SiCl_2$, leaving only SiCl on the surface. The final stage of the desorption process involves the removal of the SiCl. Whilst the etching energies appropriate to a rest atom site are generally lower than the corresponding adatom values, the minimum etching energy is found to correspond to the desorption of an $SiCl_4$ complex involving an adatom of the Si(111)7 × 7 reconstructed surface.

1. Introduction

The modification of silicon surfaces using the technique of reactive ion etching is of considerable industrial and technological importance because of its use in the manufacture of very-large-scale integrated circuits, and in the development of new electronic devices. Chlorine is widely used as a source gas in such etching processes. As a result, a number of experiments have been performed to study the etching of silicon by chlorine [1–11]. Soft-x-ray photoemission work has shown that while SiCl, $SiCl_2$, $SiCl_3$ and $SiCl_4$ are all present on an Si(111) surface exposed to atomic chlorine, the more heavily chlorinated species quickly desorb from the surface after annealing at 300 °C [1]. Desorption of these heavily chlorinated species has also been reported in XPS, temperature-programmed desorption (TPD) and laser-induced thermal desorption (LITD) studies [2, 9, 11]. The desorption kinetics of the major chlorosilicon etching products $SiCl_2$ and $SiCl_4$ are first order in the chlorine coverage below 850 K, but above 900 K the desorption of $SiCl_2$ from the Si(111) surface is found to be second order [3]. Experiments have also shown that after annealing the chlorine saturated surface to 800 K, the residual chlorine coverage is 1.0 ± 0.1 monolayer (ML). This is more than one would expect following the desorption of all of the $SiCl_x$ with $x > 1$ and suggests

0953-8984/95/367125+15$19.50 © 1995 IOP Publishing Ltd

that some of the $SiCl_x$ present on the surface dissociates when empty surface sites are released by desorption [3].

Scanning tunnelling microscopy (STM) images show that the monochloride reaction products which result from the interaction of atomic chlorine with the Si(111)7 × 7 reconstructed surface are located at the adatom sites. It has also been proposed that the dichloride and trichloride structures are produced by breaking some of the Si–Si backbonds between the adatom and its neighbouring first-layer silicon atoms and that these species reside on the bridge sites between two adjacent silicon atoms from the rest atom layer, and on top of these rest layer atoms, respectively [4].

STM experiments have shown that after annealing the chlorine-saturated Si(111)7 × 7 surface for a short time at ~ 700 K, the adatoms in some regions are displaced from the surface, leaving the rest atom layer exposed, while in other regions of the surface, Cl atoms are chemisorbed on top of the adatom sites [5, 6]. Annealing the Si(111) surface in chlorine at temperatures greater than 700 K, on the other hand, has resulted in the observation of 1 × 1 LEED [7] and RHEED [10] patterns. Heating the Si(111)/Cl system, both in ultrahigh vacuum (UHV) and in Cl_2, led to the decomposition of the $SiCl_x$ ($x > 1$) which resulted in the desorption of various reaction products to leave Si–Cl bonds on the surface. Heating in UHV for 30 s at 820 °C was found to effectively remove all of the chlorine [10].

Despite all of this experimental work, there has been relatively little investigation of the interaction of chlorine with the Si(111)7 × 7 surface from a theoretical point of view. Using a self-consistent field (SCF) Hartree–Fock (HF) linear combination of atomic orbitals (LCAO) method, and Si_4H_7, Si_4H_9, $Si_{10}H_{13}$ and $Si_{10}H_{15}$ clusters to simulate the Si(111) surface, Seel and Bagus [12] calculated the binding energy appropriate to a single chlorine atom chemisorbed at atop, open and eclipsed sites. They found that the on top site was the most energetically favourable with a binding energy of 1.63 eV and an Si–Cl equilibrium bond length of 2.24 Å. These theoretical predictions are, however, very different from the experimentally determined value for the Si–Cl bond strength of 4.76 eV [2, 13], and the Si–Cl bondlength of 1.95–2.00 Å obtained from near-edge x-ray adsorption fine structure (NEXAFS) studies of the Si(001)2 × 1 chlorinated surface [14, 15]. The aim of the present work is to employ much larger clusters to model the Si(111)7 × 7:Cl system in the hope of obtaining a more accurate and fundamental understanding of the interaction of chlorine with the Si(111)7 × 7 reconstructed surface.

2. Models and method

In this study we have employed three four-layer clusters $Si_{18}H_{27}Cl_n$, $Si_{19}H_{29}Cl_n$ and $Si_{19}H_{27}Cl_n$ ($1 \leqslant n \leqslant 7$) to simulate the adsorption of chlorine onto the Si(111)7 × 7 reconstructed surface (see figure 1). For the Si(111)7 × 7 reconstructed surface we have adopted the dimer–adatom–stacking fault (DAS) model reported by Tong *et al* [16]. According to this model, each unit cell contains 12 adatoms located at the threefold hollow (T_4) sites above the first layer, nine dimers in the second layer, a stacking fault in the fourth layer, and a corner hole. The actual atomic coordinates defining this structure have been determined using a dynamical theory of low-energy electron diffraction (LEED). In an earlier study of the chemisorption of fluorine on the Si(111)7 × 7 surface [17], it was found that there are three main chemisorption sites on this highly complex surface. These are the adatom A and adatom B sites, and the rest atom C sites (see figure 1 of [17]). The above three clusters have thus been chosen to model these particular chemisorption sites. As is

customary in these types of calculation, hydrogen atoms have been employed to saturate the bulk silicon dangling bonds.

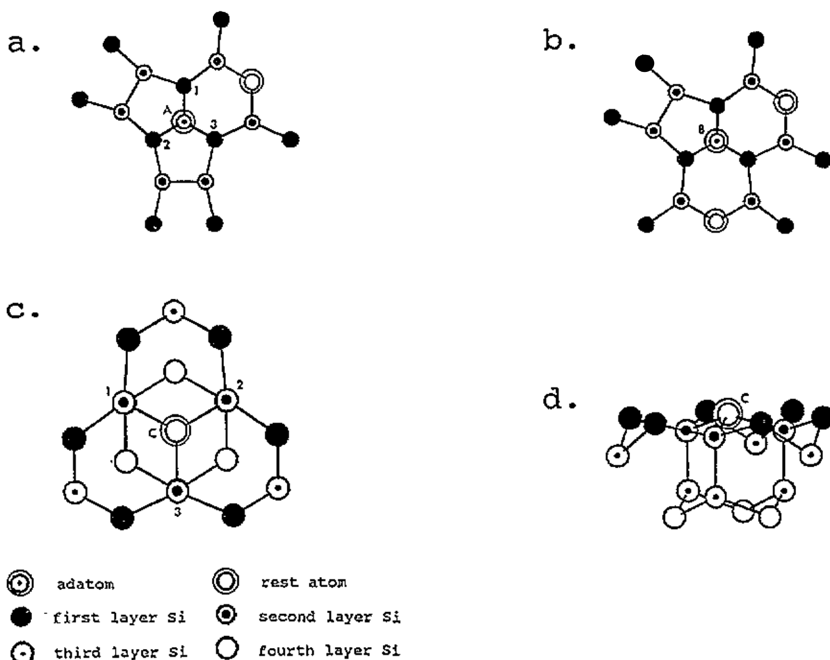

Figure 1. The various clusters employed to model the Si(111)7 × 7 reconstructed surface: (a) a top view of the $Si_{18}H_{27}$ cluster for an adatom A site: (b) a top view of the $Si_{19}H_{29}$ cluster for an adatom B site; (c) and (d) top and side views of the $Si_{19}H_{27}$ cluster employed to model the rest atom C site. The hydrogen atoms which saturate the bulk dangling bonds have been omitted for simplicity.

The equilibrium configurations have been obtained by minimizing the total energy with respect to all of the coordinates (i.e. without any symmetry constraints) of the chemisorbed chlorine and topmost silicon atoms. This is done using the Berny optimization method [18] contained within the AM1 component of the GAUSSIAN 92 code [19]. The AM1 method, which was originally formulated by Dewar *et al* [20], is a fairly sophisticated, self-consistent, semiempirical molecular orbital method which has been shown to provide a good description of many different systems [21–23].

In order to ensure that the obtained equilibrium structures were true global minima, rather than local minima, several different starting configurations were employed in each optimization. One of the major advantages in using a semiempirical method is the ability to perform an adequate search of the whole conformational space. The actual geometries which have been presented are the minimum-energy structures which we have determined in each case. It should also be pointed out that the main aim of this paper has been to study the formation and energetics of the various $SiCl_x$ ($1 \leqslant x \leqslant 4$) complexes on the Si(111)7 × 7 surface. As a result, we have only considered the effect of adding successively more chlorine to the various structures formed at the adatom and rest atom positions, and have ignored the possible chemisorption of chlorine onto other sites of the Si(111)7 × 7 surface.

3. Results

3.1. The clean Si(111)7 × 7 surface

As a basis for studying the interaction of chlorine with the Si(111)7 × 7 surface, we have first calculated the binding energies for an adatom A, adatom B and rest atom C, on this reconstructed surface using the clusters $Si_{18}H_{27}$, $Si_{19}H_{29}$ and $Si_{19}H_{27}$, respectively. In these initial binding energy calculations we have simply optimized the position of the adatom or rest atom keeping all of the other atoms fixed at their LEED-determined positions. We found that, compared to the results of Tong *et al* [16], an adatom A and an adatom B move up by 0.147 Å and 0.196 Å, while a rest atom moves down by 0.044 Å. The binding energies were determined to be 6.76 eV (adatom A), 6.12 eV (adatom B) and 7.85 eV (rest atom C). These results are in good agreement with the values of 7.40 eV and 8.46 eV which we have calculated for the adatom A and rest atom C binding energies on the Si(111)7 × 7 surface from HF cluster calculations using the 6-31G*(3df, 2p) basis set and including correlation effects via the BECKE3LYP option within GAUSSIAN 94 [24]. This treatment of electron correlation is claimed to be accurate to around 2 kcal mol^{-1} [25]. Our AM1 rest atom value of 7.85 eV is also in excellent agreement with the measured value of the binding energy of a silicon atom on the clean Si(111) surface of 7.80 eV [26].

3.2. One to seven chlorine atoms chemisorbed onto adatom A

3.2.1. Single-chlorine chemisorption. To obtain the structure appropriate to a single chlorine atom chemisorbed at an adatom A site, we have minimized the total energy of the $Si_{18}H_{27}Cl$ cluster with respect to the x, y and z coordinates of the chemisorbed chlorine and the adatom A. The equilibrium configuration corresponds to the chlorine atom sitting almost directly above the threefold adatom site with an Si–Cl bond length of 2.001 Å. This is only slightly longer than the value of 1.982 Å which we determine for free SiCl. The adatom has moved upwards by 0.007 Å compared to its clean surface equilibrium position. The Cl atom has gained 0.225e from the substrate (as determined by a Mulliken population analysis) and has an adsorption energy of 3.72 eV. These values for the Si–Cl bond length and Cl binding energy are in much better agreement with the experimental values mentioned previously than those of Seel and Bagus [12]. The prediction of the chlorine atom lying almost directly above the adatom is also consistent with the STM data at low chlorine coverage [4, 6].

In order to calculate the etching energy for the Si(A)Cl complex, we first calculate the energies of the original geometry-optimized chemisorbed system, and that corresponding to the Si(A)Cl complex sufficiently far away from the remaining substrate for their effective interaction to be negligibly small. The difference between these two energy values gives the binding energy of the Si(A)Cl complex to the substrate, and hence the net amount of energy required to remove this species from the surface. This binding energy is thus referred to subsequently as the etching energy, and has a value of 4.52 eV in this particular case. Using exactly the same method of determination, we find the etching energy for a single adatom A on the clean Si(111)7 × 7 reconstructed surface to be 6.76 eV, as indicated above, It is thus clear that the chemisorption of a single chlorine atom greatly reduces the bond strength between an adatom A and its underlying substrate.

3.2.2. Two-chlorine chemisorption. When a second chlorine atom is chemisorbed near an adatom A site, the adatom is found to move from its original threefold position to an

adjacent bridge site between two of its nearest-neighbour first-layer silicon atoms (e.g. the atoms Si(2) and Si(3) of figure 1(a)) to form an approximately tetrahedral structure, as shown in figure 2. The Si–Cl bond lengths are 2.015 Å and 2.119 Å, while the Si(A)–Si(2) and Si(A)–Si(3) bond lengths are about 5% longer than the bulk nearest-neighbour distance of 2.35 Å. The two chlorine atoms gain 0.166e and 0.244e from the nearby silicon atoms. The binding energy of the Si(A)Cl_2 configuration on the substrate is calculated to be 3.54 eV, while the total chemisorption energy for the two chlorines is 7.18 eV.

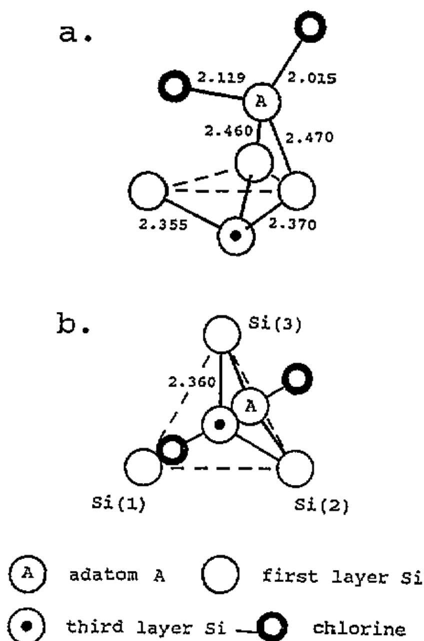

Figure 2. The optimized geometry corresponding to the chemisorption of two chlorine atoms onto an adatom A: (a) a side view, (b) a top view. All of the bond lengths in this figure, and all subsequent figures, are given in ångströms.

3.2.3. Three-chlorine chemisorption. Minimizing the total energy by varying all of the atomic coordinates of the adatom and chlorines when a third chloride atom is chemisorbed near an adatom A leads to the equilibrium configuration shown in figure 3. Rather than forming an $SiCl_3$ complex, one chlorine atom is found to saturate the dangling bond of the first-layer silicon atom, Si(2), while the other two chlorine atoms bond to the adatom A to form a slightly deformed tetrahedral structure directly above the bridge site between the silicons Si(1) and Si(3). While the Si–Cl bond lengths remain about 2.1 Å, the Si (A)–Si backbonds are slightly elongated compared to the above two-chlorine case. The etching energy for the Si(A)Cl_2 species is very similar at 3.55 eV.

3.2.4. Four-chlorine chemisorption. Adding a fourth chlorine atom to the configuration of figure 3, and optimizing with respect to the coordinates of the adatom and all four chlorines, results in the Si(A)Cl_2 complex moving essentially on top of the first-layer silicon atom Si(3), as shown in figure 4. The other two chlorine atoms lie almost directly above the neighbouring first-layer silicon atoms, Si(1) and Si(2), and saturate their dangling bonds.

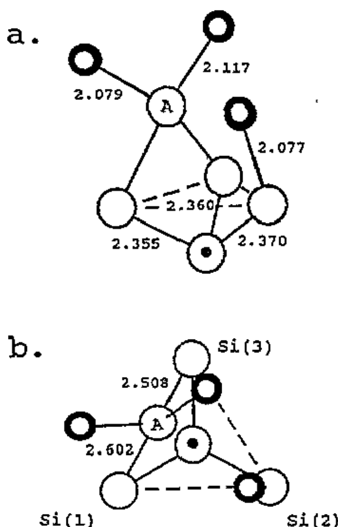

Figure 3. The minimum-energy configuration which results from the chemisorption of three chlorines near the adatom A: (a) a side view, (b) a top view. The delineation of the atoms is the same as in figure 2.

All of the Si–Cl bond lengths are around 2.06 Å and the length of the Si(A)–Si(3) bond is 2.415 Å. The energy required to desorb the Si(A)Cl_2 complex in this case is calculated to be 2.40 eV.

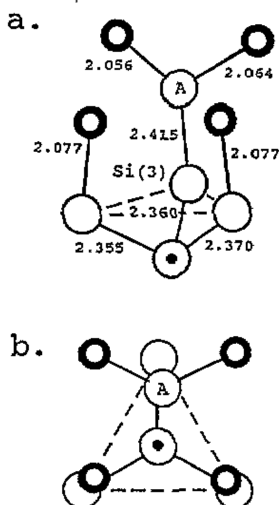

Figure 4. The equilibrium structure when four chlorine atoms are chemisorbed in the vicinity of an adatom A: (a) a side view, (b) a top view. The atom labelling is the same as in figure 2.

3.2.5. Five-chlorine chemisorption. Adding a fifth chlorine near the adatom A site results in the equilibrium structure shown in figure 5. The positions of the two chlorines saturating the dangling bonds of Si(1) and Si(2) are essentially unaltered. The additional chlorine

atom bonds to the adatom A to form an approximately tetrahedral $SiCl_3$ configuration almost directly above the first-layer silicon Si(3). The Si(A)–Si(3) bondlength is 2.433 Å, some 3.5% longer than the bulk nearest-neighbour distance. The energy required to desorb the $Si(A)Cl_3$ from this structure is found to be 0.88 eV, the bonding of the adatom A to the substrate being substantially weakened by its bonding to the three chlorines. The total charge transferred to these adatom-bonded chlorines from the surrounding silicons is predicted to be 0.924e.

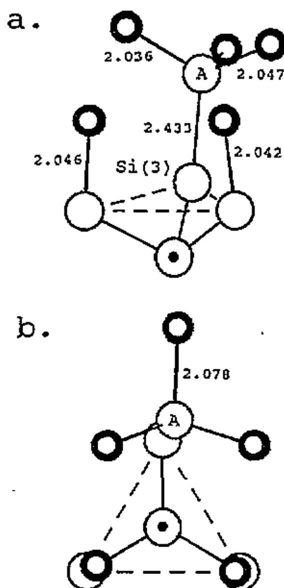

Figure 5. The optimized geometry corresponding to the adsorption of five chlorine atoms near an adatom A: (a) a side view, (b) a top view. The delineation of the atoms follows that of figure 2.

3.2.6. Six-chlorine chemisorption. The addition of a sixth chlorine atom to the above five-chlorine configuration results in the formation of a slightly deformed $Si(A)Cl_4$ structure lying above the Si(3) first-layer silicon atom, as shown in figure 6. The remaining two chlorine atoms saturate the dangling bonds of Si(1) and Si(2), as before. The adatom A is bonded no longer directly to the substrate, but indirectly via one of the adatom-bonded chlorines, Cl(6). Both the Si(A)–Cl(6) and Si(3)–Cl(6) distances, of 2.291 Å and 2.152 Å respectively, are somewhat longer than the characteristic Si–Cl bond length of around 2.05 Å. Breaking the Si(A)–Cl(6) bond to desorb $Si(A)Cl_3$,or the Si(3)–Cl(6) bond to release $Si(A)Cl_4$, is calculated to require 0.64 eV or 0.71 eV, respectively.

3.2.7. Seven-chlorine chemisorption. Adding a seventh chlorine atom to the configuration of figure 6, and minimizing the total energy with respect to the atomic coordinates of the adatom A and all seven chlorines, leads to the equilibrium structure shown in figure 7. We observe that three of the chlorines are now saturating the dangling bonds of the first-layer silicon atoms Si(1), Si(2) and Si(3). The remaining four chlorines are bonded to the adatom A to form the tetrahedral structure $Si(A)Cl_4$. This is weakly coupled to the Si(3) first-layer silicon atom via its chlorine Cl(3). The Si(A)–Cl(3) bondlength is 3.803 Å, almost

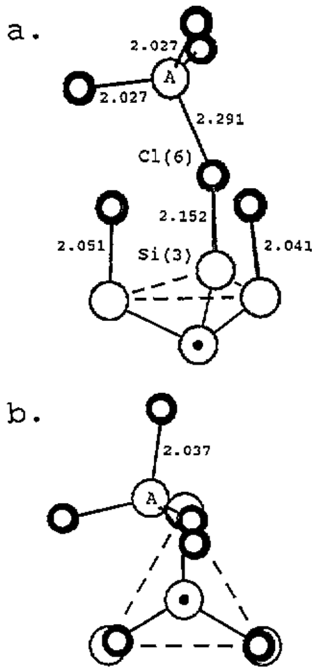

Figure 6. The minimum-energy structure for six chlorines chemisorbed adjacent to an adatom A: (a) a side view, (b) a top view. The atoms have been labelled as in figure 2.

twice the normal Si–Cl interatomic distance. As a result, the energy required to remove Si(A)Cl_4 from this chlorinated surface is only 0.024 eV.

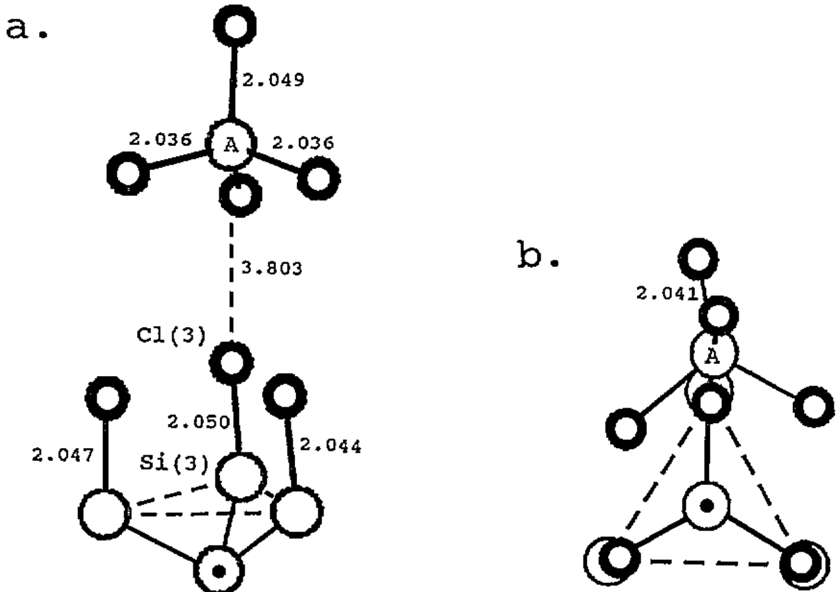

Figure 7. The equilibrium topology for seven-chlorine chemisorption near an adatom A site: (a) a side view, (b) a top view. The labelling of the atoms is identical to that of figure 2.

3.3. Chemisorption of one to seven chlorine atoms on adatom B

The behaviour of an adatom at a B site is very similar to that of an adatom at an A site with respect to chlorine chemisorption. For both sites, we have found that as successively more chlorine is chemisorbed in the vicinity of an adatom, it will move from its original clean surface threefold site (one chlorine), to an adjacent bridge site between two of its first-layer nearest-neighbour silicon atoms (two and three chlorines), and then to an on top site above one of these adjacent silicon atoms (more than three chlorine atoms). This behaviour is in good agreement with the STM data on the chlorinated Si(111)7 × 7 surface which indicates that the chlorine atoms of the monochloride structure are positioned above the adatom sites, while the $SiCl_2$ and $SiCl_3$ complexes of the dichloride and trichloride are located above the bridge sites, and at the on top sites, respectively [4].

The main results for the chemisorption of one to seven chlorine atoms at both A and B adatom sites are given in table 1. These results include the etching energies for the various $SiCl_x$ complexes ($1 \leqslant x \leqslant 4$), E_e, the total chemisorption energies for the adsorption of n chlorines ($1 \leqslant n \leqslant 7$), E_b, and the net electron transfer to the chemisorbed chlorine atoms, e_t. Not surprisingly, both E_b and e_t increase with increasing n. The etching energies of the Si(A)Cl_x and Si(B)Cl_x complexes for $0 \leqslant x \leqslant 4$, however, are found to progressively decrease from (6.76 eV, 6.12 eV) for $x = 0$, down to (0.024 eV, 0.105 eV) for $x = 4$. Thus we would expect that as the surface is annealed, the adatoms of the 7 × 7 reconstructed surface will be predominantly etched from the surface in the form $SiCl_4$, leaving the rest atom layer exposed, as indicated by Szabo *et al* [3].

3.4. Chemisorption of one to five chlorine atoms on rest atom C

3.4.1. Single-chlorine chemisorption. When a single chlorine atom is chemisorbed at a rest atom C site, and the geometry optimized with respect to the x, y and z coordinates of the chlorine and the rest atom, the chlorine is found to sit directly above the rest atom at its threefold site. The Si(C)–Cl distance is 2.06 Å and the rest atom lies 0.176 Å above its clean surface equilibrium position. The adsorption energy of the chlorine on the atop site of a rest atom C is 3.73 eV and the charge transferred to the chlorine from the substrate, as determined by Mulliken population analysis, is 0.250e. The etching energy for the SiCl is 5.62 eV.

3.4.2. Two-chlorine chemisorption. When a second chlorine is chemisorbed near the rest atom C site, we find that, in contrast to the adatom results, the rest atom moves only slightly away its original threefold site towards an adjacent bridge site, as shown in figure 8. The rest atom also moves out of the surface by an additional 0.525 Å. The Si(C)–Cl bonds are around 2.07 Å, whilst the distances between the rest atom C and the two second-layer silicon atoms to which it is bonded, Si(2) and Si(3), are approximately 2.44 Å. The energy required to desorb $SiCl_2$ from this surface is determined to be 3.03 eV, and the total adsorption energy for the two chlorines is 5.57 eV.

3.4.3. Three-chlorine chemisorption. When a further chlorine atom is chemisorbed near the above Si(C)Cl_2 configuration, and the total energy minimized with respect to the coordinates of the rest atom and all three chlorines, one obtains the structure shown in figure 9. The rest atom has now moved towards the second-layer silicon atom Si(3) to which it is bonded, with the Si(C)–Si(3) distance being 2.489 Å. The rest atom is also bonded to the three chlorines to form a distorted tetrahedral structure, with Si(C)–Cl bond lengths of 2.028 Å,

Table 1. The bonding site and etching energy, E_e, for the appropriate $SiCl_x$, the total binding energy, E_b, and the net electronic charge transferred from the substrate, e_t, for n chlorine atoms ($0 \leqslant n \leqslant 7$) chemisorbed onto the adatom A and adatom B sites.

n		0	1	2	3	4	5	6	7
Bonding site			threefold ($x = 1$)	bridge ($x = 2$)	bridge ($x = 2$)	on top ($x = 2$)	on top ($x = 3$)	on top ($x = 3, 4$)	on top ($x = 4$)
E_e (eV)	A	6.755	4.519 ($x = 1$)	3.541 ($x = 2$)	3.549 ($x = 2$)	2.398 ($x = 2$)	0.875 ($x = 3$)	0.714 ($x = 4$) 0.638 ($x = 3$)	0.024 ($x = 4$)
	B	6.122	3.850 ($x = 1$)	3.094 ($x = 2$)	4.139 ($x = 2$)	2.256 ($x = 2$)	0.648 ($x = 3$)	0.646 ($x = 4$) 0.841 ($x = 3$)	0.105 ($x = 4$)
E_b (eV)	A		3.723	7.176	9.624	14.208	17.045	20.420	23.343
	B		3.687	7.362	10.092	14.128	16.885	20.418	23.217
e_t (e)	A		0.225	0.410	0.871	1.087	1.384	1.635	2.003
	B		0.221	0.402	0.809	0.969	1.334	1.587	1.970

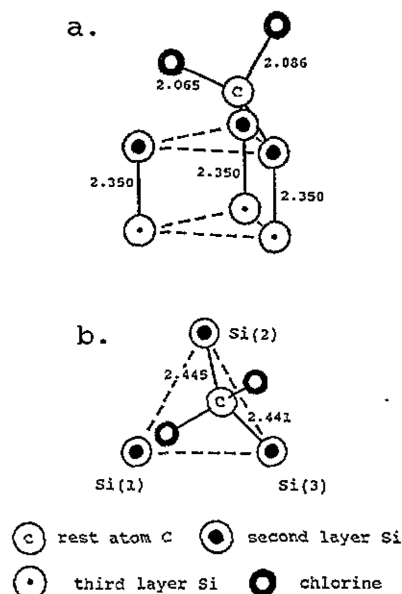

Figure 8. The optimized geometry corresponding to the chemisorption of two chlorine atoms onto a rest atom C: (a) a side view, (b) a top view.

2.028 Å and 2.183 Å. One of the chlorine atoms, Cl(3), also forms bridge bonds with the other two second-layer silicon atoms, Si(1) and Si(2). The corresponding bond lengths Si(1)–Cl(3) and Si(2)–Cl(3) are 2.175 Å and 2.184 Å, respectively. The chemisorption energy of all three chlorine atoms is 8.73 eV and the etching energy for $Si(C)Cl_2$, produced by the breaking of the Si(C)–Cl(3) and Si(C)–Si(3) bonds, is 0.49 eV.

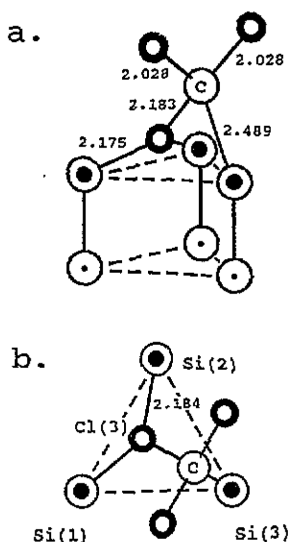

Figure 9. The minimum-energy structure for the adsorption of three chlorine atoms near a rest atom C: (a) a side view, (b) a top view. The delineation of the atoms is the same as in figure 8.

3.4.4. Four-chlorine chemisorption. The chemisorption of a fourth chlorine atom near the rest atom C is found to produce the minimum-energy structure shown in figure 10. One of the four chlorine atoms, Cl(4) say, is now positioned at the original threefold rest atom site and saturates the dangling bonds of all three second-layer silicon atoms. The rest atom C is bonded to all four chlorines with the resulting Si(C)Cl_4 configuration being approximately tetrahedral, and lying almost directly over the threefold site. The Si(C)–Cl(4) distance of 2.524 Å, however, is much greater than the other three Si(C)–Cl bond lengths of around 2.04 Å. The Si(C)–Cl(4) bond is thus relatively weak and the energy required to break this bond to yield free Si(C)Cl_3 is only 0.48 eV.

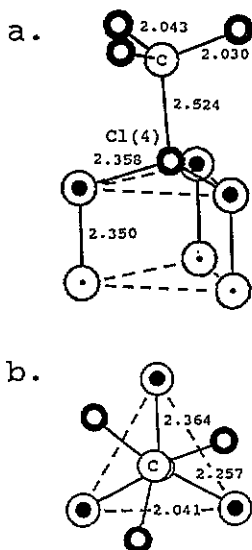

Figure 10. The equilibrium geometry which results from the adsorption of four chlorines in the vicinity of a rest atom C: (a) a side view, (b) a top view. The labelling of the atoms follows that of figure 8.

3.4.5. Five-chlorine chemisorption. The minimum-energy configuration when five chlorine atoms are chemisorbed near a rest atom C site is shown in figure 11. In this case, one chlorine is still positioned at the original rest atom threefold site. The rest atom is bonded to the four other chlorine atoms in a well defined Si(C)Cl_4 tetrahedral configuration. This complex lies essentially on top of the second-layer silicon atom Si(2) to which it is very weakly bonded via the chlorine, Cl(5). The Si(2)–Cl(5) distance is 2.649 Å, much greater than the standard Si–Cl bondlength of around 2.05 Å. As a result, the etching energy for Si(C)Cl_4 for this structure is only 0.30 eV. The total binding energy of the five chlorines is 16.56 eV. No stable configuration was found whereby an Si(C)Cl_4 complex was bonded to the surface via another chlorine atom as in the adatom case shown in figure 7.

4. Discussion and conclusions

In this paper we have investigated the chemisorption of chlorine onto the adatom and rest atom sites of the Si(111)7 × 7 reconstructed surface. Several important conclusions can be

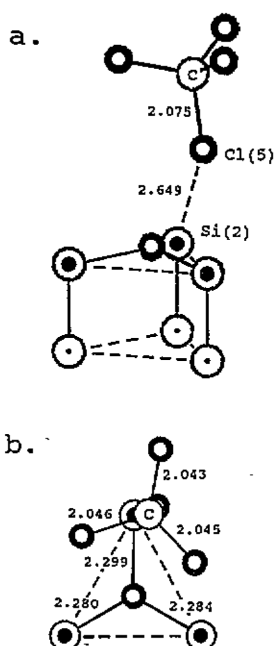

Figure 11. The optimized topology corresponding to the chemisorption of five chlorine atoms near a rest atom C: (a) a side view, (b) a top view. The atoms are labelled as in figure 8.

drawn from these theoretical calculations. Firstly, we find that when an adatom is bonded with successively more chlorines, it moves from its original threefold site (one chlorine), to an adjacent bridge site between its neighbouring first-layer silicon atoms (two and three chlorines), and then to a position essentially on top of one of these neighbours (more than three chlorines). The smallest etching energies correspond to the desorption of $SiCl_4$ and are 0.024 eV for the adatom A sites, and 0.105 eV for the adatom B sites. These etching energies, however, correspond to the $SiCl_4$ complexes bonding to the substrate via chlorine bridging bonds as shown in figure 7. Such configurations would only be expected to occur at fairly high chlorine exposure.

Secondly, we have found markedly different chemisorption behaviour between the rest atom and adatom sites. In contrast to an adatom, a rest atom bonding with up to four chlorine atoms remains close to its original threefold site. The minimum etching energies for $SiCl_2$, $SiCl_3$ and $SiCl_4$ for the rest atom site are all significantly lower than the corresponding adatom values (excluding the above-mentioned $n = 7$ adatom configuration). The total binding energy corresponding to a given number of chemisorbed chlorine atoms is also smaller for a rest atom site than for either an adatom A or adatom B site. We believe that these variations are due to the different orientations of the dangling bonds which would characterize the first- and second-layer silicon atoms of the Si(111)7 × 7 reconstructed surface. For a first-layer silicon atom, the dangling bond is directed upwards, almost perpendicular to the surface. As a result, a monochloride structure on a threefold site, a dichloride configuration on a bridge site, and a trichloride topology on an atop site, corresponds to a very stable tetrahedral structure for such first-layer silicon atoms, with little deformation of their associated dangling bonds. The dangling bonds which would result from a second-layer silicon atom, on the other hand, are oriented at a relatively small angle to the surface, towards the rest atom sites. This prevents the rest atom from forming

stable tetrahedral structures at its adjacent bridge and on-top sites, and constrains it to remain near its original threefold site.

Finally, our results predict that the etching energies of the various $SiCl_x$ ($1 \leqslant x \leqslant 4$) complexes satisfy the general relation $E_e(SiCl) > E_e(SiCl_2) > E_e(SiCl_3) > E_e(SiCl_4)$. Since the most stable $SiCl_4$ configuration yields an etching energy of 0.71 eV, we would expect to observe all species on an Si(111)7×7 surface exposed to atomic chlorine at low temperature, in agreement with experiment. The minimum etching energies for the various species are predicted to be 3.85 eV (SiCl:adatom site), 0.49 eV ($SiCl_2$:rest atom), 0.48 eV ($SiCl_3$:rest atom) and 0.024 eV ($SiCl_4$:adatom). Thus, as the temperature is increased, our results predict that one should first observe $SiCl_4$ desorption from the adatom sites, followed by the etching of $SiCl_2$ and $SiCl_3$ from the rest atom sites. At intermediate temperatures, all of the $SiCl_3$ and $SiCl_4$ should have been removed from the surface, leaving just some of the $SiCl_2$, and all of the SiCl. These results are consistent with the available experimental evidence. Matsuo *et al* [1] observed that the heavily chlorinated species $SiCl_2$, $SiCl_3$ and $SiCl_4$ quickly desorbed from the Si(111) surface after annealing at 300 °C. In addition, Schnell *et al* [11] have reported that SiCl is the only stable species remaining on the Si(111) surface above 400 °C while Szabo *et al* have suggested that some $SiCl_x$ with $x > 1$ is present on the Si(111) surface even after annealing to 800 K [3]. At sufficiently high temperatures, our results suggest that only SiCl will remain on the Si(111)7×7 surface. Moreover, since the SiCl etching energy is significantly larger for the rest atom site than the adatom site, we would expect the high-temperature phase of the chlorine-chemisorbed surface to correspond to single chlorine atoms bonding to the rest atom sites. This is in agreement with the STM work of Villarrubia and Boland [6] which indicates that the high-temperature-annealed surface consists of the rest atom layer of the DAS structure with each rest atom terminated by a single chlorine atom.

Acknowledgments

We would like to thank the Australian Government for the award of a DITAC collaborative exchange grant, and the University of Newcastle and the National Science Foundation of China for providing additional financial support. We would also like to thank Dr M W Radny for his interest and helpful comments during the course of this work.

References

[1] Matsuo J, Karahashi K, Sato A and Hijiya S 1992 *Japan. J. Appl. Phys.* **31** 2025
[2] Whitman L J, Joyce S A, Yarmoff J A, McFeely F R and Terminello L J 1990 *Surf. Sci.* **232** 297
[3] Szabo A, Farrall P D and Engel T 1994 *Surf. Sci.* **312** 284
[4] Suguri M, Shudo K, Komori F and Murata Y 1993 *J. Phys.: Condens. Matter* **5** 6607
[5] Suguri M, Hashizume T, Hasegawa Y, Sakurai T and Murata Y 1992 *J. Phys.: Condens. Matter* **4** 8435
[6] Villarrubia J S and Boland J J 1989 *Phys. Rev. Lett.* **63** 306
Boland J J and Villarrubia V S 1990 *Phys. Rev.* B **41** 9865
[7] Florio J V and Robertson W D 1969 *Surf. Sci.* **18** 398
[8] Sullivan D J D, Flaum H C and Kummel A C 1993 *J. Phys. Chem.* **97** 12051
[9] Gupta P, Coon P A, Koehler B G and George S M 1991 *Surf. Sci.* **249** 92
[10] Aoto N, Ikawa E, Kikkawa T and Kurogi Y 1991 *Surf. Sci.* **250** 235
[11] Schnell R D, Rieger D, Bogen A, Himpsel F J, Wandelt K and Steinmann W 1985 *Phys. Rev.* B **32** 8057
[12] Seel M and Bagus P S 1983 *Phys. Rev.* B **28** 2023
[13] Weast R C (ed) 1977 *CRC Handbook of Chemistry and Physics* 59th edn (Boca Raton, FL: Chemical Rubber Company) pp F219

[14] Thornton G, Wincott P L, McGrath R, McGovern I T, Quinn F M, Norman D and Vvedensky D D 1989 *Surf. Sci.* **211/212** 959
[15] Purdie D, Muryn C A, Prakash N S, Purcell K G, Wincott P L, Thornton G and Law D S L 1991 *J. Phys.: Condens. Matter* **3** 7751
[16] Tong S Y, Huang H and Wei C M 1988 *J. Vac. Sci. Technol.* A **6** 615
[17] Cao Pei-Lin and Smith P V 1995 *J. Phys.: Condens. Matter* **7** 7113
[18] Schegel H B 1982 *J. Comput. Chem.* **3** 214
[19] Frisch M J *et al* 1992 *GAUSSIAN 92* Revision E3 (Pittsburgh, PA: Gaussian)
[20] Dewar M J S, Zoebisch E G, Healy E F and Stewart J J P 1985 *J. Am. Chem. Soc.* **107** 3902
[21] Dewar M J S and Jie C X 1989 *Organometallics* **8** 1544
[22] Jalaliheravi M, McManus S P, Zutaut S E and McDonald J K 1991 *Chem. Mater.* **3** 1024
[23] Brewster M E, Huang M J, Kaminski J J, Pop J J and Bodor N 1991 *J. Comput. Chem.* **12** 1278
[24] Frisch M J *et al* 1995 *GAUSSIAN 94* Revision B.1 (Pittsburgh, PA: Gaussian)
[25] Becke A D 1993 *J. Chem. Phys.* **98** 5648
[26] Dieleman J 1983 *Le Vide les Couches Minces Suppl.* **218** 3