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

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

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Abstract. The chemisorption and etching of fluorine on the Si(111)7×7 surface has been studied using $Si_{90}H_{74}F_n$ ($1 \leqslant n \leqslant 5$) clusters and the atom superposition and electron delocalization molecular orbital (ASEDMO) method. At low coverage, the fluorine atoms are adsorbed onto the dangling bonds. As more fluorines are added, however, a fluorine-bonded adatom is found to move from its original threefold site (one fluorine atom), to an adjacent bridge site (two fluorine atoms) and then to a neighbouring on-top site (three or more fluorine atoms), while the rest atoms remain fixed near their original threefold equilibrium sites. The lowest etching energy is found to be 0.35 eV for SiF_4 desorption from a rest atom site.

1. Introduction

Reactive ion etching of silicon surfaces has become the foremost technique in microelectronic device fabrication. To selectively etch silicon in a plasma reactor, fluorine containing gases such as CF_4 and NF_3 are employed. While the actual etching mechanism is fairly complex, it is widely accepted that the primary chemical reaction is between Si and atomic fluorine. For most basic studies of the surface science aspects of the etching of silicon surfaces, XeF_2 has been used as the source of high-purity atomic fluorine. Although the Si etching rates are different for XeF_2 and atomic fluorine, the surface chemical reactions are similar [1, 2].

A variety of experiments have been performed on Si/F systems [1–6]. The main gas phase product produced in the spontaneous etching of silicon by XeF_2 at room temperature is SiF_4 (~85%) with some Si_2F_6 and Si_3F_8. At higher temperature ($T = 800$ K), however, the major etch product is SiF_2, and the minor etch product SiF_4. The results of soft x-ray photoemission spectroscopy (SXPS) show that during the initial stages of XeF_2 etching of the Si(111)7×7 surface (30 L exposure of XeF_2), the S_2 peak in the photoemission intensity, which corresponds to the core level shift of the surface rest atoms, disappears. The adatom S_1 peak is also reduced, while SiF, and a small amount of SiF_2, appears. At 90 L exposure, the S_1 peak has gone and SiF, SiF_2 and SiF_3 are all present. After greater XeF_2 exposure, some SiF_4 is observed [1]. The etch rate for an initially clean surface increases, reaches a maximum and then decreases as a function of fluence [2].

There have been relatively few theoretical investigations of the interaction of fluorine with the Si(111) surface [7–9]. The activation energy for SiF_4 formation on the Si(111) surface was estimated by Garrison and Goddard to be 1.0 ± 0.2 eV using the configuration $F + F_3Si–SiH_3$ [7]. Van de Walle *et al* [8] studied the interaction of a single fluorine atom with the ideal Si(111)1 × 1 surface and suggested that the precursor to etching was the

introduction of fluorine atoms into the Si–Si backbonds of the surface region. More recently, Gadiyak and Morokov [9] have employed the MINDO/3 method to determine optimized geometries for SiF_x $(1 \leqslant x \leqslant 4)$ chemisorption on Si(111) using the small clusters Si_4H_9, Si_6H_9 and $Si_{10}H_{13}$. Despite these theoretical studies, however, the equilibrium geometries for fluorine chemisorption on the Si(111)7 × 7 surface, and the basic Si–F reactions, are still poorly understood. Our aim in the present study is to improve our understanding of the interaction of fluorine with the Si(111) surface by employing much larger clusters of up to 169 atoms to accurately model the Si(111)7 × 7:F system.

2. Models and method

Five-layer silicon–fluorine cluster models of the form $Si_{90}H_{74}F_n$ $(1 \leqslant n \leqslant 5)$ have been employed to simulate the adsorption of fluorine and its reaction with the Si(111)7 × 7 surface. For this reconstructed surface, which is shown in figure 1, we have used the DAS (dimer–adatom–stacking fault) model reported by Tong *et al* [10]. According to this model, each unit cell contains 12 adatoms 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 were determined empirically by Tong *et al* using the dynamical theory of low-energy electron diffraction. In order to saturate the Si dangling bonds at the extremities of the clusters we have simply employed hydrogen atoms, as in most previous studies.

The calculations have been performed using the atom superposition and electron delocalization molecular orbital (ASEDMO) method which has been successfully applied to many systems [11–14]. In this approach, the extended Hückel energy represents the binding part of the interaction energy which is due to electron delocalization while the atom superposition energy is the sum of the repulsive interatomic interactions. Use of this very fast semiempirical method enables a complete search of configuration space for a variety of different starting geometries. The equilibrium structure in each case is taken to be the final optimized geometry with minimum energy. The various atomic parameter values which we have employed in our calculations are listed in table 1 [12, 15, 16]. These parameters provide a good description of the geometry of the SiF_4 and Si_2F_6 molecules. They also predict a binding energy of 6.28 eV for the removal of a single fluorine atom from the SiF_4 molecule, in reasonable agreement with the experimental value of 6.95 eV [8].

Table 1. The atomic parameters used in the calculations for the valence band s and p states: principal quantum number (n), ionization potential in electron volts (IP) and Slater orbital exponent in atomic units (ζ).

Atom	s			p		
	n	IP	ζ	n	IP	ζ
Si	3	14.68	1.6344	3	8.08	1.4284
H	1	10.40	1.2000			
F	2	40.00	2.5638	2	18.10	2.5500
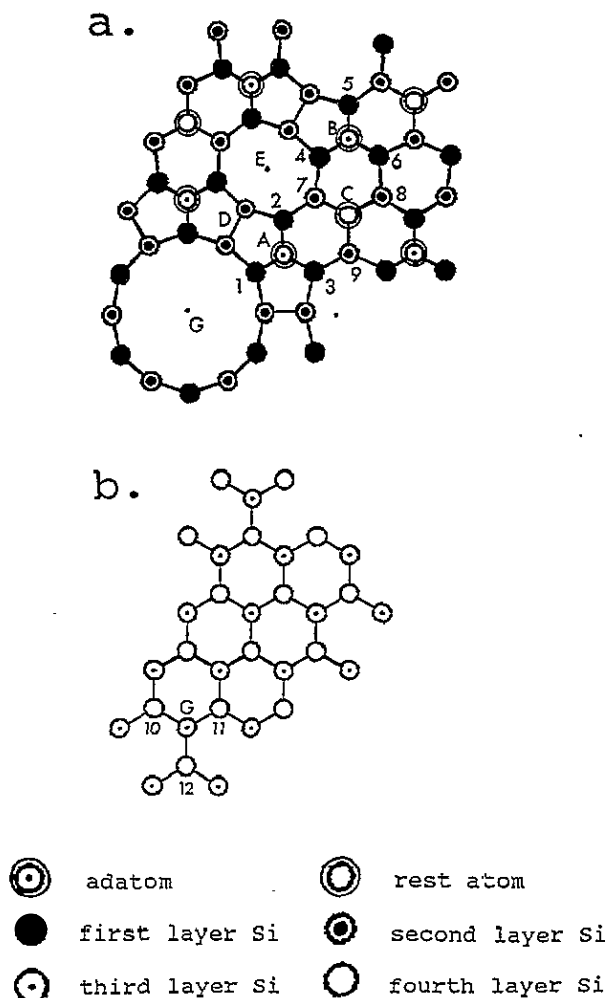
Figure 1. The cluster model Si90H74 used to simulate the Si(111)7 × 7 surface. The hydrogens which have been employed to saturate the bulk dangling bonds are not shown. (a) The adatoms and first- and second-layer silicon atoms; (b) the third- and fourth-layer silicon atoms.

3. Results and discussion

3.1. The clean Si(111)7 × 7 surface

To provide a basis for studying the interactions between chemisorbed fluorine and the Si(111)7 × 7 surface, we have first calculated the binding energies appropriate to the adatoms A and B, and the rest atoms C and G (see figure 1), as well as the associated bond orders of these surface silicon atoms with their nearest neighbours. The latter measure the degree of wavefunction overlap between each pair of sites, and hence, indirectly, the strength of the corresponding bonds. The results are presented in table 2. The calculated binding energies of 6.44 eV and 6.64 eV for adatoms A and B, and 7.60 eV and 7.71 eV for the rest atoms C and G, are in excellent agreement with the values which have been obtained using the semiempirical AM1 method [17]. They are also in reasonably good agreement

with the adatom and rest atom binding energies of 7.40 eV and 8.46 eV which we have determined from *ab initio* Hartree–Fock calculations using 6-31G*(3df, 2p) basis functions and including correlation via the BECKELYP option within GAUSSIAN94 [18]. This latter procedure is claimed to yield binding energies to within 2 kcal mol^{-1} [19]. The bond orders for the adatoms and their nearest neighbours lie in the range 0.70–0.74, while the corresponding rest atom values are slightly higher at 0.76–0.80.

Table 2. Binding energies (in electron volts) of an adatom A, adatom B, rest atom C and rest atom G on the Si(111)7 × 7 surface, and their bond orders with their nearest neighbours.

	Adatom A	Adatom B	Rest atom C	Rest atom G
Binding energy	6.440	6.640	7.602	7.706
Bond order	A-1 A-2 A-3	B-4 B-5 B-6	C-7 C-8 C-9	G-10 G-11 G-12
	0.702 0.723 0.725	0.740 0.741 0.727	0.802 0.803 0.792	0.759 0.765 0.765

Table 3. Various properties characterizing the adsorption of a single fluorine atom onto an adatom or rest atom site of the Si(111)7 × 7 surface: adsorption energy of the fluorine in electron volts (E_c), optimized Si–F bondlength in ångströms, number of electrons transferred to the fluorine (e_t), energy required to remove SiF from the surface in electron volts (E_e), and bond orders between the surface adatom or rest atom and its nearest-neighbour silicon atoms.

	Adatom A	Adatom B	Rest atom C	Rest atom G
E_c (eV)	4.293	4.495	5.282	5.242
Si–F bondlength	1.673	1.679	1.684	1.677
e_t	0.340	0.357	0.403	0.414
E_e (eV)	4.384	4.692	6.567	7.037
Bond order	A-1 A-2 A-3	B-4 B-5 B-6	C-7 C-8 C-9	G-10 G-11 G-12
	0.586 0.608 0.603	0.621 0.617 0.609	0.706 0.712 0.709	0.709 0.714 0.713

3.2. Single-fluorine chemisorption on the Si(111)7 × 7 surface

Six possible adsorption sites were considered for the chemisorption of a single fluorine atom onto the Si(111)7 × 7 surface. These were the sites directly above adatoms A and B, rest atoms C and G, the dimer bridge site D, and the small hole site E. In each case, the height of the fluorine was adjusted to minimize the energy. For the on-top sites, the vertical position of the adatom or rest atom was also optimized. The resulting adsorption energies and optimized F–Si distances are given in table 3. We find that neither the dimer bridge site not the small hole site is a stable chemisorption site. Single fluorine atoms are, however, readily adsorbed onto the dangling bonds which exist at the adatom and rest atom sites of the Si(111)7 × 7 surface. While fluorine chemisorption occurs spontaneously onto the A, B and C sites, the rest atom G sites are found to be characterized by an activation energy of 0.34 eV. This suggests that fluorine chemisorption is less likely to occur at the rest atom G sites. We have therefore restricted our attention in the remainder of this paper to just the adatom A, adatom B and rest atom C adsorption sites. Moreover, since our main interest in the present work is in the formation of the various SiF$_x$ ($1 \leqslant x \leqslant 4$) species observed in the etching of the Si(111)7 × 7 surface, we have only considered the addition of progressively more fluorine at these adatoms and rest atom sites, and have ignored any fluorine adsorption which may occur at other sites on the surface.

In order to more fully characterize the interaction of the chemisorbed fluorine with the neighbouring silicon atoms, three additional properties have been evaluated. These are the number of electrons transferred from the substrate to the chemisorbed F atoms (as determined by a Mulliken population analysis), the bond orders between the fluorine-bonded surface silicon atoms and their nearest neighbours and the binding energy of each SiF complex on the silicon surface. This latter energy we refer to as the etching energy. Values for these three properties are also presented in table 3. Not surprisingly, we observe that each fluorine atom gains a charge in the range 0.34–0.41 e from the substrate.

Comparing the results in tables 2 and 3, it is clear that the bond orders are reduced by around 0.1 as a result of the adsorption of a single fluorine atom. This reduction in the bond orders implies a weakening of the bonds between the F-bonded adatoms or rest atoms and the substrate. Chemisorbing a single fluorine atom on top of the adatom site A, for example, leads to a reduction in the bond orders from (0.702, 0.723, 0.725) to (0.586, 0.608, 0.603). This represents a net decrease of 0.353, consistent with the chemisorbed fluorine gaining 0.34 e. The binding energy of this Si(A)F configuration is 4.38 eV, significantly less than the value of 6.44 eV required to remove an adatom A from the clean surface. It thus follows that an adatom A is easier to remove from the fluorine-exposed surface, as part of an SiF complex, than directly from the clean surface. Similar results apply for the rest atom sites although the energy difference is substantially smaller.

3.3. Two to five fluorines adsorbed onto an adatom A

3.3.1. Two-fluorine chemisorption. When two fluorines are adsorbed onto an adatom A, three different chemisorption sites need to be considered. These are the original threefold site, the nearby bridge site and a site directly above one of the immediately adjacent first-layer silicon atoms (an atop site). For each of these possibilities, we have optimized the F–Si(A) bondlengths, the F–Si(A)–F angle and the height of the adatom. Our results show that the binding energy of Si(A)F$_2$ on the bridge site (4.08 eV) is much larger than that on the threefold (1.74 eV) and atop (0.031 eV) sites. We would thus expect to observe the formation of SiF$_2$ predominantly at the bridge sites. In this case, the F–F direction is found to be perpendicular to the bridging direction so that the F$_2$–Si(A)–Si$_2$ configuration is tetrahedral. The F–Si(A) bondlengths are 1.68 Å, the F–F distance is 2.91 Å, and the Si(A)–Si bondlengths are 2.42 Å. The bond orders of Si(A) with its three original silicon neighbours are 0.626, ∼0.0 and 0.646. We also find no evidence of an energy barrier between the threefold sites and their neighbouring bridge sites. This suggests that a silicon adatom A which bonds to two fluorine atoms will move spontaneously from its threefold site to the immediately adjacent bridge site. The total chemisorption energy for this two-fluorine bridge site adsorption process is 8.24 eV.

3.3.2. Three-fluorine chemisorption. When a third fluorine atom bonds to an adatom A, this adatom is found to move spontaneously from the bridge site to one of its neighbouring atop sites (such as the site Si(3) in figure 1). The topology of the resulting Si(3)–Si(A)F$_3$ configuration is again essentially tetrahedral with the distance between the fluorines and the adatom being ∼1.66 Å, and the Si(A)–Si(3) bondlength being 2.455 Å. The binding energy of the Si(A)F$_3$ complex to the substrate is 2.87 eV and the adatom A bond orders are now (∼0.0, ∼0.0, 0.616).

3.3.3. Four-fluorine chemisorption. Addition of a fourth fluorine atom results in the formation of a tetrahedral $Si(A)F_4$ structure in which one of the fluorine atoms, $F(4)$, bonds directly to one of the neighbouring first-layer silicon atoms (e.g. $Si(3)$), as shown in figure 2. The distance between $F(4)$ and $Si(3)$ is 1.711 Å, and the $F(4)$–$Si(A)$ distance is 1.663 Å. The energy required to break the $F(4)$–$Si(3)$ bond to yield $Si(A)F_4$ is 3.94 eV, while that needed to break the $F(4)$–$Si(A)$ bond to liberate the $Si(A)F_3$ is 5.43 eV.
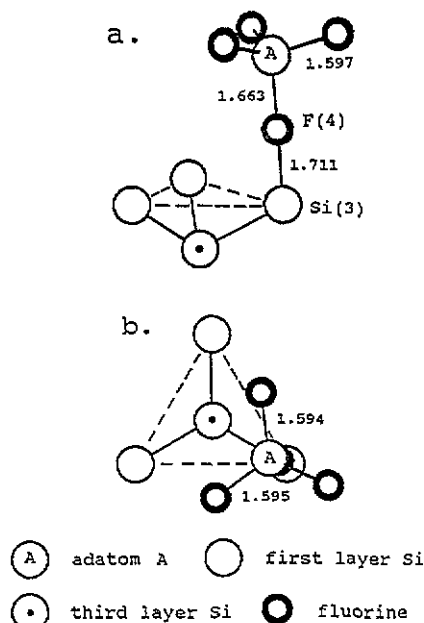
Figure 2. The optimized structure for SiF_4 resulting from the adsorption of four fluorine atoms onto an adatom A: (a) side view; (b) top view. All of the bond lengths in this figure, and all subsequent figures, are given in ångströms.

3.3.4. Five-fluorine chemisorption. Chemisorption of a fifth fluorine atom results in the formation of a slightly deformed $Si(A)F_4$ structure which bonds via a fifth fluorine atom, $F(5)$ say, to the underlying substrate, as shown in figure 3. The bond lengths between $F(5)$ and $Si(3)$, $F(5)$ and $Si(A)$, and $Si(A)$ and the other four fluorine atoms are 1.689 Å, 1.780 Å and ~1.62 Å, respectively. The corresponding bond orders are 0.614, 0.327 and 0.57. It follows that the strength of the bond between $F(5)$ and $Si(A)$ is much weaker than that between $F(5)$ and $Si(3)$, and hence it is easier to break the $Si(A)$–$F(5)$ bond to obtain $Si(A)F_4$. Our calculated etching energy in this case is 1.14 eV.

3.4. Chemisorption of two to five fluorine atoms on an adatom B

The results in this case are very similar to those discussed above for an adatom A, and are presented together with the adatom A results in table 4. As before, successive chemisorption of one, two and three fluorines onto an adatom B site results in the adatom first sitting on top of the threefold site, then moving spontaneously from the threefold site to the bridge site and then finally shifting to a position immediately above one of the adjacent first-layer
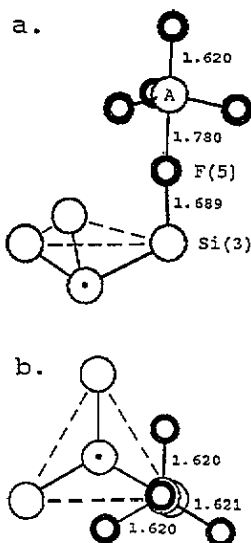
Figure 3. The minimum-energy configuration which results from the chemisorption of five-fluorines onto an adatom A: (a) side view; (b) top view. The delineation of the various atoms is the same as in figure 2.

silicon atoms. This behaviour is in excellent agreement with that determined by Suguri *et al* [20] in a recent scanning tunnelling microscopy study of the Si(111)7 × 7 chlorinated surface. They found that in the monochloride the chlorine atoms are located above the adatom sites, whilst for the dichloride and trichloride the $SiCl_2$ and $SiCl_3$ complexes are positioned above the bridge site and on top of the neighbouring silicon atoms, respectively. It is hoped that similar results will soon be available for the Si(111)7 × 7:F system for direct comparison with the present work.

Table 4. The F_n $(1 \leqslant n \leqslant 5)$ chemisorption sites, and the corresponding SiF_x etching energies in electron volts, E_e, for both adatom A and adatom B[a].

		$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$[a]
Bond site		threefold	bridge	on top	on top	on top
E_e	A	4.384	4.079	2.873	3.943	1.141
	B	4.692	4.340	2.999	3.991	1.142

[a] In this case SiF_4 is bonded to the underlying first-layer silicon atom via a fifth fluorine, as shown in figure 3. The desorption product, however, is still SiF_4.

3.5. Chemisorption of two to five fluorine atoms on a rest atom C

3.5.1. Two-fluorine chemisorption. When two fluorine atoms are chemisorbed onto a rest atom C, we find that this atom simply displaces upwards by 0.69 Å rather than moving to the adjacent bridge site as for adatom chemisorption. The F–F direction is perpendicular to one of the bridging directions (e.g. Si(7)–Si(8) in figure 1) and the bond orders between the rest atom and its neighbouring second-layer silicon atoms are reduced to 0.453 (Si(C)–Si(7)), 0.466 (Si(C)–Si(8)) and 0.175 (Si(C)–Si(9)). The calculated binding energy of the

Si(C)F$_2$ complex to the substrate (i.e. its etching energy) is 2.38 eV (see table 5) while the total chemisorption energy of the two fluorines is 5.42 eV. These values are smaller than the corresponding results for the adatom sites. We believe that this variation in behaviour is directly related to the different orientation of the Si–Si bonds appropriate to the first- and second-layer atoms of the Si(111)7 × 7 reconstructed surface. For a first-layer silicon atom, the dangling bonds which would result from the removal of an adatom would be directed upwards, essentially perpendicular to the surface. Such dangling bonds need to be only slightly deformed to yield a very stable tetrahedral configuration for the monofluoride structure on a threefold site, the difluoride complex on a bridge site or the trifluoride configuration on an atop site. In the case of a rest atom, on the other hand, the dangling bonds which would result from the removal of that rest atom would simply be directed towards that vacant site. The rest atoms thus remain close to their original positions even when bonded with two or more fluorines. Movement to one of the adjacent bridge or on-top sites, as in the adatom case, would require a great deal of bond distortion which is, of course, energetically unfavourable.

Table 5. The etching energies in electron volts, E_e, for the SiF$_x$ species resulting from the chemisorption of n fluorine atoms ($1 \leqslant n \leqslant 5$) at a rest atom C site.

n	1	2	3	4	5
E_e (eV)	6.57 ($x = 1$)	2.38 ($x = 2$)	2.55 ($x = 2$)	0.65 ($x = 3$)	2.60 ($x = 3$)
			2.24 ($x = 3$)	0.48 ($x = 4$)	0.35 ($x = 4$)

3.5.2. Three-fluorine chemisorption. When three fluorine atoms are chemisorbed on the rest atom C, the minimum-energy structure is as shown in figure 4. One of the fluorine atoms, F(1), bridges between the rest atom C and one of the neighbouring silicon atoms, Si(7), while the other two fluorine atoms are bonded directly to the rest atom. The rest atom has moved 0.868 Å out of the surface (compared to its original clean surface position) and slightly closer to the bridge site between the other two neighbouring silicon atoms, Si(8) and Si(9). Two etching processes are thus possible: either the Si(C)–F(1) bond will break to yield Si(C)F$_2$, or the Si(7)–F(1) bond will break to produce Si(C)F$_3$. The corresponding etching energies are 2.55 eV and 2.24 eV, respectively.

3.5.3. Four-fluorine chemisorption. The optimized structure when four fluorines are chemisorbed near the rest atom C site is shown in figure 5. As before, the fluorine atom F(1) bridges between the rest atom C and the neighbouring silicon, Si(7). The remaining three fluorines are bonded directly to the rest atom with a bond length of approximately 1.61 Å. The rest atom C is now 1.385 Å above its clean surface position and shifted slightly towards the adjacent Si(8). The energy required to remove Si(C)F$_3$ from this fluorine-chemisorbed surface, via the breaking of the Si(C)–F(1) bond, is calculated to be 0.65 eV, while the etching energy for the Si(C)F$_4$ complex, which is liberated by the breaking of the Si(7)–F(1) bond, is 0.48 eV.

3.5.4. Five-fluorine chemisorption. Our optimized structure when an additional fluorine is chemisorbed near the above four-fluorine configuration is shown in figure 6. In this case, two fluorine atoms, F(1) and F(5), occupy bridging sites between the rest atom and the neighbouring silicon atoms Si(7) and Si(9), whilst the three remaining fluorine atoms are
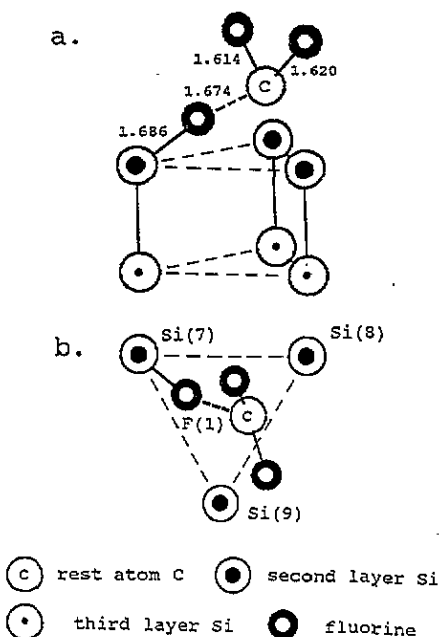
a.

b.

Figure 4. The equilibrium geometry produced by the chemisorption of three fluorine atoms onto a rest atom C: (a) side view; (b) top view.
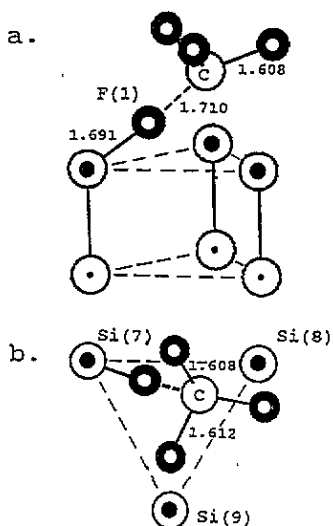
a.

b.

Figure 5. The optimized structure which occurs when four fluorines bond at a rest atom C site: (a) side view; (b) top view. The atom labelling is the same as in figure 4.

bonded directly to the rest atom with an Si–F distance of approximately 1.62 Å. The rest atom has moved slightly away from the adjacent silicon Si(8) and vertically upward by an additional 0.125 Å. The calculated etching energy for Si(C)F$_4$, with either F(1) or F(5)

remaining on the surface to saturate the Si(7) or Si(9) dangling bond, is 0.35 eV. By contrast, the etching energy for Si(C)F$_3$, with both F(1) and F(5) remaining on the surface to saturate the Si(7) and Si(9) dangling bonds, is 2.60 eV. The very low etching energy which we have calculated for SiF$_4$ suggests that this species should be very easy to desorb from the surface even at room temperature. Moreover, comparison with the adatom SiF$_4$ etching energy of 1.14 eV leads to the conclusion that etching of this species should occur preferentially at the rest atom sites. This is consistent with the soft-x-ray spectroscopy studies [1].
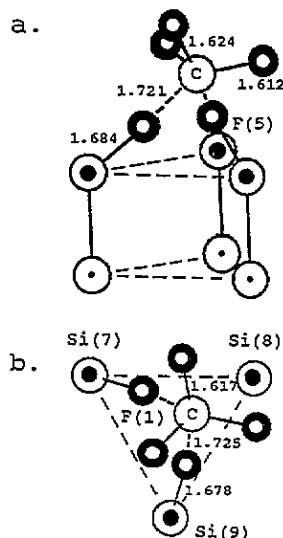

Figure 6. The minimum-energy configuration corresponding to five-fluorine-atom chemisorption onto a rest atom C: (a) side view; (b) top view. The delineation of the various atoms is the same as in figure 4.

4. Conclusions

Several important conclusions can be drawn from this work. Firstly, we observe that when both adatom and rest atom silicons become bonded to fluorine there is a transfer of charge, from the overlap region between these silicons and their immediate neighbours, to the fluorine atoms. This results in a reduction of the bond orders appropriate to these surface silicon atoms and their adjacent silicons, and a substantial decrease in the strength of these Si–Si 'backbonds'.

Secondly, we have found that as successively more fluorine atoms bond to an adatom it moves from its original threefold site (one fluorine atom) to a neighbouring bridge site between two adjacent Si atoms (two fluorine atoms), and then to an atop site above one of these nearest-neighbour silicon atoms (three or more fluorine atoms). The minimum etching energy for SiF$_x$ ($1 \leqslant x \leqslant 4$) at an adatom site is 1.14 eV for SiF$_4$.

Finally, we have found that a fluorine-bonded rest atom is unable to move to its neighbouring bridge or atop sites to form stable tetrahedral structures as in the adatom case, but essentially just moves normal to the surface, close to its original position. This is a direct consequence of the orientation of the dangling bonds at the rest atom sites and

leads to rather unusual bonding configurations when several fluorine atoms are chemisorbed in the vicinity of a rest atom site. As a result, the etching energies for the SiF$_x$ complexes with $x \geqslant 2$ are lower for the rest atom sites than the adatom sites, with the lowest value being only 0.35 eV for SiF$_4$. We would thus expect the dominant etching mechanism to result from the desorption of SiF$_4$ from the rest atom sites. This is in good agreement with the soft-x-ray photoemission spectroscopy experiments.

Acknowledgments

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