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Chemisorption of fluorine and chlorine on a Si (111) surface

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Abstract. The total energy profiles along the onefold on-top site axis and the threefold hollow site axis of chemisorption of fluorine and chlorine on a Si (111) surface have been determined by using the CNDO method. Clusters of 19 and 23 silicon atoms, respectively, are used to simulate onefold-site and threefold-site chemisorbed systems. The distance between the on-top site and the nearest silicon atoms is found to be 2.18 Å, which compares favourably with the experimental value of 2.03 Å. We also find that the fluorine atom can penetrate into the silicon substrate while the chlorine atom cannot. The on-top site is the most stable site for both chemisorbed systems.

1. Introduction

The study of laser-induced chemical etching of solid surfaces by halogen gases has been actively pursued in recent years (see, e.g., Chuang 1983, 1984). It is well recognised that the laser-induced etching process promises well as a potential technique for processing electronic materials. Understanding the basic mechanism of chemisorption of halogens on semiconductor surfaces is the first step towards process control and optimisation of various parameters for this powerful technique.

In the present paper, we use a self-consistent semi-empirical molecular method—namely the complete neglect of differential overlap (CNDO) method—to study the chemisorption of fluorine (F) and chlorine (Cl) on silicon (111) surfaces. The variation of the total energy profile with the perpendicular distance of the chemisorbed atom from the surface is carefully determined.

2. Theory

The CNDO method involves self-consistent calculations yielding solutions similar to Hartree–Fock solutions and giving total energies and wavefunctions. It is described as semi-empirical because some of the matrix elements corresponding to the electron overlap in the Fock matrix are either neglected or approximated by semi-empirical parameters. The semi-empirical parameters introduced are (i) the orbital exponent ξ, (ii) the electronegativity E and (iii) the bonding parameter β. Each orbital of the valence electrons of an atom has particular values of these three parameters. One of the attractive features of the CNDO method is that it can yield information on the excited states,

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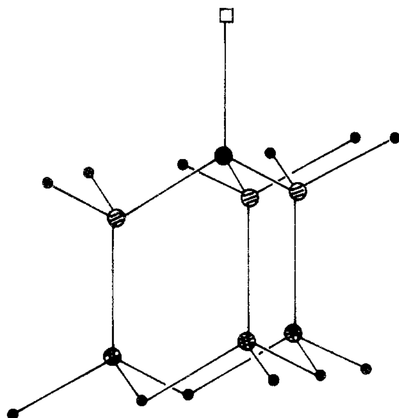

Figure 1. The 19-atom cluster used in the present work to simulate halogen chemisorbed on the on-top site of Si (111). Open square: halogen atom; large full circle: Si atoms at the first layer; hatched circles: Si atoms at the second layer; cross-hatched circles: Si atoms at the third layer; small full circles: Si* pseudo-atoms.

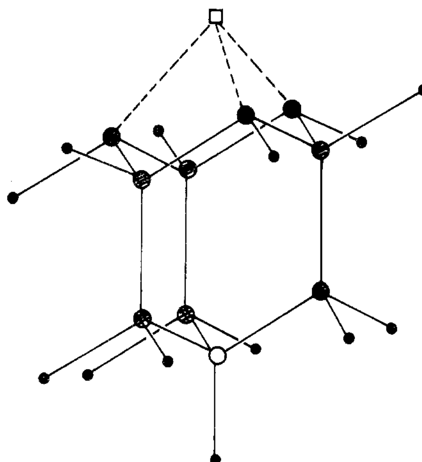

Figure 2. The 23-atom cluster used in the present work to simulate halogen chemisorbed on the threefold site of Si (111). The key is as for figure 1, but in addition there is an open circle representing Si atoms at the fourth layer.

although achieving convergence to self-consistency in excited states may be difficult sometimes. The information on excited states is particularly useful in the study of solid–gas interface systems subjected to laser beam irradiation. Furthermore, using the CNDO method we are able to calculate and compare the Mülliken charge transfers among the various atoms in the cluster, both at ground states and at excited states. The CNDO method has been employed successfully in the studies of defects in Si (Stoneham 1985, Ong and Khoo 1987) and the reconstructed Si (100) surface (Ong and Chan 1988).

3. Calculation clusters and CNDO parameters

There are two possible chemisorbed sites for halogen atoms on Si (111) surfaces, namely the on-top site and the threefold site. The clusters used to simulate the Si (111) surface for each site are similar to those proposed by Seel and Bagus (1983). The cluster for the on-top site is shown in figure 1. It consists of three surface layers—a total of seven silicon atoms. The first layer has one atom, while the second and third each have three. The dangling bonds at the edges of the silicon cluster are saturated by 12 pseudo-atoms, Si*, consisting of one or two sp^3 hybrids. The cluster for the three-fold site is shown in figure 2. It consists of four surface layers—a total of ten silicon atoms; three atoms each at the first, second and third layer, while there is only one atom at the fourth layer. The dangling bonds at the edges of the silicon cluster are also saturated by 13 pseudo-atoms. The CNDO parameters used are summarised in table 1. The Si parameters are those determined by Harker and Larkins (1979). The parameters for Si* are similar to those for Si except for the bonding parameter, which is set to zero, as discussed by Khoo and Ong (1987).

To investigate the suitability of the CNDO parameters for F and Cl given by Pople and Beveridge (1970) (hereafter termed standard parameters) in the present study, we

Table 1. The CNDO parameter used. Standard parameters for Cl and F are given in brackets.

Atoms	Orbital exponents, ξ (au^{-1})	Bonding parameters, β (eV)	Electronegativity, E_s (eV), E_p (eV)
Si	1.54	−6.4	6.3, 4.5
Si*	1.54	0	6.3, 4.5
Cl	2.03	−16.1	16.00, 7.00
	(2.03)	(−12.2)	(16.00), (7.00)
F	2.68	−47.1, −6.0	32.2724, 11.08
	(2.6)	(−39.0) (−6.0)	(32.2724), (11.08)

carried out CNDO calculations for the free SiF_4 and $SiCl_4$ molecules. The Si–F and Si–Cl equilibrium bond lengths and the respective bond energies were also calculated. The calculated values and the experimental values are listed in table 2. Using the standard parameters for F and Cl, the calculated bond lengths are about 10–20% larger than the experimental values, and the calculated bond energies are very much lower ($\simeq$40%) than the experimental values. In the present study of the chemisorption of F and Cl on a Si (111) surface, the bond energy has to be determined accurately. We therefore decided to reparametrise the Cl and F parameters. The new set of CNDO parameters for F and Cl were obtained by altering the standard parameters until the calculated bond energies agreed with the experimental values for SiF_4 and $SiCl_4$ respectively. The calculated Si–F (Si–Cl) bond lengths in the SiF_4 ($SiCl_4$) molecules obtained using the new F and Cl parameters are about 8–10% larger than the experimental values, and also agree well with the sums of the covalent radii (compiled by Kittel 1976) of the constituent atoms. Since the environment of chemisorbed atoms F (Cl) on the Si (111) surface is similar to that of F (Cl) in the SiF_4 ($SiCl_4$) molecules, the new set of Cl (F) parameters determined in the present work, together with the set of Si parameters determined by Harker and Larkins (1979), can be used to study the chemisorption of F (Cl) on the Si (111) surface. We used the Harwell computer code MOSES to perform the CNDO calculation (Harker and Lyon 1979).

Table 2. Predicted bond lengths and binding energies for SiF_4 and $SiCl_4$.

	Bond length (Å)				Bond strength (eV)		
	Present calculation				Present calculation		
	Standard parameter	New parameter	Experiment†	Sum of covalent radii‡	Standard parameter	New parameter	Experiment†
SiF_4	1.81	1.75	1.54	1.81	3.88	5.85	5.85
$SiCl_4$	2.23	2.16	2.01	2.16	1.97	3.95	3.95

† Bailar *et al* (1973).
‡ Kittel (1976).

4. Calculations and results

The two most probable chemisorption sites for adatoms are onefold on-top and threefold hollow bridging sites (Seel and Bagus 1983). Many experimental and theoretical results suggest that the onefold on-top site is the most stable site for adatoms Cl and F (Rowe *et al* 1977, Seel and Bagus 1983). However, the electronegativities of adatoms Cl and F are much larger than that of the substrate Si atoms. As a result, chemisorption of Cl or F at the threefold hollow bridging sites may also be stable. For chemisorption at the threefold sites, the adatom may be outside the substrate surface or it may penetrate into the surface, lying between the first and the fourth layer. Recent SEXAFS measurements conducted by Citrin *et al* (1983) accurately determined the bond length between the on-top-site Cl adatom and the substrate Si atom to be 2.03 ± 0.03 Å by comparing the SEXAFS data for the Si–Cl phase shift and the corresponding distance in $SiCl_4$.

In the present calculation, we assume that the substrate surface remains in its primitive (1 × 1) surface structure after chlorination and fluorination. This assumption has been confirmed by the LEED experiment of Rowe (1975a, b) for the case of Cl–Si (111) chemisorption. We calculate the total energy profile of the chemisorbed system by varying the vertical distance between the adatom and the first (outermost) Si substrate layer along the on-top axis and the threefold axis. Along the on-top axis, only one minimum-energy site is obtained for both the Cl and F chemisorbed systems. The calculated equilibrium Cl–Si (111) distance of 2.18 Å (see table 3) agrees very well with the experimental value of 2.03 Å obtained by Citrin *et al* (1983). For the case of the threefold axis, there are two minimum-energy chemisorbed sites for F; one is outside the surface and the other inside the substrates (see figure 3). For Cl, only the chemisorbed site is found outside the surface. In figure 3 we note that the F adatom outside the surface needs about 0.3 eV in order to overcome the barrier and penetrate into the Si substrate. The fact that it is the F and not the Cl adatom that can penetrate into the Si substrate agrees well with the observations in plasma etching (Winters and Houle 1983) and a Hartree–Fock calculation (Seel and Bagus 1983). The results of the present calculation, the results of previous theoretical investigations and the experimental data are summarised in table 3. Among the various theoretical investigations, Zhang and Ye (1980) and Tang *et al* (1986) used the extended Hückel method, Bachelet and Schluter (1983) used the pseudopotential method, and Seel and Bagus (1983) used the Hartree–Fock method in their investigation. The binding energy reported in table 3 is calculated by using the formula below:

$$B = E_{\mathrm{Si+A}} - (E_{\mathrm{Si}} + E_{\mathrm{A}})$$

where E_{Si} is the total energy of the silicon cluster, E_{A} is the total energy of the adatom atoms and $E_{\mathrm{Si+A}}$ is the total energy of the Cl or F chemisorbed surface. This method is similar to that used by Seel and Bagus (1983).

5. Conclusions

We found that the on-top site is the most favourable site for both F and Cl chemisorbed systems. The distance between the optimum on-top site and its nearest silicon neighbour is nearly equal to the sum of the covalent radii. The binding energy is slightly larger than the bond strength of the respective silicon molecules. In the threefold site, the F atom can either stay outside of the silicon surface or penetrate into the silicon substrate, and

Table 3. Calculated equilibrium vertical distances (d) of the chemisorbed atoms from the outermost surface Si layer and the binding energies for the chemisorption. Results from previous theoretical investigations and the experimental data are included for comparison. Negative d-values indicate that the adatom has penetrated into the lattice.

	F				Cl			
	On-top site		Threefold site		On-top site		Threefold site	
	d (Å)	E (eV)	d (Å)	E (eV)	d (Å)	E (eV)	d (Å)	E (eV)
Experiment (Citrin *et al* 1983)	—	—	—	—	2.03	—	—	—
Present calculation	1.78	−5.92	0.72	−0.94	2.18	−4.27	1.02	−1.50
			−0.92	−1.21				
Zhang and Ye (1980)	—	—	—	—	1.85	−3.81	—	—
Tang *et al* (1986)	1.53	−4.7	−2.2	−3.1	—	—	—	—
Bachelet and Schluter (1983)	—	—	—	—	2.02	0	1.53	+1.30
Seel and Bagus (1983)	1.68	−3.25	1.3	−0.56	2.24	−1.63	1.9	−0.4
			−1.4	−0.49				

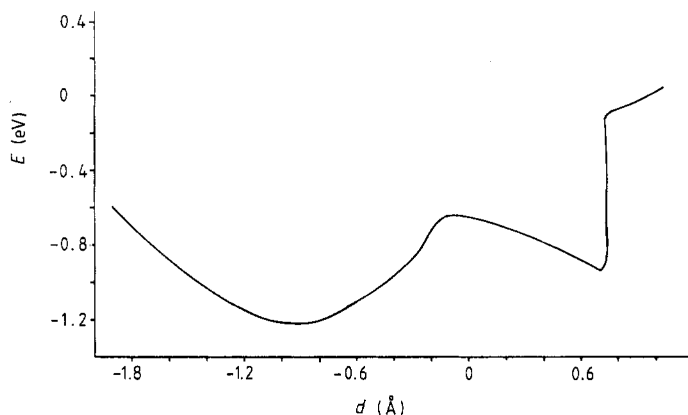

Figure 3. The binding energy (E) profile of the F–Si (111) chemisorbed system. d is the vertical distance of the chemisorbed atoms from the outermost surface Si layer along the threefold site axis. Negative d-values indicate that the adatom has penetrated into the bulk silicon and positive d-values indicate that the adatom is outside the silicon surface.

the site inside the substrate is found to be more stable than the one outside; this is also observed in the experiment of Chuang (1984). This behaviour is probably due to the Coulomb interaction of charge transfer between the F and Si atoms favouring the site inside the substrate. The distance between the F atom and its nearest-neighbour silicon is found to be 2.26 Å (2.23 Å) for F lying outside (inside) the substrate. However, the nearest silicon neighbour of the F atoms inside the Si substrate are those at the second layer. In the Cl–Si (111) chemisorbed system, the Cl atom cannot penetrate into the substrate. The distance between the Cl and its nearest silicon neighbours is 2.16 Å, which is shorter than that for the F–Si system.

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