Cl-Cl interaction and chlorine adsorption mechanism on Si(100)2*1

Cl–Cl interaction and chlorine adsorption mechanism on Si(100) 2 × 1

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Abstract. The characterization and interaction between Cl atoms on the Si(100) 2 × 1 surface have been studied by the atom superposition and electron delocalization molecular orbital theory, using 2 × 1 symmetric- and buckled-dimer models for this surface. Two stable adsorption sites for Cl bonding have been found in the symmetric-dimer model. One is along the surface dangling bond, with a Cl–Si bond length of 1.97 Å and a bond angle of 21° to the surface normal; the other is the bridge site with a Cl–Si bond length of 1.99 Å. The adsorbed Cl atom on the bridge site will block further adsorption on the dangling-bond site in the same Si dimer. A reasonable explanation for slowing chlorine adsorption kinetics at a coverage of about 0.7 Cl/Si is given. In the buckled-dimer model, Cl is predicted to adsorb onto the dimer up-atom site, with a Cl–Si bond length of 1.92 Å and a bond angle of 19°. We guess that the buckled dimer on the Si(100) 2 × 1 surface will be converted into a symmetric dimer after Cl adsorption.

1. Introduction

Study of the adsorption of chlorine on silicon surface is of both fundamental and technological importance, particularly in view of the potential application of halogens as an etching agent in the manufacture of patterned silicon substrates for very-large-scale integrated circuits. Meanwhile, the simplicity of the expected monovalency of halogens may help us to learn how the chemisorption depends on the reconstruction of the substrate and how the chemisorption itself influences the surface relaxation [1–8].

The adsorption of chlorine on the Si(100) surface has always been studied using various surface science techniques [3, 4, 9–14]. However, some controversial conclusions are reported in the literature. For example, earlier measurements involving surface polarization-dependent near-edge x-ray adsorption fine structure (NEXAFS) at the Cl(ads) K edge [12] indicated that the Si–Cl bond length is about 1.95 Å, with the Si–Cl bond tilted about 25° off normal. UV photoemission studies of Cl_2 adsorption on Si(100) 2×1 at room temperature [9] also indicated a tilted Cl–Si bond. However, studies of chlorine adsorption on Si(100) 2 × 1 at about 500 K [10, 11] using a vicinal single-domain surface conclude that the Si–Cl bond is perpendicular to the (100) surface (within 10°) based on the polarization dependence of the Cl(ads) K edge NEXAFS measurements. This perpendicular bond geometry is proposed to result from atop bonding of Cl on a buckled (asymmetric) dimer with a Si–Cl bond length of about 2.00 Å. Later, two Cl adsorption states which are terminally bonded Cl and bridge-bonded Cl are observed on the Si(100) 2 × 1 surface, using the digital electron-stimulated desorption ion angular distribution (ESDIAD) method [14]. The tilt angle for terminally bonded Cl is 25 ± 4° off normal. The irreversible conversion from bridge-bonded Cl to

terminally bonded Cl occurs over a temperature range 273–673 K, forming the more stable terminally bonded Cl species. Cl_2 adsorption at 120 K resulting in a decrease in surface order is indicated by the reduction in the relative intensity of the one-half-order LEED beams [14].

In our recent study of Br on Si(100) 2×1 [15], two stable adsorption sites for Br bonding have been found in the symmetric-dimer model. One is along the surface dangling bond, with a Br–Si bond length of 2.16 Å and a bond angle of 19° with the surface normal; the other is the bridge site with a Br–Si bond length of 2.13 Å. As our data for Br on Si(100) 2×1 are similar to the recent ESDIAD study [14] of Cl on Si(100) 2×1 and the foregoing controversial reports, it is worthwhile to calculate the system of Cl on Si(100) 2×1 to obtain a deeper insight into the mechanism of this adsorption.

The AES results on Cl_2 adsorption by Gao *et al* [14] show that Cl_2 adsorption at about 100 K has a relatively high adsorption rate initially up to about 0.7 Cl/Si and then undergoes a sudden reduction in adsorption rate. These results are attributed to the repulsive interactions between Si–Cl species by Gao *et al*. In this paper, we have studied this kinetic break and a new model to explain the break is proposed.

2. Models and method

A four-layer silicon cluster model $Si_{31}H_{36}Cl_x$ ($x = 1, 2$) is adopted to simulate the Cl bonding, migration and interaction between Cl adatoms on Si(100) 2×1. For the Si(100) surface, we use both the 2×1 symmetric- and the asymmetric-(buckled)dimer models reported by Roberts and Needs [16]. For the symmetric model, the displacements of the first-layer Si atoms making up each dimer are 0.331 Å in the [100] direction (closer to the second layer) and ±0.803 Å in the [011] direction (to form dimers), and the second-third- and fourth-layer Si atoms also have some small displacements with respect to their unreconstructed bulk places; for the 2×1 asymmetric-dimer model, the buckling angle is about 6.9°, and the displacements of the above four-layer atoms are more complex. Details have been given in [16]. In our calculations, the coordinates of Si substrates are frozen unless specially needed. The H atoms in the cluster are used only to saturate the bulk Si dangling bonds (DBs) as in most studies concerning silicon surfaces.

The atom superposition and electron delocalization molecular orbital theory is used in the present calculation. This fast semi-empirical method has been applied to the study of adsorption on both metal and semiconductor surfaces and has proved to be reliable in determining the bonding geometries and force constants [17–19]. The parameters used in the calculations are listed in table 1 [20, 21].

Table 1. Atomic parameters in calculations; principal quantum number n; ionization potential I_p and Slater orbital exponent ζ.

Atom		S			P	
	n	I_p (eV)	ζ (au)	n	I_p (eV)	ζ (au)
Si	3	14.69	1.6344	3	7.59	1.4284
H	1	11.61	1.20			
Cl	3	22.54	2.3561	3	10.97	2.0387

3. Results and discussion

First, we study the Cl adsorption using the 2×1 symmetric-dimer model. For each adsorption site, including the pedestal A, bridge B, cave C, valley bridge D, side bridge E, atop F and DB G (figure 1), the total energies (TEs) of the cluster versus the adsorption height are calculated in detail. The pedestal, cave, valley bridge and side bridge sites are found to be unfavourable since there are negative binding energies for the Cl atom on these sites, while the bridge, atop and DB sites are capable of adsorbing a Cl atom with binding energies of 1.55 eV, 0.88 eV and 1.67 eV, respectively. When the Cl–Si bond length l and angle θ to the surface normal are carefully varied, further calculations show that the most favourable site is on the DB site with $l = 1.97$ Å, $\theta = 21°$ and a bond energy of 1.672 eV (figure 2).

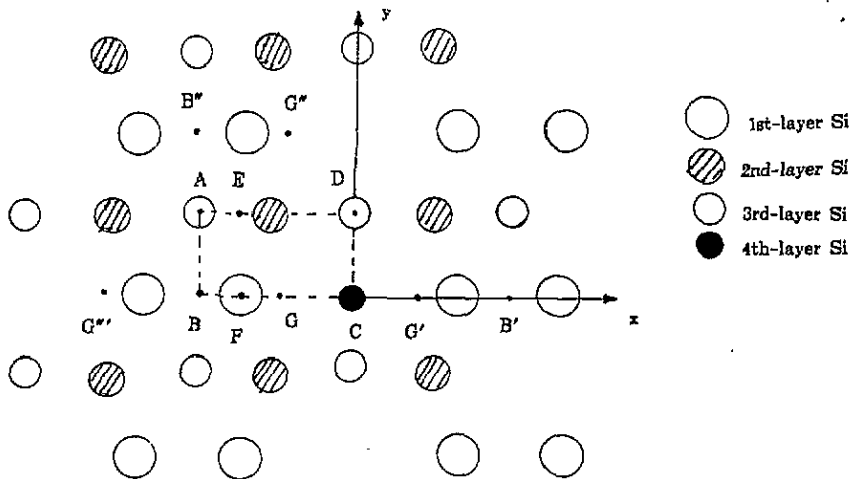Figure 1. Cluster model $Si_{31}H_{36}Cl_x$ ($x = 1.2$) for Cl adsorption on the Si(100) 2 × 1 surface and the possible adsorption sites: A, pedestal; B, bridge; C, cave; D, valley bridge; E, side bridge; F, atop; G, DB. For convenience, the H atoms saturating the bulk DBs are not plotted.
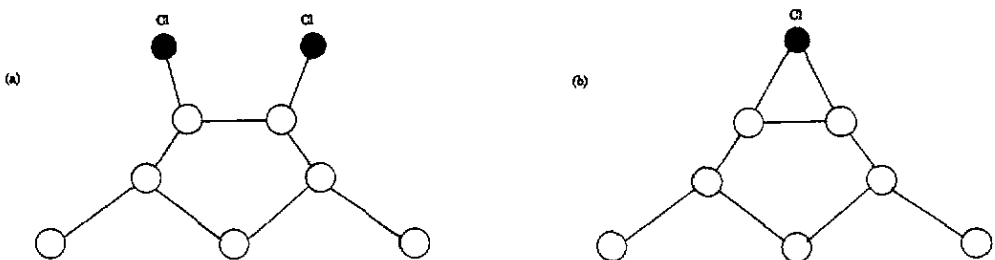

Figure 2. Schematic diagrams of Cl adsorption geometries on the DB and bridge sites.

In order to obtain the properties of these bonds, we have employed a Morse-type expression to simulate the TE curve versus the bond length (bond angle, adsorption height, etc) near the equilibrium values [22]:

$$E(x) = E(x_0) + [a + b(x - x_0) + c(x - x_0)^2]\{1 - \exp[-\alpha(x - x_0)]\}^2$$

where x is the bond length (bond angle, adsorption height, etc), $E(x)$ is the TE at x, and x_0, $E(x_0)$, a, b, c, and α are the parameters to be determined. Using this optimum technique, we may find an accurate bond length, binding energy and force constant $(k = \mathrm{d}^2E/\mathrm{d}^2x|_{x=x_0} = 2a\alpha^2)$.

For the DB site Cl, a bond length of 1.97 Å and $\theta = 21°$ are obtained, which agree with the NEXAFS result of about 1.95 ± 0.04 Å [12] and the ESDIAD result of $25 \pm 4°$ off normal [14]. As we know, the sum of the respective covalent radii is 2.16 Å and, for ideal tetrahedral bonding, the above angle would measure 19.47°. Our result on the Cl–Si bond length is only slightly shorter than the sum of the respective covalent radii but somewhat longer than our calculated bond length in $SiCl_4$ of 1.90 Å (the experimental value is 1.996 Å). As the bond between one dimer atom and its nearest atom beneath whose length is 2.286 Å longer than the bond length in $SiCl_4$, and the angle to the dimer direction is 72.17°, also larger than ideal tetrahedral bond angle, we think that it is reasonable that the Cl–Si bond angle to surface normal is slightly larger than 19.47° because of the decrease in repulsive interaction between the Cl adatom and substrate. The Cl–Si bond stretching and bending frequencies are calculated to be 555 cm^{-1} and 163 cm^{-1}, respectively, in good agreement with the observed frequency of 550–600 cm^{-1} [14] (no experimental bending frequency) as in our recent work on C_2H_2–Si(100) 2×1 [18] and C_2H_4–Si(100) 2×1 [19].

Except for the DB site, the bridge site is found to have a binding energy of 1.55 eV, only 0.12 eV less than that of the DB site. The bond length is 1.99 Å, and the perpendicular and parallel vibrational frequencies are 570 cm^{-1} and 355 cm^{-1}, respectively. Since our calculated perpendicular vibrational frequency is in contrast with spectra obtained by HREELS [14] in which this mode in general is expected to be the most intense, we suggest that the actual vibrational mode of the bridge-bonded Cl adatom perhaps deviates from the normal to the surface.

In order to determine the stability of the Cl adatom on the bridge and atop site, we calculated the binding energy and adsorption heights for various positions between the bridge and DB sites. The results are shown in figure 3. It is obvious that the Cl adatom on the atop site will migrate to the DB site with no barrier, but the bridge site is also a stable equilibrium site, and the migration barrier for Cl adatom transition from the bridge site to the DB site is about 1.0 eV. The high migration barrier indicates that the Cl adatoms cannot easily migrate from the bridge site to the DB site, which is in agreement with HREELS and ESDIAD results [14]. These results show that the transformation is completed at about 673 K.

The Cl–Cl interactions on Si(100) 2×1 are calculated and the results are listed in table 2. Our results show that no or little interaction between Cl adatoms on the adjacent or same dimer DB sites is found. However, the repulsive interaction between B and DB (see figure 1) is so large that, when one Cl atom occupied the bridge site, the binding energy of the Cl atom on the DB in the same dimer will be negative. This implies that the bridge-bonded Cl will block two DB sites in the same dimer.

Table 2. Interaction energies (IES) between two Cl adatoms on sites G and B, etc.

Sites	G–B	G–G′	G–G″	G–G‴	G–B′	G–B″	B–B′	B–B″
IE(eV)	7.97	−0.11	0.00	−0.52	0.03	0.01	0.04	0.01

Because there is little repulsive energy between bridge-bonded Cl and dangling-bonded Cl in a different dimer, the Cl atom can be adsorbed in a disordered manner onto these two
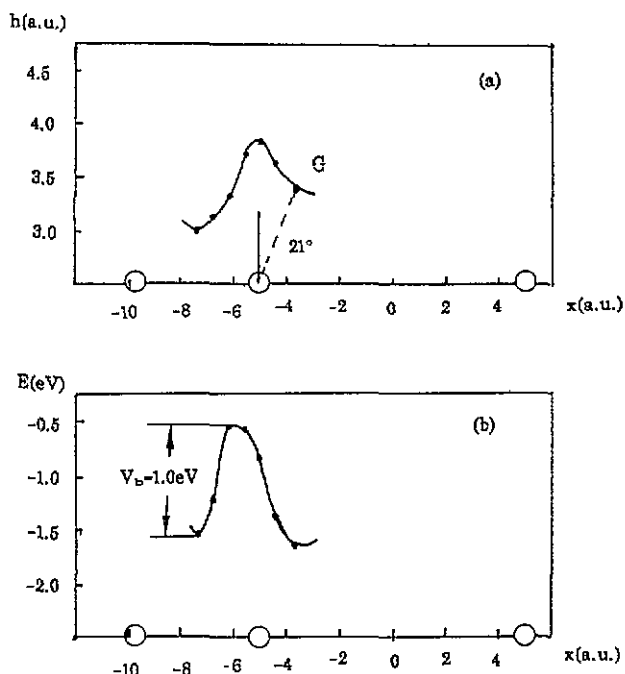
h(a.u.)

E(eV)

Figure 3. Adsorption heights and the corresponding TE for the Cl adatom on various positions between the bridge site and the neighbouring DB site. Here, we have adopted the TE for the Cl adatom at infinity as zero.

kinds of adsorption site. This indicates that chlorine adsorption results in a decrease in the surface order, which is in agreement with the LEED result of the reduction in the relative intensity of the one-half-order LEED beams [14].

As shown in [14], the adsorption of Cl on Si(100) 2 × 1 at about 100 K has a relatively high adsorption rate initially and then undergoes a sudden reduction in adsorption rate at a coverage of about 0.7 Cl/Si. Because the binding energies of Cl on the bridge site and on the DB site are almost equal, it is a reasonable assumption that the adsorption coefficients on the DB sites and on the bridge sites are equal. As mentioned above, a Cl adatom on the bridge site will block two DB sites in the same dimer; generally speaking, every two dimers can adsorb three Cl atoms at most, two on the DB sites in one dimer and another on the bridge site in the other dimer, i.e. about 0.75 Cl/Si is expected. After that, only if the adsorbed Cl atom on the bridge site surmounts the energy barrier and migrates to the DB site, can one more Cl atom occupy the other DB site in the dimer. We think that this is a reasonable interpretation for slowing the chlorine adsorption kinetics on Si(100) 2 × 1 at the coverage of about 0.7 Cl/Si as indicated in [14].

Since a scanning tunnelling microscopy (STM) study [23] and first-principles calculations [16] have both shown that non-buckled and buckled dimers coexist on the Si(100) surface, a buckled-dimer model must be included in our calculation. Detailed calculations have been performed for Cl adsorption on the buckled-dimer surface. Cl atoms are found to adsorb onto the dimer up-atom, down-atom and bridge sites with binding energies of 2.22 eV, 0.35 eV and 1.58 eV, respectively. For the bridge site and the dimer down-atom site, Cl–Si bond lengths of 1.99 Å and 1.97 Å, and bond angles of 7° and 12° to the surface normal, respectively, are found. However, the most favourable site is on the dimer up-atom with a

Si–Cl bond length of 1.92 Å and a bond angle of 19° to the surface normal. As we know, the surface buckling angle is about 6.9°; thus one should expect the bond angle to decrease to 14°, according to results using the symmetric-dimer model. The analogous problem is also found in our recent work of Br on Si(100) 2 × 1 using the buckled-dimer model [15]. We think that the repulsive interaction between the Cl adatom on the up-atom site and the Si substrate further decreased for the same reason that there is an increase in the Cl–Si bond angle to the surface normal in the symmetric model. This difference between our calculation results and the expected value is under further investigation. Meanwhile, the stretching and bending frequencies slightly decrease to 531 cm^{-1} and 157 cm^{-1}, respectively.

Furthermore, the number of the buckled dimers is temperature dependent [24]. Unfortunately, our model cannot simulate temperature dependence completely. We vary the coordinates of the dimer atoms onto which Cl adatoms adsorbed from buckled-dimer sites to symmetric-dimer sites and calculate the TEs. We find that the binding energy increases by 0.08 eV after one Cl adatom is adsorbed onto the bridge site. For the case when two Cl adatoms are adsorbed onto the DB sites, the TE decreases by 0.33 eV. Therefore, we guess that the buckled dimer on the Si(100) 2 × 1 surface will be converted into a symmetric dimer after Cl adsorption.

4. Conclusions

The bond configuration, migration, interaction between Cl atoms, and vibration properties of Cl adatoms on the Si(100) 2 × 1 surface have been studied in this paper. Some important results are summarized as follows.

(1) There are two stable adsorption sites for Cl on the Si(100) 2 × 1 symmetric-dimer surface: one is the surface DB site with a Si–Cl bond length of 1.97 Å and a bond angle of 21° to the surface normal, and the other is the bridge site with a Si–Cl bond length of 1.99 Å. The binding energy on the DB site is slightly larger than that on the bridge site. The migration barrier from the bridge site to the DB site is 1.0 eV.

(2) On the DB site, the Cl–Si stretching frequency is determined to be 555 cm^{-1}, in agreement with the recent HREELS results. On the bridge site, the Cl parallel vibration frequency is 355 cm^{-1} and the perpendicular mode is 570 cm^{-1}.

(3) The bridge-bonded Cl blocks two DB sites in the same dimer. On average, every two dimers can adsorb three Cl atoms, two on the DB sites in one dimer and another on the bridge site in the other dimer, which is a reasonable explanation for showing chlorine adsorption kinetics at the coverage of about 0.7 Cl/Si.

(4) In the buckled-dimer model, Cl is predicted to adsorb onto the dimer up-atom site favourably. We guess that the buckled dimer on the Si(100) 2 × 1 surface will be converted into a symmetric dimer after Cl adsorption since TEs decrease when we vary the coordinates of the dimer atoms onto which Cl adatoms adsorbed from buckled-dimer sites to symmetric-dimer sites.

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