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J. Phys.: Condens. Matter **10** (1998) 4515–4522. Printed in the UK PII: S0953-8984(98)91371-6

The effect of Cl coverage on Si(100) surface reactivity: implications for Cl etching of Si

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Received 3 February 1998

Abstract. We have carried out first-principles calculations of the potential energy as a function of the distance from the Cl to the surface normal for various Si(100)–(2 × 1) surface sites. A comparison between the potential energies of the clean and Cl-covered (1 ML) surfaces indicates a significant change in Si surface reactivity. Our results suggest that it is critical to consider the effect of Cl coverage when simulating Cl plasma etching of Si. With regard to the mechanism responsible for Cl etching of Si(100), we have ruled out the pathway where Cl penetrates into the Si substrate via adsorption on top of the exposed second-layer Si atoms. Both of the pathways via the exposed third- and fourth-layer Si atoms are found to be energetically possible. Finally, we have found, in contrast to the findings of previous theoretical studies, that the bridge-bonded Cl structure is stable with the Si–Si dimer bond remaining intact, in agreement with the experimentally suggested structure.

1. Introduction

Chlorine plays an important role in very-large-scale integrated circuit technologies such as etch and chemical vapour deposition [1]. As feature sizes on silicon wafers continue to decrease, traditional design approaches based on trial experiments become prohibitively expensive. Thus, for the advancement of semiconductor manufacturing, development of accurate simulation tools is critically needed, which requires a detailed description of chlorine–silicon surface chemistry.

In the past two decades, extensive experimental and theoretical studies have revealed much about the surface chemistry relevant to Cl etching of Si [2], but our understanding is still far from complete. For example, one issue that is still under debate is the structure of the bridge-bonded Cl on Si(100)–(2 × 1) and in particular whether the underlying Si–Si dimer bond is broken or remains intact. We use the term bridge-bonded Cl here and throughout the article to refer to all possible configurations in which a Cl atom is adsorbed in between two Si surface atoms. The presence of a bridge-bonded configuration was first suggested by Yates and co-workers on the basis of electron-stimulated-desorption ion angular distributions (ESDIAD) and high-resolution electron energy-loss spectroscopy (HREELS) [3, 4] and further supported by the STM work of Boland [5]. Yates and co-workers proposed that the bridge-bonded structure consisted of Cl adsorbed in between the two atoms of an intact Si dimer [4].

Previous theoretical studies have found bridge-bonded Cl configurations which differ from that proposed by Yates and co-workers. Cl adsorption on Si(100) at a coverage of 1 ML was investigated by Kruger and Pollmann [6] using density functional theory (DFT) and by Craig and Smith [7] using a semi-empirical total-energy method. Despite the qualitative

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differences between their predicted energetics for a Cl coverage of 1 ML, both studies found that the Si–Si dimer bond is broken with the underlying (2 × 1) Si surface reverting to its unreconstructed form. At a Cl coverage of 1 ML each surface Si atom is bonded to two Cl adatoms, and therefore has a bonding environment similar to that in bulk Si, which explains why the unreconstructed geometry is favoured. However, for coverages up to 1 ML (saturation coverage) it is observed experimentally that the majority of the Cl adatoms are bonded to Si dangling bonds and only a small percentage are bridge bonded. Therefore, it is likely that the bridge-bonded Cl adatoms will be adjacent to Cl atoms bonded to Si dangling bonds, and not other bridge-bonded Cl adatoms as in the calculations. Recently, a lower Cl coverage of 0.125 ML was studied theoretically by de Wijs and Selloni [8] using DFT. They also found that the formation of a stable bridge-bonded structure requires breaking of the Si–Si dimer bond. This result is surprising to us since breaking this bond requires a fairly large amount of energy (∼1.6 eV/dimer [9]). In addition, de Wijs and Selloni suggest that the bridge-bonded Cl structure with an intact Si dimer, as proposed by experiment, is not a minimum but rather a saddle point for Cl intra-dimer diffusion.

A critical issue which has not even been addressed previously is the effect of adsorbed Cl on Si surface reactivity. Under steady-state etching conditions, Si surfaces are saturated by Cl. If coverage by Cl significantly changes the Si surface reactivity, then much of the previous work concerning Cl adsorption onto clean Si surfaces cannot be applied directly to modelling of the etching process. It seems clear that surface conditions should play an important role in the chemistry of etching, and our goal here is to address this question quantitatively.

The primary focus of the present work is on evaluating the influence of Cl coverage on the Cl etching mechanism for the technologically important Si(100)–(2 × 1) surface. We accomplish this goal by comparing Si–Cl potential energies as a function of the Cl-to-surface-normal distance for both clean and Cl-covered Si surfaces for various adsorption sites, as obtained from first-principles DFT calculations. Our first-principles potential energy results can be used as a database for developing Si–Cl interaction potentials. In addition, we have examined the controversial bridge-bonded Cl structure on the clean Si(100)–(2 × 1) surface.

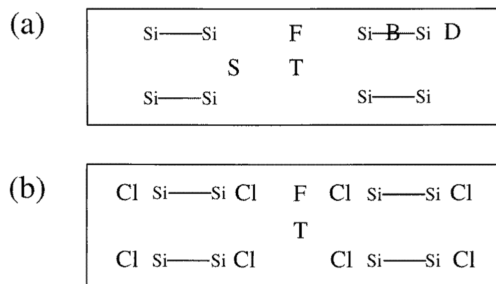

Figure 1. A schematic illustration of Cl adsorption sites on (a) clean Si(100)–(2 × 1) and (b) Cl-covered Si(100)–(2 × 1).

2. The surface model and computational details

We have used the mono-chlorinated surface (1 ML): Si(100)–(2 × 1):2Cl, illustrated schematically in figure 1(b), to represent the Cl-covered Si surface, where all of the surface

dangling bonds have been saturated by Cl adatoms. We modelled both the clean and Cl-covered surfaces by periodically repeated supercells containing six (100) layers of Si. Convergence with respect to the number of layers was checked by comparing the energetics and geometries obtained from six- and ten-layer Si(100) supercells, with no significant difference being found. In addition, the supercells include a vacuum region equivalent in width to nine Si(100) layers.

Si(100)–(2×1) (illustrated schematically in figure 1(a)) has a highly open surface structure with Si substrate atoms up to the fourth layer directly exposed to gas-phase Cl reagents. We have studied the five possible reactive geometries on the clean Si(100) surface, those for which Cl adsorbs directly on top of the atoms in each of the first four Si layers. Each surface unit cell contains two Si atoms and one Cl adatom (coverage of 0.5 ML). In figure 1(a), D and B indicate the dangling bond and bridge sites near a surface Si dimer, while S, T, and F refer to the adsorption sites located directly above the atoms in the second, third, and fourth Si layers, respectively. Within the (2×1) surface unit cell, there are two distinct T as well as F sites. However, we have studied only those in between the Si dimer rows which are more easily accessible and thus are expected to be more reactive with respect to Cl reagents. In the case of the Cl-covered surface, the adatoms in the initial Cl layer are all chosen to occupy D sites, which we found to have the lowest adsorption energy, thus saturating all of the dangling bonds. We then investigated the adsorption of additional Cl atoms only on the S, T, and F sites where we expect a smaller Cl–Cl repulsion.

The total-energy calculations were performed using the plane-wave pseudopotential method within the local density approximation (LDA) [10]. Although LDA overestimates total adsorption energies due to its poor description of isolated atoms, it has been shown that in comparison to gradient-corrected methods it provides accurate relative energies for Cl adsorption on Si surfaces (within 0.2 eV) [8]. Norm-conserving Si and Cl pseudopotentials were generated using the Troullier and Martins scheme [11] and were used to represent the valence–core electron interactions. We used the Ceperley–Alder exchange–correlation potential, as parametrized by Perdew and Zunger [12]. A kinetic energy cut-off of 40 Ryd was used for the plane-wave basis set. Special $\boldsymbol{k}$-points were generated using the Monkhorst–Pack [13] algorithm with a shifted mesh of $2 \times 4 \times 2$ in the full Brillouin zone.

Table 1. Calculated adsorption energies of Cl on the clean Si(100)–(2×1) surface relative to that of the D site. These values correspond to fully relaxed equilibrium structures.

Site	D	B	S	T	F
Relative energy (eV)	0.0	1.0	1.3	1.4	1.0

The total-energy calculations were performed for both rigid and relaxed Si substrates. Rigid-substrate results are particularly useful for developing Si–Cl interatomic potentials derived from first principles, since the contribution from the Si substrate is kept constant. The rigid substrate results also provide convenient starting points for full geometry relaxation where all of the atoms are allowed to move. For the rigid Si(100)–(2×1) surface the Si dimers were kept in their symmetric positions for computational convenience. The adsorption energy of Cl on the clean Si(100)–(2×1) surface is defined relative to this symmetric structure plus an isolated, spin-polarized Cl atom [14]. Since the energy difference between the symmetric and asymmetric dimer structures is relatively small (only about 0.01–0.07 eV/atom) [6], we have ignored the difference. Additional force and total-

Table 2. Structural parameters for a fully relaxed and mono-chlorinated Cl–Si–Si–Cl surface fragment corresponding to the D site.

	Present work	Experiments	Other theory
θ	19.1°	25° ± 4° [3, 4], <25° [16], ∼20° [17]	15.0° [6], 14.8° [7]
R(Si–Cl)	2.06 Å	2.00 ± 0.02 Å [15], 1.95 ± 0.04 Å [16]	2.05 Å [6], 2.050 Å [7]
R(Si–Si)	2.41 Å		2.40 Å [6], 2.451 Å [7]

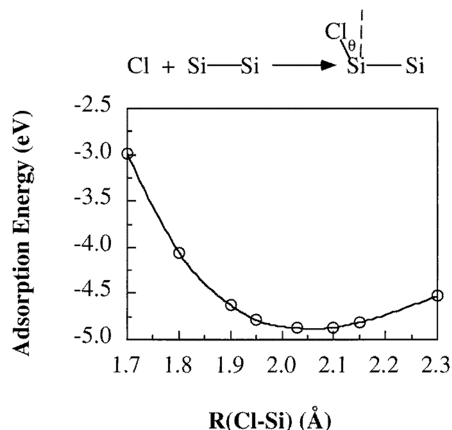

Figure 2. The Cl adsorption energy as a function of the Si–Cl separation for Cl approaching the dangling bond of a symmetric Si dimer on a rigid substrate.

energy calculations were performed to determine whether each of the stationary points is a minimum or a saddle point.

3. Results and discussion

3.1. Cl adsorption on clean Si(100)–(2 × 1)

Table 1 lists the calculated Cl adsorption energies, relative to that of the dangling-bond site D, for the fully relaxed equilibrium structures corresponding to the five different adsorption sites considered here on the clean Si(100)–(2 × 1) surface. We find, consistently with previous work [2], that the D site is the most stable adsorption geometry. Table 2 gives the structural parameters for the equilibrium, mono-chlorinated surface fragment Cl–Si–Si–Cl corresponding to the D site (see figure 1(b)). The resulting Si–Cl bond length, R(Si–Cl) = 2.06 Å, and tilt angle of the Si–Cl bond axis relative to the surface normal (see figure 2), $\theta = 19.1°$, are both in good agreement with previously reported experimental [3, 4, 15–17] and theoretical values [6, 7] (see table 2). Our calculated Cl binding energy for the D site is 4.90 eV/atom, which is similar to the value of 4.77 eV/atom obtained in a recent LDA cluster calculation [18]. The binding energy may be underestimated in the finite-cluster model since the substrate is not fully relaxed. However, our result is larger than that of an earlier LDA crystal calculation by Kruger and Pollmann (4.14 eV [6]), obtained using a Green function method and a Gaussian basis set.

In figure 2 we plot the Cl adsorption energy as a function of the Si–Cl separation, R(Si–Cl), for Cl bonded to the dangling bond of a symmetric Si dimer and at a fixed tilt

angle of 19°. No energy barrier was found along this pathway, consistent with expectations for a radical recombination reaction. This rigid-surface calculation for a Si–Si–Cl surface fragment has a minimum in the total energy at R(Si–Cl) = 2.06 Å with a corresponding bond energy of 4.90 eV/atom. This result is identical to that from the fully relaxed Cl–Si–Si–Cl calculation, indicating that the interaction between the two Si–Cl components of the Cl–Si–Si–Cl surface fragment is negligible at a Cl coverage of 1 ML.

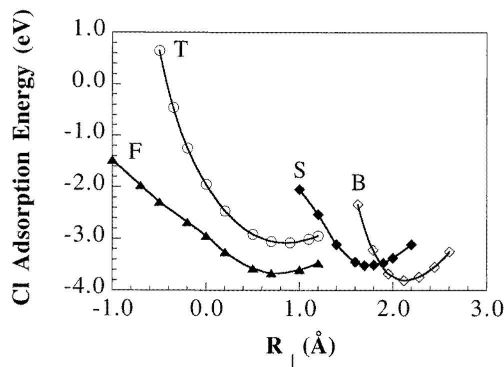

Figure 3. Adsorption energies as a function of Cl-to-surface-normal distance $R_\perp$ for the B, S, T, and F sites of the clean Si(100)–(2 × 1) surface, with the substrate held rigid.

Figure 3 gives the adsorption energies as a function of the Cl-to-surface-normal separation, $R_\perp$, for the B, S, T, and F sites on the clean Si(100)–(2 × 1) surface. Along the vertical direction, the interaction between Cl and each of these sites is strongly attractive with no energy barrier, which is consistent with the high initial sticking probabilities for Cl on Si(100) as measured by experiment [2]. By comparing the rigid-substrate results in figure 3 with the relaxed-substrate calculations of table 1, we find that the substrate relaxation is a small effect. In particular, the maximum energy difference between the equilibrium relaxed- and rigid-substrate calculations is 0.2 eV/atom for the S site.

Among the five adsorption sites investigated, D, B, and T are found to be local minima, while the F and S sites are identified as saddle points for intra- and inter-dimer-row diffusion, respectively. The TS2 and TS3 sites of de Wijs and Selloni [8] are also saddle points and appear to correspond to our S and F sites while their LM1 site is a local minimum and appears to correspond to our local-minimum T site. Our LDA adsorption energies for the S and F sites, relative to that of the D site, are +1.3 and +1.0 eV/atom, respectively, which are similar to the LDA values of 1.2 and 0.9 eV obtained by de Wijs and Selloni for their TS2 and TS3 sites. However, the T site is 1.4 eV higher in energy than the D site, while LM1 is only 0.7 eV higher.

As regards the controversial B site, we find it to be a local minimum with the Si dimer remaining intact. The calculated Si–Si dimer bond length, R(Si–Si) = 2.290 Å, is similar to that of the clean surface while the Si–Cl bond length is found to be 2.435 Å. Our structure is consistent with the experimentally suggested structure [4], but, in contrast, de Wijs and Selloni find this geometry (labelled TS1) to be a saddle point. The structural parameters for the TS1 site were not reported in reference [8], and therefore cannot be compared to ours. In addition, our calculated B-site adsorption energy is 1.0 eV above that of the D site, while de Wijs and Selloni find that the TS1 site is only 0.6 eV higher in energy than the D site. There are a number of possible reasons for the differences between our work and that of de Wijs and Selloni: (1) they use a smaller kinetic energy cut-off of 12 Ryd whereas we

use 40 Ryd, (2) they use only Γ-point sampling while we sample at four irreducible points in the Brillouin zone, and (3) our supercell is smaller, with the result that our calculations correspond to a higher coverage. Kruger and Pollmann [6] used a unit cell which is identical to ours and obtained similar energetics for the B site (0.96 eV above the D site), but they studied a higher Cl coverage and thus found a different local structure.

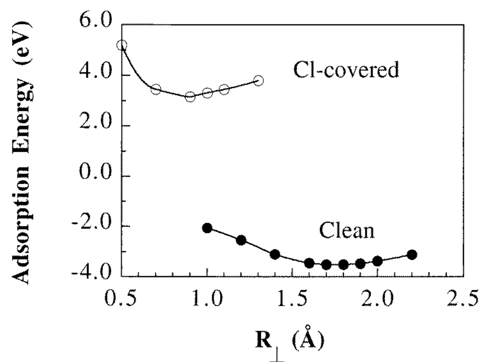

Figure 4. Cl adsorption energies as a function of $R_\perp$ in the S geometry for both the clean and Cl-covered surfaces, with the substrates held rigid.

3.2. Cl adsorption on Cl-covered Si(100)

Calculations for the Cl-covered Si surface were carried out with 1 ML of Cl atoms at the D sites with additional Cl atoms located at the S, T, and F sites. Figure 4 shows the Cl adsorption energies plotted as a function of $R_\perp$ for additional Cl atoms at the S site on the rigid clean (solid circles) and Cl-covered (empty circles) surfaces. Our calculations exhibit a dramatic change in the nature of the interaction between Cl and the S site: from strongly attractive to highly repulsive as the Cl coverage increases from 0 to 1 ML. The decrease in the reactivity of the S site is the result of strong repulsion between the existing D-site Cl adatoms and the Cl atom approaching the S site. This result implies that Cl does not penetrate into the Si substrate via this site and therefore the etching of Si by vertical penetration of Cl into the second Si layer is ruled out.

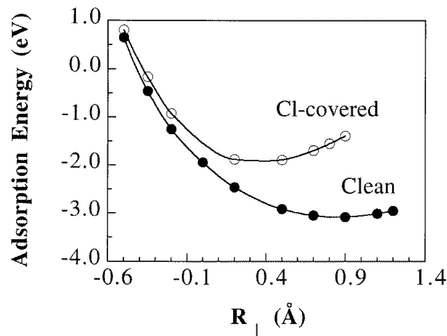

Figure 5. Cl adsorption energies as a function of $R_\perp$ in the T geometry for both the clean and Cl-covered surfaces, with the substrates held rigid.

Cl adsorption at the T and F sites was also found to change significantly as a result of pre-existing Cl coverage, although the forces between the incoming Cl and these two surface sites are still attractive. In figures 5 and 6 the adsorption energies of Cl on the T and F sites on a rigid Si(100) substrate are reduced by more than 1.0 eV/atom due to Cl–Cl repulsion. Neglecting the effect of substrate relaxation, the calculated adsorption energies for the T and F sites are 1.9 eV and 1.6 eV, respectively. Including substrate relaxation increases these numbers to 2.3 and 1.8 eV/atom, respectively. We also find that the additional Cl atoms sit closer to the Si substrate for the covered surface as compared to the clean surface. For example, in the case of the T site on the Cl-covered surface, the Cl adatom sits above the first Si layer by only 0.024 Å, while for the F site the Cl adatom is actually located beneath the first Si layer by 0.531 Å. However, the effect of the Cl coverage is localized to the first layer of the Si substrate. For example, the potential energies for Cl adsorption at the T site for the clean and Cl-covered surfaces start to merge at about 1.0 Å below the surface (see figure 5). In contrast to the case for the clean surface, where the F site is more stable, for the Cl-covered surface the T site is more stable.

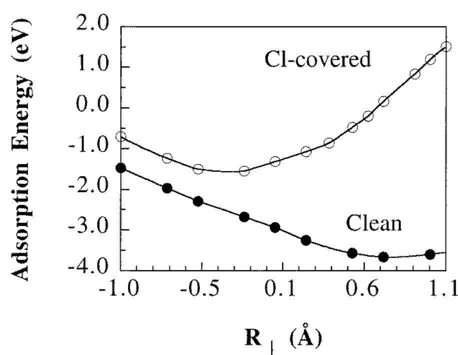

Figure 6. Cl adsorption energies as a function of $R_\perp$ in the F geometry for both the clean and Cl-covered surfaces, with the substrates held rigid.

4. Summary

In summary, we have obtained first-principles potential energies for Cl approaching various surface adsorption sites. The comparison between the potential energies of the clean and Cl-covered surfaces indicates a significant change in Si surface reactivity as the pre-existing Cl coverage increases from 0 to 1 ML (close to saturation coverage). Our results suggest that it is critical to consider the effect of Cl coverage when simulating Cl plasma etching of Si. For the mechanism of Cl etching of Si(100), we have ruled out the pathway of Cl penetrating into the Si substrate via the second Si layer (S site). The two pathways via the third (T site) and fourth (F site) Si layers are found to be possible. Further calculations of Cl bulk diffusion are needed to determine actual energy barriers, but are beyond the scope of the present work. In addition, we have investigated the controversial B site and found it to be a local minimum with the dimer bond remaining intact. This result contradicts previous theoretical studies, but it is in agreement with the experimentally suggested structure.

Acknowledgments

We would like to thank L H Yang for providing the plane-wave pseudopotential code used in this work. This work was performed under the auspices of the US Department of Energy at the Lawrence Livermore National Laboratory under contract No W-7405-ENG-48.

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