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First-principles study of chlorine adsorption and reactions on Si(100)

G. A. de Wijs*
Centre Européen de Calcul Atomique et Moléculaire (CECAM), ENSL, Lyon, France

A. De Vita
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), INR-Ecublens, CH-1015 Lausanne, Switzerland

A. Selloni
Department of Physical Chemistry, University of Geneva, CH-1211 Geneva, Switzerland

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First-principles local-density-functional calculations on the interaction of chlorine with the Si(100)-2×1 surface are presented. Cl_2 adsorption and a number of reactions relevant to etching via desorption of $SiCl_2$ species are considered, both at the defect-free surface, and in the presence of small surface defects. The formation of $SiCl_2$ species via an isomerization mechanism, their stabilization and desorption are studied. Whereas this is a likely route towards spontaneous etching of the surface in the limit of low Cl coverage (θ_{Cl}), at $\theta_{Cl}\sim 1$ it is energetically very costly. In the high coverage limit the formation of $SiCl_2$ by either a Cl atom reacting with a monochloride surface species or by dissociative chemisorption of hyperthermal Cl_2 molecules is investigated. For the latter, a barrier for dimer-bond breaking of 0.5–1 eV is estimated. Our results show that both the Cl_2 adsorption energy and the $SiCl_2$ desorption energy decrease significantly with increasing the local chlorine concentration above one monolayer. [S0163-1829(98)08015-1]

I. INTRODUCTION

The adsorption of chlorine on Si(100) has been extensively investigated for many years as a prototype example of adsorbate/surface interaction.[1] The Cl/Si(100) system is of great interest also from the technological point of view due to the important role of halogen etching in the production of very-large-scale integrated devices.[2] On this surface, Cl_2 molecules adsorb dissociatively and the stable Si-Cl bonding configuration consists of Cl atoms saturating the dangling bonds (DB's) of the surface dimers (terminal bonding).[1,3] However, also metastable Si-Cl bridge-bonded structures,[4–10] particularly on Si(100) surfaces containing a high concentration of surface dimer vacancies (DV's),[11,12] are believed to occur.

The etching of Si(100) with chlorine is a complex process that depends on many parameters.[13–28] Temperature programmed desorption experiments reveal that the main reaction products are $SiCl_4$ and $SiCl_2$ of which the first generally evolves at lower (~150 and 200 K) and intermediate temperatures (~450 K) and the second at intermediate and higher temperatures (~900 K), depending slightly on the experiment. In practical applications the etching is usually stimulated by various techniques which affect the nature of the desorption mechanism. Inert gas ion bombardment simultaneous to chlorine exposure can be employed to yield higher etching rates. This was studied by Feil *et al.*[29] who found that ion bombardment helps disrupting the Cl-passivated surface. Their results are consistent with the observation of Sesselmann *et al.*[22] that a fully chlorinated Si(100) surface has very low reactivity. For the related F/Si(100) system similar inhibition of etching was found for a fully saturated surface in simulations by Carter and Carter.[30] This study suggests that for a fully fluorinated surface sustained etching can only occur in the presence of surface defects.

Different etching conditions can be created by different kinds of surface preparation, or predissociation of the etchant Cl_2 molecules to form Cl atoms. A significant enhancement of etching can also be obtained using hyperthermal beams composed of Cl radicals and Cl_2 molecules:[17–21] Campos *et al.*[17] used beams with a wide range of kinetic energies going up to 6 eV/Cl_2. They found enhancement by a factor of ~10 over thermal beam etching. However, when a threshold of ~3 eV was passed etching could be enhanced even more to a factor of ~30. At higher temperatures (800 K), Teraoka and Nishiyama showed that $SiCl_2$ is evolved by a hyperthermal Cl/Cl_2/He beam after an energy threshold of 2.1 eV has been overcome.[21]

We have studied the interaction of chlorine with Si(100) at the microscopic level by means of first-principles local-density-functional (LDF) calculations. In this paper we will focus on several surface chemical reactions involving Cl_2 and the (high-temperature) etching desorption product $SiCl_2$, at both defect-free and defected Si(100). After a short overview of the computational techniques employed (Sec. II), we discuss Cl_2 adsorption at surface dimers (Sec. III), and the formation of $SiCl_2$ by means of an isomerization mechanism (Sec. IV). Part of this work has been published elsewhere.[31] In Sec. V, the binding and diffusion of an excess Cl atom on a fully chlorinated 2×1 surface is considered, in order to assess the possibility that this adatom reacts with a surface monochloride to yield a $SiCl_2$ species. Further we present results on the energetics of various reactions involving adsorption of gas phase Cl_2 molecules and $SiCl_2$ formation accompanied by bond breaking on a fully chlorinated surface (Sec. VI). Cl_2 adsorption and $SiCl_2$ formation on a defected Si(100) surface are presented in Sec. VII. Results are dis-

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TABLE I. Energies of some reactions involving Cl_2, $SiCl_2$, and $SiCl_4$. The plane-wave kinetic energy cutoff is $E_{cut}=12$ Ry.

	E_{cal} (eV)		E_{exp} (eV)
Nonlocal projectors	s	sp	
Si(solid) + 2 $Cl_2(g) \rightarrow SiCl_4(g)$	−6.28	−7.05	−6.78[a]
$Cl_2+SiCl_2(g) \rightarrow SiCl_4(g)$	−4.53	−5.3	−5.06[a]

[a] *CRC Handbook of Chemistry and Physics*, 1st student ed., edited by R.C. Weast (CRC, Boca Raton, 1988).

cussed in the context of some recent experiments.[11,12] Summary and conclusions can be found in Sec. VIII.

II. COMPUTATIONAL DETAILS

Our calculations are based on LDF theory within the framework of the Car-Parrinello approach.[32] The surface is modeled by means of a periodically repeated slab of six layers of Si atoms. Each layer has 16 (in some cases 24) atoms forming a 4×4 (6×4 or 4×6) cell, and periodic boundary conditions are applied. Slabs are separated by a vacuum region of 9 Å or more. On the upper surface the Si atoms give rise to 8 (12) surface dimers, while the two lowest layers are kept in a bulk-terminated configuration and hydrogen atoms ensure that no unsaturated electrons remain. On the upper surface, Cl atoms are introduced in various configurations. The positions of all Cl atoms as well as those of the four topmost Si layers are fully optimized using a quenched molecular-dynamics algorithm.

Only valence electronic states at the Γ point of the surface Brillouin zone are treated explicitly using a plane-wave expansion with a kinetic energy cutoff of 12 Ry, while electron-ion interactions are described in terms of separable[33] norm-conserving pseudopotentials.[34] To check the accuracy of our approach we considered several reactions involving crystalline silicon, Cl_2, $SiCl_2$ and $SiCl_4$ molecules. Using sp nonlocality, the calculated reaction energies agree with experimental data by better than 5% (See Table I). For s nonlocality larger discrepancies occur. Although, for computational convenience, most of the calculations in this paper were carried out using s projectors only, for several structures calculations were checked using s and p projectors. Tests on the Cl_2 and $SiCl_4$ molecules (See Table II) indicate that structural parameters are rather well described using s projectors only.

Some calculations (see Sec. V) were carried out in a slightly modified geometry with respect to that previously described. We employed a nine-layer slab of which *both* sides had a fully chlorinated dimer structure, and a $p(\sqrt{8}\times\sqrt{8})R45°$ surface unit cell (i.e., four surface dimers along the diagonal of the supercell). An excess Cl atom was put on the upper surface of this slab. The lower half of the slab, including the middle layer, was kept fixed during relaxation of the upper layers. Periodic images of the slab were separated by a vacuum layer of ≈ 9.5 Å. Unlike the case where only one surface of the slab is covered by Cl, this geometry has the advantage that the electric field in the vacuum region (associated to the Cl-Si dipole) is practically zero. Therefore it also provides the opportunity to test whether the artificial field present in the calculations using the larger 4×4 cell has an appreciable effect. As a test, we calculated the desorption energy of a $SiCl_2$ species from the LM2 state [see Sec. V and Fig. 3(b) below] for both cells. For the unsymmetric slab (Cl on one side only, with hydrogen saturating the bonds at the other side, 4×4), we obtained 2.74 eV, for the ''symmetric'' slab [Cl on both sides, $p(\sqrt{8}\times\sqrt{8})R45°$] the result was 2.62 eV. This reasonably small difference indicates that it is justified to use the computationally more convenient unsymmetric slab without the need to introduce extra correction terms in the Hamiltonian.

TABLE II. Equilibrium distance of the Cl_2 and $SiCl_4$ molecules. E_{cut} is the kinetic energy cutoff on the plane-wave expansion of the wave functions.

	R_{cal} (Å)			R_{exp} (Å)
E_{cut} (Ry)	12	12	24	
Nonlocal projectors	s	sp	sp	
Cl_2	2.03	2.02	1.99	1.99[a]
$SiCl_4$	2.07	2.04		2.03[a]

[a] *CRC Handbook of Chemistry and Physics*, 60th ed., edited by R.C. Weast (CRC, Cleveland, 1981).

III. ADSORPTION AND PAIRING AT DB SITES

It is well known,[35] although not yet entirely beyond debate (see, e.g., Ref. 36), that on Si(100) surface atoms reconstruct to buckled dimers and that on the same row neighboring dimers have opposite buckling.[37] This buckling lifts the degeneracy of the two half-filled dangling bond (DB) states of a flat dimer and results in the opening of a gap at the Fermi level.[38] Adsorption of a monovalent adatom such as H or Cl, resulting in saturation of one dangling bond, creates an unpaired DB at the Fermi level. Similarly, when Cl_2 dissociatively adsorbs onto the surface in such a way that the two Cl atoms end up on different surface dimers, two unpaired DB's are created. Vice versa, if the two Cl's end up on one dimer only, no unpaired bonds result, and therefore this configuration should be energetically more favorable. This effect, known as pairing, has been clearly observed in a scanning tunneling microscopy (STM) study of H/Si(100).[39] This is confirmed also by the energetics of our calculations: we find that the configuration with two Cl atoms on the same dimer (Fig. 1) has ~0.4 eV lower total energy than if the two Cl atoms are far apart on the surface.[40]

For the dissociative adsorption energy of Cl_2 on a dimer of clean Si(100) (see Fig. 1) we obtained $E_a=5.4(5.3)$ eV using only s (sp) nonlocality,[6] to be compared to the experimental value of 5.2 eV.[24] This value is independent of coverage, from very low up to one monolayer coverage, i.e., as long as unoccupied dimer DB's are present.

IV. $SiCl_2$ FORMATION AND DESORPTION VIA AN ISOMERIZATION MECHANISM

At high temperatures, etching may be simply caused by desorption of $SiCl_2$ species which are formed spontaneously on the surface via a thermally activated mechanism. We consider two Cl atoms adsorbed at both ends of a surface dimer.

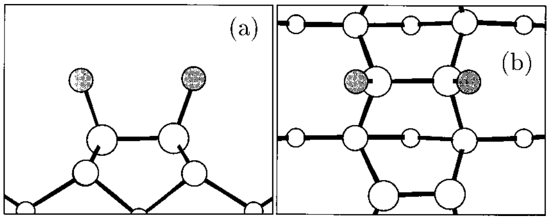

FIG. 1. Surface Si dimer with two Cl adsorbed at the dangling bonds [lhs Eq. (1)] on an undefected surface without additional Cl atoms. Views are along a dimer row (a) and from above the surface (b). First, second, and third layer atoms are depicted by large, medium and small sized white spheres, respectively. Shaded spheres represent the Cl atoms. The Si-Cl distance and dimer bond length are $d_{\text{Si-Cl}}=2.12$ Å and $d_{\text{Si-Si}}=2.44$ Å.

Starting from this (energetically favored) configuration, $SiCl_2$(a) may be formed by a movement of one of the Cl atoms towards the other, so that they will both end up being bonded to the same Si atom (Fig. 2). In this monochloride-dichloride *isomerization* process the dimer bond is broken and a twofold-coordinated silicon atom, Si(s), remains. Schematically:

$$2\,\text{SiCl(a)} \rightleftharpoons \text{SiCl}_2\text{(a)} + \text{Si(s)}, \tag{1}$$

where 2SiCl(a) denotes the two monochlorinated Si atoms of a surface dimer.

We studied this mechanism in the limits of low (only two Cl atoms on an otherwise empty Si surface) and high θ_{Cl} (in which all DB's are saturated by chlorine). The low θ_{Cl} results have been reported in detail in Ref. 31, where this mechanism of $SiCl_2$ formation and desorption has been applied to discuss the growth of linear pits as observed in the STM experiments carried out at low θ_{Cl} by Chander *et al.*[13] Here, for completeness, these results are shortly summarized.

A. Low coverage

We estimated the barrier for $SiCl_2$(a) formation from a set of constrained minimizations. The transition state energy is about 2.1 eV above the energy of the left-hand side (lhs) of Eq. (1) (Fig. 1). Once the Cl has moved over the barrier the energy drops by 0.7 eV on reaching the rhs configuration (Fig. 2), so that the energy cost of $SiCl_2$ formation is 1.4 eV.

In Ref. 31 we found that the Si(s) atom can move onto the reconstructed surface and diffuse away, thereby preventing occurrence of the inverse isomerization reaction, and stabilizing the $SiCl_2$ species. Since the barrier confining Si(s) near the $SiCl_2$ is ~1.0 eV, i.e., only slightly larger than the barrier of 0.7 eV for the inverse isomerization, this process has a reasonable chance to occur.

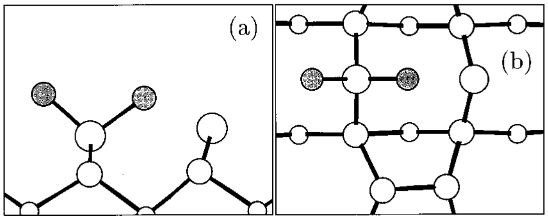

FIG. 2. Surface $SiCl_2$ after the isomerization step [rhs Eq. (1)] on an undefected surface without additional Cl atoms. Views are along a dimer row (a) and from above the surface (b). Si-Cl distances are 2.13 and 2.21 Å.

The inverse isomerization reaction being rendered impossible, the $SiCl_2$ is further stabilized in a dynamical fashion. Moving one Cl atom of $SiCl_2$ onto a neighboring dimer atom costs 0.3 to 0.6 eV (depending on onto which of the surrounding Si atoms the Cl is placed). Moving both Cl atoms onto a dimer far away from the original $SiCl_2$ does not change the total energy within the accuracy of our calculations. Therefore the $SiCl_2$ might (effectively) live long enough to find an opportunity to overcome the desorption barrier, for which a value of 3.2 eV is calculated. This corresponds to the effective barrier for etching. After desorption of $SiCl_2$, a dimer vacancy is formed on the surface. In this way an etch pit is initiated.[13]

B. High coverage

On the saturated surface, forming a $SiCl_2$ species via the isomerization reaction, Eq. (1) is found to cost 1.3 eV. Subsequent desorption of the $SiCl_2$ unit costs 3.5 eV. Both these values are close to those obtained at low θ_{Cl}. However, contrary to what can happen at low θ_{Cl}, diffusion away of the remaining Si(s) atom is unlikely, because the neighboring surface dimers are all occupied by Cl atoms. Instead, a Cl atom (coming from a neighboring dimer) may move on this empty Si(s) atom, thereby suppressing the inverse isomerization reaction, in a way substantially analogous to that proposed for the low coverage regime. However, also, this stabilization process remains unlikely, since it is found to have an energy cost of about 0.9 eV. In the absence of a mechanism for $SiCl_2$ stabilization, the effective barrier for etching is the sum of the $SiCl_2$ formation and desorption energies, i.e., $1.3+3.5=4.8$ eV. Such a high value suggests that at $\theta_{\text{Cl}}\sim 1$ etching via the isomerization mechanism is an extremely rare event.

V. ADSORPTION AND REACTIONS OF A Cl ATOM ON A SATURATED SURFACE

In this section we study the interaction of a Cl atom with a Si(100) surface whose DB's are already saturated by chlorines. This study should be relevant to the case where atoms, rather than molecules, are used as etching agents. The Cl atom may also result from other surface reactions, e.g., from the interaction of a Cl_2 molecule with an isolated DB on a locally saturated surface. A Cl_2 molecule arriving at such an isolated reactive site dissociates and one of the two Cl atoms ends up saturating the dangling bond, while the other Cl atom may remain on the locally fully saturated surface. This is what we actually found by direct simulation for an incident Cl_2 molecule of ~0 kinetic energy. We shall then try to assess the possible effect of such a reactive species on the fully chlorinated surface. First we consider the binding sites and diffusion properties of the Cl adatom. Then we consider the possibility that the Cl adatom combines with a monochloride surface species and desorbs as $SiCl_2$.

To identify the binding sites of the Cl adatom on the saturated surface we calculated the two-dimensional energy surface $E(x,y)$: the excess atom is kept fixed at various po-

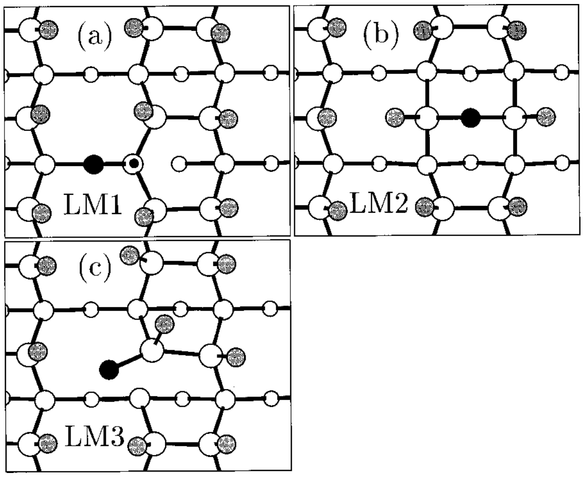

FIG. 3. Binding sites for an excess Cl atom (black) on a Si(100) surface having all DB's saturated by chlorines. Top view showing the three outermost layers of Si atoms (empty circles) and the chlorines (shaded spheres). (a) LM1: the Cl adatom binds with the second row Si atom labeled with ●, $d_{\text{Si-Cl}}=2.29$ Å. (b) LM2: $d_{\text{Si-Cl}}=2.29$ Å. (c) LM3: Si-Cl distances are 2.18 and 2.20 Å.

sitions (x,y) relative to the surface, whereas it is relaxed along [100] (z), i.e., perpendicular to the surface, such as to minimize the total energy. Also all surface coordinates are allowed to relax. This approach generally yields reliable results for a highly reactive surface like Si(100), see, e.g., Refs. 41, 42. From $E(x,y)$ we obtained indications about three local minima (LM), which were unambiguously identified after additional unconstrained minimization. The LM of lowest energy, that we shall denote LM1 [see Fig. 3(a)], has the Cl adatom residing in the valley between two dimer rows, where it is bound to a second row Si atom. This results in an elongation of a bond between this Si atom and a third layer atom to 2.69 Å. LM2 [Fig. 3(b)] is a bridge-bonded configuration, where a dimer bond has been broken and the Cl is in a position bridging the two Si dimer atoms. Finally in LM3 [see Fig. 3(c)] the excess Cl binds to a dimer Si atom, and a Si-Si backbond is broken ($d_{\text{Si-Si}}=2.63$ Å). LM2 and LM3 are both ~0.2 eV higher in energy than LM1.[43] Note that for LM3 a surface $SiCl_2$ unit has been created.

Essentially two paths are available for the diffusion of the excess Cl atom along the rows: on top of the dimers and through the valley in between two dimer rows. For the latter, we find that the LM1→LM1 barrier is ~0.3 eV. For the former our sampling of the potential energy surface shows that the bottleneck is the moving away from LM2. A more dense series of constrained minimizations yields an LM2→LM2 barrier of 0.4 eV. These results indicate that diffusion along the direction of the rows is rather easy, certainly at temperatures of ~850 K where surface etching occurs.[4,14]

Estimation of the barrier for diffusion perpendicular to the rows turned out to be more difficult. This is due to the occurrence of large hysteresis effects, related to the breaking and formation of bonds. Excluding the possibility of exchange processes, the only way a Cl atom can cross a dimer row, is by passing in between two adjacent dimers (otherwise it would bump into other Cl atoms). This route is bound to pass through LM3, as indeed we experienced when releasing the symmetry constraints imposed in the potential energy sampling. From the total energy halfway the LM1→LM1 transition crossing a row, we infer a lower bound for the barrier of 0.4 eV. However, since the Cl atoms are quite large, large movements of the Cl at the DB sites are necessary when the excess Cl atom crosses the dimer row. Therefore it is not unlikely that the actual value of this barrier is significantly larger. This would imply that the motion of the excess Cl is anisotropic, and takes place mostly along the rows.

At temperatures where etching (via $SiCl_2$ desorption) occurs, the LM states discussed above can be easily occupied by excess Cl atoms. Thus a surface $SiCl_2$ unit (LM3), or something very similar (LM2), can be formed. Desorption of $SiCl_2$ from both LM2 and LM3 is found to cost ~2.7 eV. The desorbing species is effectively mobile on the surface: at 850 K the Cl atom can diffuse easily (at least along the rows) and it can attempt to desorb at each LM2 and LM3 visited. This might account for a considerable enhancement of the prefactor for desorption[44] and therefore this may be a relevant $SiCl_2$ desorption channel in the etching of Si by Cl atoms.

VI. Cl_2 ADSORPTION ACCOMPANIED BY BOND BREAKING AND $SiCl_2$ FORMATION AT HIGH COVERAGE

Recently several studies involving molecular beams of Cl_2, F_2, etc., impinging on silicon surfaces have been reported.[17–19,24,25,29,30,45–47] With these techniques some of the reaction mechanisms involved in the etching process can be investigated in a simplified and more detailed way. For the interaction of Cl_2 with Si(100) incident energies up to 6 eV have been considered, and several studies have shown substantially higher etch rates for Cl_2 translational energies higher than 2 to 3 eV.[17,28] In this section we try to make contact with these experiments and focus on the structure and energetics of models of $SiCl_2$ surface species that do not come about spontaneously (i.e., via thermal activation), but result from the bond-breaking adsorption of Cl_2 molecules (of sufficiently high translational energy) on a (locally) fully chlorinated surface.

A. Energetics of formation and structure of $SiCl_2$ species

At the surface two inequivalent kinds of Si-Si bond can be broken: (a) a dimer bond, and (b) a backbond connecting a dimer atom with a second row atom. A Cl_2 molecule breaking these bonds results in (a) two or (b) one surface $SiCl_2$ units, respectively, (see Fig. 4). The calculated adsorption energy for both (a) and (b) is ~1.9 eV (i.e., the energy is reduced upon adsorption). From Fig. 4 it is apparent that the surface structure relaxes significantly. In the situation depicted by Fig. 4(a) Cl atoms clearly try to maximize their distances in order to reduce their repulsive interactions. Distortion in the configuration shown in Fig. 4(b) is also quite severe.

For case (a) we obtained also an approximate estimate of the barrier by performing two sets of constrained minimizations for different orientations of the incoming Cl_2 molecule. We first considered an incident Cl_2 molecule parallel to the

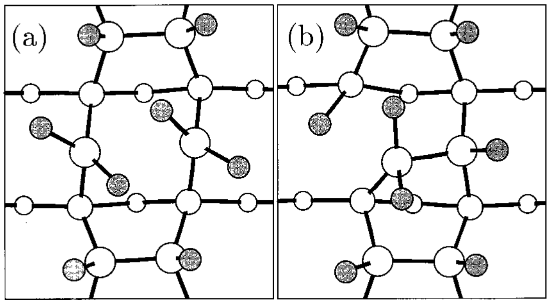

FIG. 4. Surface $SiCl_2$ units resulting from Cl_2 adsorption causing dimer-bond (a) and back-bond (b) breaking on a saturated surface. To minimize repulsions between Cl atoms, the surface undergoes severe distortions. In (a) the distance between the two central Cl atoms is 2.96 Å.

surface and perpendicular to the dimer bond [Fig. 5(a)]. Additionally we kept the Cl_2 and Si dimer flat and constrained their centers of mass to coincide along the dimer row and dimer bond directions. In this way we found that the Cl_2 dissociation barrier (i.e., the energy threshold relative to the case where Cl_2 is at very large distance from the surface) is 0.9–1.0 eV. The final configuration for the adsorbed Cl_2 molecule is that shown in Fig. 4(a), with *two* surface $SiCl_2$.

We also considered the case where the incident Cl_2 is perpendicular to the surface and its trajectory passes through the center of a Si-Si dimer bond [Fig. 5(b)]. The resulting barrier is 0.5 eV above the energy of the Cl_2 at infinite distance. In agreement with these results, recent LDF calculations by Ohno for the case where one Cl atom (instead of a Cl_2 molecule) attacks the surface found that the barrier to break a dimer bond is 0.5 eV.[48] In our calculations, the final configuration [Fig. 5(c)] has one of the attacking Cl atoms incorporated in the surface at a bridging position in the middle of the broken dimer bond, while the other Cl atom does not appear to react immediately with the surface. Among the possible ''fates'' for this atom are either to be scattered back (abstraction) (see, e.g., Refs. 30,45) or to ''land'' on the surface where it may disrupt the bridge bonded structure of Fig. 5(c), until the configuration of Fig. 4(a) (which has ~1.8 eV lower energy) is reached. Which of the various possibilities will actually prevail will presumably depend also on the kinetic energy of the incoming molecule.

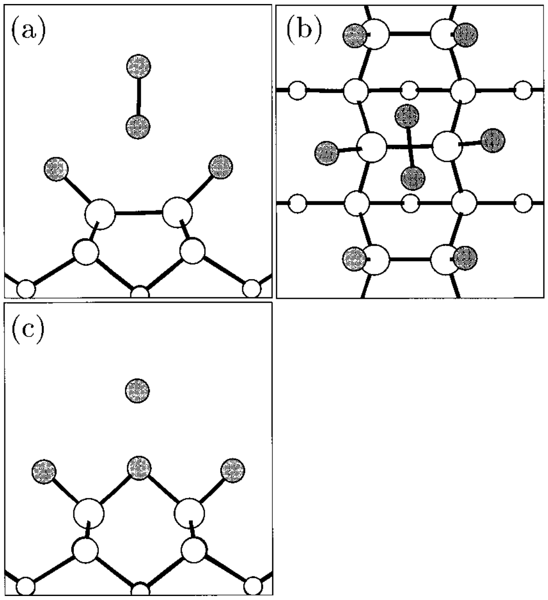

FIG. 5. Dimer-bond breaking via Cl_2 adsorption. Starting configurations for constrained minimizations with incoming Cl_2 perpendicular (a) and parallel (b) to the surface. The final configuration for Cl_2 perpendicular to the surface is shown in (c): the Cl-Cl distance is 2.64 Å, Si-Cl distances for the bridging Cl atom are 2.29 Å.

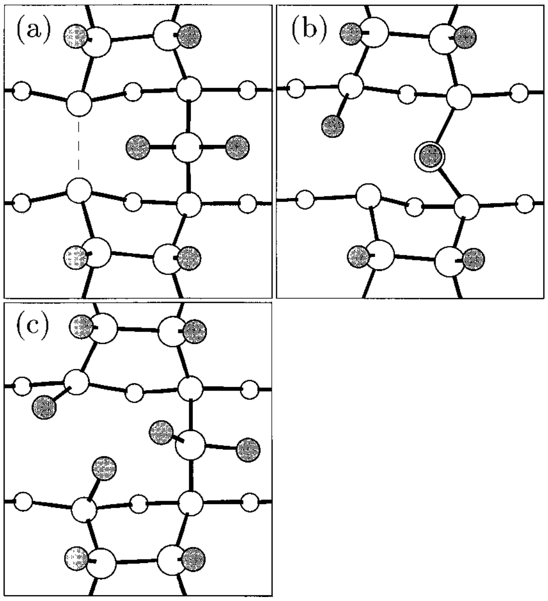

FIG. 6. (a) and (b) Configurations obtained after $SiCl_2$ desorption from the configurations shown in Fig. 4(a), respectively 4(b). The dashed line indicates where there is a tendency towards rebonding. (c) Configuration obtained from either (a) or (b) after saturation of all second layer dangling bonds with Cl.

B. $SiCl_2$ desorption

It is plausible to assume that $SiCl_2$ desorption is an event without an additional barrier, i.e., the desorption energy coincides with the desorption barrier. In fact, after the $SiCl_2$ has desorbed a partially rebonded structure, and therefore a reactive site, remains there where the $SiCl_2$ was originally bonded to the surface [Figs. 6(a) and 6(b)]. Since also the $SiCl_2$ itself possesses a few unsaturated bonds, it is likely that the inverse process of desorption — should it occur — is entirely spontaneous. As a consequence, the desorption is not expected to have an additional barrier.

We checked the above assumption for case (a): We carried out a few constrained minimizations where we fixed the height of the Si atom of the desorbing $SiCl_2$ molecule relative to the height of the center of mass of the two second row Si atoms to which it was bonded on the surface. Following the $SiCl_2$ until it was 7 Å above the second row Si atoms, no additional barrier was found.

We calculated the energies required for $SiCl_2$ desorption from (a) and (b), and obtained 1.4 and 1.9 eV, respectively. The final configurations are shown in Figs. 6(a) and 6(b). From configuration (a), the second $SiCl_2$ may desorb at a cost of 2.9 eV. This is far larger than the cost for desorbing the first $SiCl_2$, which can be explained by the release of

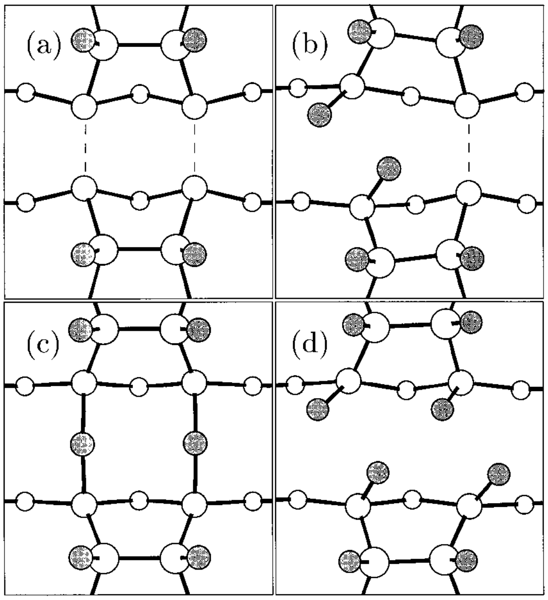

FIG. 7. Bonding structures for chlorine at a dimer vacancy. (a) Bare DV with two rebonds (of length 2.76 Å), (b) and (c) DV with two Cl adsorbed, (d) DV with four Cl adsorbed. Outside the DV the surface dangling bonds are fully saturated by Cl atoms. Dashed lines indicate weak bonds.

strain resulting from the desorption of the first $SiCl_2$ unit. With two $SiCl_2$ units next to each other, the surface deforms so as to avoid that the Cl atoms approach one another too close. Once one $SiCl_2$ has desorbed, the other $SiCl_2$ is in no way hindered anymore by other surface species. After also the second $SiCl_2$ has desorbed, a DV is formed on the saturated surface. Cl_2 adsorption at such defect is discussed in the next section.

Instead of the second $SiCl_2$ desorbing, a Cl_2 molecule may first dissociate and saturate the dangling bonds of the (not completely) rebonded second layer dimer [Fig. 6(c)]. For (a) this releases 3.1 eV, for (b) 3.7 eV, resulting in the same final configuration for both (a) and (b). Now $SiCl_2$ desorption has become slightly less expensive and the second $SiCl_2$ may leave the surface at a cost of 2.5 eV. The resulting configuration is shown in Fig. 7(b).

Whatever the desorption/adsorption sequence, one may finally end up with a DV with four Cl atoms saturating the dangling bonds [Fig. 7(d)]. The overall exothermicity of the process leading from a Cl-saturated dimer to a DV with four Cl atoms is 4.4 eV.

VII. ADSORPTION ON DEFECTED Si(100)

In this section we consider adsorption and reactions at or near dimer vacancies which may have formed during the etching process. At the same time, we shall try to make contact with recent electron stimulated desorption ion angular distribution (ESDIAD) and high-resolution electron-energy-loss spectroscopy experiments by Yang *et al.*[11] on the influence of surface defects on chlorine adsorption on Si(100). Yang *et al.* found that with increasing surface damage the Cl^+ ESDIAD pattern develops a component normal to the surface in addition to the off-normal components that occur for a nondamaged surface. This off-normal ESDIAD signal is caused by desorption of Cl^+ atoms that saturate the DB's of the surface Si dimers, while the normal ESDIAD signal is assigned to Cl at surface DVs.[49] Another finding of Yang *et al.* is the enhanced Cl saturation coverage on defective Si(100) which is also attributed to excess adsorption of Cl at DV's or larger defects.

A. Adsorption at single dimer vacancies

We consider Cl_2 adsorption at a DV on a surface where the DB's of the dimers are all saturated by Cl atoms. For the bare DV [Fig. 7(a)] we find that the second layer Si atoms approach to a distance of 2.76 Å, thus forming two weak bonds. This behavior is similar to that found for DV's on the bare Si(100) surface.[50] Adsorption of Cl_2 may occur in various ways. We considered two possibilities, one in which Cl atoms end up on one side of the row only [Fig. 7(b)], and the other where the Cl occupy positions bridging the second layer Si atoms, thus breaking the ''rebonds'' [Fig. 7(c)]. The latter corresponds to model I of Yang *et al.* The two configurations are found to have the same total energy, corresponding to a Cl_2 adsorption energy of 3.5 eV. Due to exothermicity of the adsorption, at high coverages these states are likely to be populated. However, since adsorption at DB sites is more favorable (by $5.4-3.5=1.9$ eV) these states are only metastable. This is consistent with the finding of Yang *et al.* that their normal ESDIAD signal reduces upon annealing.

Breakup and adsorption of a second Cl_2, leading to the configuration shown in Fig. 7(d), releases 3.3 eV. Since adsorption of a second Cl_2 at the DV is almost just as exothermic as adsorption of the first, this configuration (which corresponds to model II of Yang *et al.*) may account for an excess uptake of two Cl atoms (at one monolayer coverage the DV has 2 Cl). The calculated geometry [Fig. 7(d)], shows that, in order to minimize their mutual repulsions, the Cl atoms bend both upwards and aside. For the configuration depicted in Fig. 7(d) the angles between the Cl-Si bonds and the surface normal range from 31° to 44°.

B. Adsorption at double dimer vacancies

The calculated relaxed configuration for a bare double DV (DDV) on the Cl-saturated surface is shown in Fig. 8(a). The second layer Si atoms in the center have a lot of freedom to relax along the direction of the row, and therefore two strong rebonds with a bondlength of 2.51 Å are present. Saturating the remaining dangling bonds in the DDV with two Cl_2 molecules gives a total energy reduction of 5.9 eV/Cl_2 [Fig. 8(b)]. This is even more than the 5.4 eV for adsorption on the undefected surface. This can be partly explained by the fact that the Cl atoms in the DDV are at sufficiently large distances so that their repulsive interactions are negligible. Moreover their adsorption does not affect the buckling pattern as it does on the undefected empty surface.

To adsorb more Cl_2 in the DDV is far less advantageous: the adsorption energy for another Cl_2 is only 1.7 eV [Fig. 8(c)].[51] Adding a further Cl_2, i.e., finally having eight Cl in the DDV [Fig. 8(d)], releases just 1.1 eV. These low adsorption energies can be explained by the energetic cost of breaking the (strong) rebonds, combined with the fact that the Cl atoms tend to get too close together, thus forcing additional distortions. From these results we infer that the structure of Fig. 8(b) is a particularly stable one, i.e., the DDV tends to

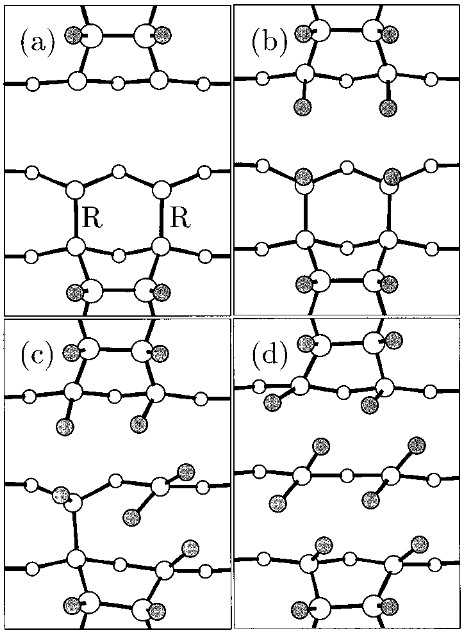

FIG. 8. Bonding structures for chlorine at a double dimer vacancy (DDV). (a) DDV without Cl atoms adsorbed (length of rebonds, denoted by R, is 2.51 Å), (b) DDV with four Cl atoms adsorbed without the rebonds being broken, Si-Cl distances are 2.13 and 2.21 Å, (c) DDV with six Cl adsorbed (Ref. 51), (d) DDV with eight Cl adsorbed: note the two second layer $SiCl_2$ units.

be occupied by four Cl atoms (two Cl_2 molecules) only, with no excess Cl over one monolayer.

C. $SiCl_2$ formed in the proximity of a Cl-saturated dimer vacancy

Starting from the configuration in Fig. 7(d) we consider Cl_2 adsorption with $SiCl_2$ formation via dimer-bond breaking on a neighboring dimer along the row [see Fig. 9(a)]. We find that the energy released in this reaction is 2.2 eV, which is slightly (0.3 eV) larger than the corresponding energy in an undamaged region of the surface, i.e., it is somewhat more favorable to break a dimer bond near a (saturated) DV than in a defect-free part of the surface.[52] However, the desorption energies of the resulting $SiCl_2$ units are found to be extremely low, ~0.0 and ~1.0 eV for the first and second $SiCl_2$, respectively. The vanishing desorption energy for the 1st $SiCl_2$ can be rationalized by considering that in this process both the strain due to the tilt of the $SiCl_2$ units is released and a (complete) rebonding of second layer Si atoms occurs [see Fig. 9(b)]. Desorbing the second $SiCl_2$, leading to the configuration in Fig. 8(b), only brings the advantage of rebonding, so that the energy cost is higher, but still very low, 1.0 eV. These low desorption energies indicate that the configuration of Fig. 9(a) is energetically unfavorable, and it will quickly evolve to that of Fig. 8(b). As mentioned previously, the latter configuration is very stable, and attack of the rebonds by Cl_2 molecules, to yield second row $SiCl_2$ species [see Fig. 8(d)] is not energetically advantageous. Therefore this reaction seems unlikely to occur, except at very high $Cl_2(g)$ concentrations, where it may open a channel towards surface corrugation.

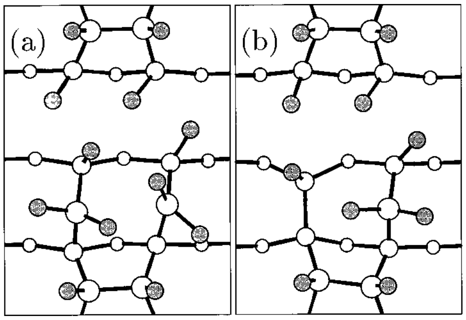

FIG. 9. (a) Two $SiCl_2$ species formed via Cl_2 adsorption accompanied by bond breaking next to a Cl-saturated DV. (b) The $SiCl_2$ unit on the left has desorbed from (a). A strong rebond has been formed with $d_{\text{Si-Si}}=2.51$ Å. The remaining $SiCl_2$ has substantially relaxed.

VIII. SUMMARY AND CONCLUSIONS

In the preceding sections several aspects of the interaction of chlorine with Si(100), that are — in a general sense — relevant to the etching process, have been studied.

First we studied chlorine adsorption and the formation of $SiCl_2$ species, the most important product of chlorine etching of Si(100) at higher temperatures. We considered $SiCl_2$ formed through the isomerization mechanism in Eq. (1), its stabilization and subsequent desorption. In the limit of low θ_{Cl} this process can explain the terrace pitting and etching as observed by Chander *et al.* by means of STM.[13,31] In the limit of high θ_{Cl} this process has higher energy cost and should thus play a very small role in the actual etching.

Next we considered a surface for which the DB's are already saturated by chlorines, and discussed both the interaction of a Cl atom with this surface and $SiCl_2$ formation by bond breaking through dissociative adsorption of Cl_2 molecules with sufficiently high kinetic energy. In agreement with a previous theoretical estimate referring to etching with Cl atoms,[48] we determined a barrier for dimer bond breaking of 0.5–1 eV. These results may be related to experimental molecular-beam studies which found substantially higher etch rates for Cl_2 translational energies higher than 2 eV.[17,18,20,21]

In the last part of this paper we considered a defected Si(100) surface and studied Cl_2 adsorption at single and double dimer vacancies. This allowed us to make contact with experiments that provide evidence for the occurrence of surface defects through the presence of an ESDIAD signal directed normal to the surface.[11,12] We also considered the energetics of $SiCl_2$ formation and desorption near a dimer vacancy, on a fully saturated surface. We found that dimer-bond breaking is easier in proximity of a preexisting vacancy and that the structure of Fig. 8(b) is particularly favored.

An interesting feature which emerges from our study is the dependence of the Cl_2 adsorption and $SiCl_2$ desorption energies on the local Cl coverage, both quantities decreasing strongly with increasing θ_{Cl}, for coverages above one monolayer. The decrease of the Cl_2 adsorption energy with coverage is primarily related to the fact that at high θ_{Cl}, i.e., when all DB's are already saturated, any further Cl_2 uptake implies that bonds need to be broken. Thus the clean surface adsorption energy of ~5.2 eV (Ref. 24) drops to about 2 eV when a dimer bond or back bond is broken. An intermediate value, ~ 3.5 eV, is obtained for the adsorption at a dimer vacancy, which implies the breaking of a weak bond, whereas breaking of the strong rebonds at a DDV (see Fig. 8) leads to adsorption energies as low as 1.7–1.1 eV. A second effect which also contributes to reduce the adsorption energy with increasing θ_{Cl} is the fact that, in order to minimize the mutual repulsive interactions between Cl atoms, the surface must distort, which has a further energetic price. In this respect the Cl/Si system may behave differently from systems with smaller halogen atoms, namely F/Si.

The same effects can also explain the decrease of the $SiCl_2$ desorption energy with increasing θ_{Cl}. Also for this quantity very important variations have been found, with values ranging from 3.2 to 3.5 eV (desorption of $SiCl_2$ species spontaneously formed via isomerization), to values of 1.4–2.9 eV for desorbing the $SiCl_2$ units formed via dimer-bond or back-bond breaking on a saturated surface (see Fig. 4). In the presence of a high local Cl concentration, the surface is highly strained in an attempt to minimize the repulsions among the Cl atoms. Thus $SiCl_2$ desorption tends to have a lower energetic price. In addition, if in the region where $SiCl_2$ desorption has occurred, rebonding can take place, then a further energy gain can occur. This is particularly evident for the case of Fig. 9(a), where the energies to desorb the two $SiCl_2$ units are found to be extremely low (see Sec. VII C).

In summary, in the case of a Si(100) surface with very small (or vanishing) defect concentration, the Cl_2 uptake tends to become very small when the Cl coverage exceeds one monolayer. In addition, the excess chlorine tends to be eliminated quickly via $SiCl_2$ desorption leading to a rebonded structure. This means that building up a chlorosilyl layer[2] is difficult, because chlorine is mostly confined on the outermost layer, and thus the etching is not very efficient. Possible ways to overcome these difficulties are either to use beams of highly energetic Cl_2 molecules or to introduce extended surface defects via, e.g., inert gas ion bombardment.

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*Present address: Electronic Structure of Materials, RIM, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands.

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[52] In Ref. 31 an analogous result was found for $SiCl_2$ formation via the monochloride-dichloride isomerization reaction. In fact formation of this species is about 0.3 eV less costly in proximity of a DV along a row than in an undamaged region of the surface.