Mechanism for $SiCl_2$ Formation and Desorption and the Growth of Pits in the Etching of Si(100) with Chlorine

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A mechanism for $SiCl_2$ formation and desorption in the etching of Si(100)-(2 × 1) at low chlorine coverages is analyzed using first-principles calculations. We find that the two monochlorinated Si atoms of a surface dimer can rearrange into a metastable $SiCl_2(a)$ adsorbed species plus a Cl-free Si atom. Desorption of $SiCl_2$ occurs via a two-step mechanism, in which the adsorbed species is preliminarily stabilized by the diffusion away of the free Si atom. The energy barrier to form $SiCl_2(a)$ is lower on a dimer next to a dimer vacancy than in an undamaged region of the surface, consistent with recent STM observation of preferential linear growth of etch pits along dimer rows. [S0031-9007(97)03410-8]

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Etching is a surface chemical reaction which occurs when a gas-phase species removes part of the surface atoms. Understanding the basic microscopic mechanisms underlying this reaction is important both from the fundamental point of view and because it may lead to a better control of this process in technological applications. In particular, much attention is focused on the etching of silicon surfaces with halogen molecules and atoms, which is a process playing a crucial role in microelectronic device fabrication [1]. It is known that the products and rates of the etching reaction depend strongly on various parameters, including the temperature, the properties of the gas phase species, the surface characteristics (e.g., the defect concentration), as well as the possible presence of simultaneous inert gas ion bombardment. In this Letter we study the *spontaneous etching* (i.e., with no ion bombardment) of a *perfectly ordered* (initially defect-free) Si(100)-(2 × 1) surface at *low* Cl-coverage θ_{Cl}, a system for which a number of interesting experimental observations are available.

For this surface, the growth of the etch pits induced by low Cl_2 fluxes (corresponding to $\theta_{Cl} \sim 30\%$) at ~850 K has been recently studied by Chander *et al.* (CGAW) using scanning tunneling microscopy (STM) [2]. They found that pitting is initiated by the creation of *single dimer vacancies on terraces,* and that these one-layer deep pits grow preferentially along the dimer row direction, with some occasional branching to an adjacent row. CGAW suggested that creation of a dimer vacancy (DV) proceeds via desorption of a $SiCl_2$ unit, while the other Si atom (originally forming a dimer with the desorbed Si) is either etched in a fashion similar to the first or it is ejected onto the surface where it can contribute to the formation of a Si regrowth island. However, the mechanism leading to the desorption of $SiCl_2(a)$, which is expected to be a short-lived species [2], is not understood in detail. Moreover, to explain the observed growth pattern, CGAW proposed that DV complexes elongated along a dimer row are energetically more stable than aggregates of DV's in adjacent rows, both being lower in energy than isolated DV's. The relative stability of different DV cluster structures on the Si(100) surface is, however, a controversial issue [3], and the way this may be affected by the presence of a Cl submonolayer coverage is not known.

To get insight into these issues, we have carried out first-principles local density functional calculations for the energetics of formation and desorption of $SiCl_2$ species, which are responsible for the etching of Si(100) at temperatures of ~850 K and low θ_{Cl} [4,5]. Previous theoretical investigations of halogen etching of silicon have been mostly concerned with fluorine [6–9,11], and examined other aspects of this process [6–11]. Starting from two Cl atoms adsorbed at the dangling bonds (DB's) of a surface dimer, we find that a $SiCl_2(a)$ species can be formed via a monochloride-dichloride isomerization reaction which costs ~1.4 eV. These $SiCl_2(a)$ species are short-lived, with an estimated lifetime of the order of 50 ns at 850 K. Thus their direct desorption, requiring an energy of about 3 eV (and a typical time of the order of tens or hundreds seconds), is very unlikely. Instead, we propose that $SiCl_2$ desorption occurs via a two-step mechanism where the twofold coordinated free Si atom next to $SiCl_2(a)$ first diffuses away on the surface, thus inhibiting the decay of this species. The resulting etching rate maintains no apparent memory of $SiCl_2(a)$ formation, and its activation energy is in reasonable agreement with available experimental results. We also find that the formation of a $SiCl_2$ on a dimer next to an existing pit along a row has a significantly lower activation barrier than anywhere else on the surface. We suggest that the energetics of $SiCl_2$ formation is essential for explaining

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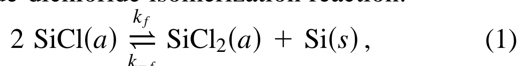
the experimental finding of preferential etch pit growth along dimer rows.

In our calculations, which employ the Car-Parrinello approach [12], the surface is modeled by means of a silicon slab six layers thick, containing 16 atoms per layer. Periodic boundary conditions are applied. On the upper surface the Si atoms give rise to 8 surface dimers per unit cell, while the lower surface is kept in a bulk-terminated configuration and its dangling bonds are saturated with hydrogen atoms. For several calculations larger slabs, having 24 atoms per layer (12 surface dimers), are also used. On the upper surface, a few Cl atoms in different configurations are introduced. 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. Constraints in the optimization procedure are introduced using the "shake" algorithm [13]. Only valence electronic states at the Γ point of the surface Brillouin zone are treated explicitly using a plane wave expansion, while electron-ion interactions are described in terms of norm-conserving pseudopotentials. To check the accuracy of our approach, we considered several reactions involving crystalline silicon, Cl_2, $SiCl_2$, and $SiCl_4$ molecules. Calculated reaction energies agree with experimental data by better than 5%. Moreover, for the (dissociative) adsorption energy of Cl_2 on Si(100), we obtained $E_a = 5.4$ eV, to be compared to the experimental value of 5.2 eV [14].

We first examine the process of creating a single dimer vacancy. Because of a pairing mechanism analogous to that for H/Si(100)-(2 × 1), on Si(100) terraces two Cl atoms preferentially occupy the DB's of the same surface dimer [15]. Starting from this configuration, we consider formation of a $SiCl_2(a)$ adsorbed species via the monochloride-dichloride isomerization reaction:

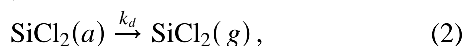


$$2\,\mathrm{SiCl}(a) \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} \mathrm{SiCl}_2(a) + \mathrm{Si}(s)\,, \qquad (1)$$

where 2 SiCl(a) and Si(s) denote the two monochlorinated Si atoms and a free silicon surface atom, respectively. In the following we assume that all elementary rates, such as k_f and k_{-f}, have a simple Arrhenius-like expression, e.g., $k_f = \nu_f \exp(-E_f^*/k_B T)$, where E_f^* is the activation energy, ν_f is the prefactor, k_B is Boltzman's constant, and T is the temperature.

We find that formation of $SiCl_2(a)$ via the reaction (1) costs an energy $E_f = 1.4$ eV, and causes the dimer bond to break [see Figs. 1(b) and 1(c)]. The formation barrier E_f^* was determined from a series of constrained minimizations, where the reaction coordinate was the intradimer distance Si1-Si2. We obtained $E_f^* = 2.1$ eV, so that the barrier for the inverse isomerization reaction is $E_{-f}^* = E_f^* - E_f = 0.7$ eV (see Fig. 2). From this we estimated a lifetime $k_{-f}^{-1} \sim 50$ ns for the metastable $SiCl_2(a)$ state at 850 K [16].

Desorption of $SiCl_2(a)$ to yield a $SiCl_2(g)$ gas-phase species (at rate k_d),



$$\mathrm{SiCl}_2(a) \xrightarrow{k_d} \mathrm{SiCl}_2(g)\,, \qquad (2)$$

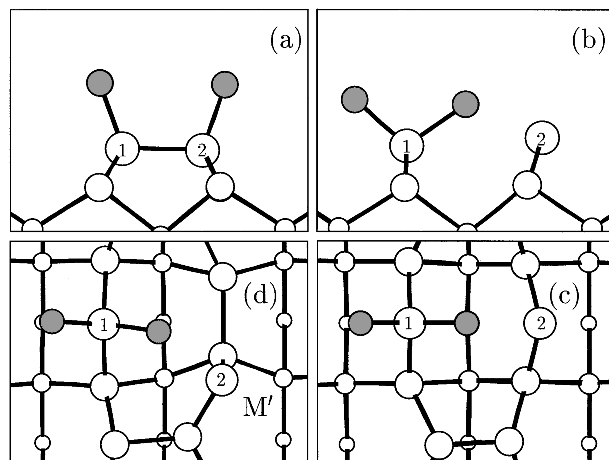


FIG. 1. Atomic structure of: (a) two Cl atoms at the DB's of a surface dimer [2 $SiCl_2(a)$]; (b,c) $SiCl_2(a)$ + Si(s); (d) M', a local minimum for the diffusion of Si2 along the dimer row (see Fig. 2). (c) and (d) are top-views. Grey spheres: Cl atoms; white spheres: Si atoms. Atoms in deeper layers have smaller size. In (b) and (c) the distance Si1-Si2 is 4.1 Å, Si-Cl distances are 2.13 and 2.21 Å, whereas the distance between the Cl in the "quasibridging" position in the middle of the dimer and Si2 is 2.54 Å.

implies the breaking of two Si-Si back bonds. For this process we find a barrier $E_d^* \sim E_d \sim 3.2$ eV [17]. Using a simple kinetic model [18], we can express the overall etching rate R_d for the direct $SiCl_2(a)$ formation-desorption mechanism in terms of k_f, k_{-f}, and k_d. Since $k_f, k_{-f} \gg k_d$, $R_d \sim (k_f/k_{-f})k_d$. This corresponds to an overall activation energy $E_{\mathrm{etch}}^* = E_d^* + E_f^* - E_{-f}^* = 4.6$ eV. Experimentally, in Ref. [5], the activation energy for desorbing the so-called β state (a mixture of $SiCl_2$ and

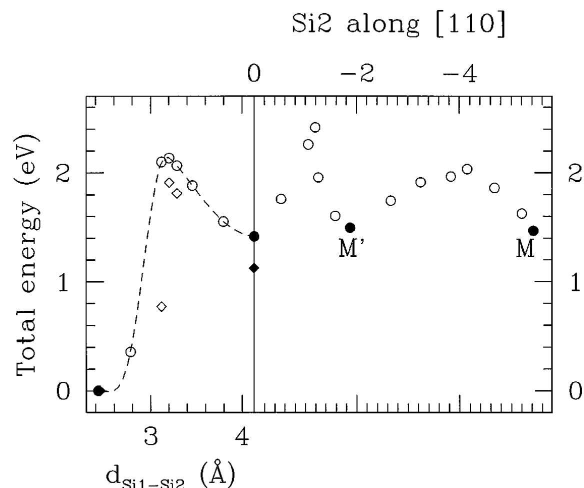


FIG. 2. Left panel: barrier for $SiCl_2$ formation (circles: on a perfect surface; diamonds: near a DV). Right panel: diffusion of Si2 to the M site (see text), along the dimer row. The zero of energy corresponds to the configuration of Fig. 1(a). Full symbols: local minima on the potential energy surface. Open symbols: results of constrained minimizations (see text). The dotted line is a guide for the eye.

$SiCl_4$) was estimated to $\sim$2.4 eV, while in the fluorine etching of Si(100) the typical values of $E^*_{\rm etch}$ for initial F coverages $\lesssim$ 1 monolayer were in the range 3–3.7 eV (depending on the experimental technique) [19]. It is evident that the $E^*_{\rm etch}$ that we have obtained for the direct $SiCl_2$ formation-desorption mechanism is at least 1 eV too large with respect to experiment, indicating that this mechanism is very unlikely.

The structure of $SiCl_2(a)$ [see Figs. 1(b) and 1(c)] shows that, due to the dimer bond breaking, Si2 has become twofold coordinated. This suggests that Si2 can easily diffuse away over the surface. Diffusion barriers for a Si adatom on Si(100)-(2 × 1) are in the range 0.6–1.0 eV (see, e.g., Ref. [20]), and can be thus easily overcome at $T \sim 850$ K. We find that moving Si2 to the equilibrium Si adatom site in between two dimers at the side of a row [20] (this site will be denoted M) costs only a negligible amount of energy, i.e., $\sim$0.03 eV. Alternatively, once moved onto the surface, Si2 can get attached to a step edge (in particular, we find that moving it into a reservoir with bulk chemical potential releases $\sim$0.5 eV). We estimated the barrier for the diffusion of Si2 to a neighboring M site, by performing various sets of constrained minimizations. As in the case of Si adatom diffusion, the barrier for motion along the dimer row, $E^*_{\rm diff} \sim 1.0$ eV (see Fig. 2), is lower than the barrier for jumping across the rows, $\sim$1.3 eV. The value of $E^*_{\rm diff}$ is not much higher than the barrier $E^*_{-f} = 0.7$ eV confining $SiCl_2(a)$, notably if we take into account that, due to our reduced sampling of the potential energy surface, $E^*_{\rm diff}$ is only an upper bound to the real diffusion barrier of Si2. This suggests that the diffusion away of Si2 after the formation of $SiCl_2(a)$ is a process which has a reasonable chance to occur. To approximately evaluate the overall rate $R_{\rm out}$ of this process, we start by noting that once Si2 has moved onto the surface, there are so many places where it can go (e.g., it can get attached to a step edge) that its return to the original dimer site is statistically ruled out. From simple kinetics we then get $R_{\rm out} \sim (k_f/k_{-f})k_{\rm diff}$, where $k_{\rm diff}$ is the elementary rate for Si2 leaving its original site. The corresponding activation energy is $E^*_{\rm out} = E^*_{\rm diff} + E^*_f - E^*_{-f} \sim 2.4$ eV (see Fig. 2). Using a typical value of 10^{13} s^{-1} for the prefactor $\nu_{\rm diff}$, and an approximate value $(\nu_f/\nu_{-f}) \sim 40$ [21], we obtain $R_{\rm out} \sim 2$ s^{-1} at 850 K. For comparison, we note that this rate is some factors of ten higher than that estimated for the spontaneous formation of a single or dimer vacancy on undefected Si(100)-(2 × 1) at the same temperature [22], and about one order of magnitude higher than the largest rates which have been reported for the etching of Si(100) with fluorine in the case of initial F coverages $\lesssim$ 1 monolayer [19,23]. In spite of its crudeness, our estimate of $R_{\rm out}$ indicates that the diffusion away of Si2 after the formation of $SiCl_2(a)$ is indeed a process which is quite likely to occur.

The removal of Si2 stabilizes the remaining $SiCl_2(a)$ unit (hereafter denoted $SiCl_2'$) since the reverse isomerization reaction in Eq. (1) is inhibited unless another Si atom falls into the single atom vacancy, which—as mentioned above—is unlikely for entropic reasons. We also found that moving *one* of the Cl atoms from $SiCl_2'$ to a neighboring (unoccupied) dimer has a significant energy cost, between $\sim$0.3 and $\sim$0.6 eV (somewhat different values are obtained for "up" and "down" atom sites of buckled dimers located in the same and in different rows). Moving *both* Cl atoms from $SiCl_2'$ to the DB's of a surface dimer far away changes the total energy by less than 0.05 eV; i.e., the two Cl atoms are just as "happy" on $SiCl_2'$ as when they saturate the DB's of an unbroken surface dimer. This implies an effective pairing of the two chlorines at $SiCl_2'$, so that $SiCl_2'$ species are most of the time fully occupied (except perhaps at extremely low $\theta_{\rm Cl}$) [24]. The overall etching rate can be expressed as the coverage of $SiCl_2'$ species times their elementary desorption rate. Our estimate of the $SiCl_2'$ formation rate $R_{\rm out}$ and the fact that these are *stable* surface species indicate that the etching is limited by the rate of $SiCl_2'$ desorption, i.e., $R_d \sim k_d$. The resulting activation energy is $E^*_{\rm etch} \sim E_d \sim 3.1$ eV [25], in reasonable agreement with experiment [5,19]. Note the "loss of memory" of the initial $SiCl_2(a)$ formation which has been caused by the (irreversible) Si2 diffusion and subsequent $SiCl_2$ stabilization.

The calculations presented so far refer to the removal of one dimer from an otherwise undefected Si(100)-(2 × 1) surface, i.e., to the initiation of a pit. The essential features of this process do not change if we now consider a dimer at the end of a preexisting pit. In Ref. [2], CGAW studied the growth of Cl-induced etch pits under low coverage and slow etching conditions. They found that the preferential linear growth of etch pits along dimer rows is not due to coalescence of isolated (diffusing) DV's, but to the successive etch-removal of neighboring dimers along the growing pit. To explain these results, they proposed that the energy cost of removing a dimer next to a DV along a row is $\sim$0.1 eV lower than that of removing a neighboring dimer from the adjacent row, both processes requiring less energy than the removal of an isolated dimer from a terrace.

To verify these suggestions, we have studied the energetics of two-DV complexes located along a row and in adjacent rows by using supercells with 24 Si atoms/layer. In agreement with experiment [2,3], our results indicate that it is energetically preferable to have two DV's at nearest neighbor positions (either along a row or in adjacent rows) than at larger distances. However, we find the binding energies of neighboring DV's to be substantially the same within the accuracy of our calculations; we obtained 0.10 and 0.08 eV for the two DV's positioned along a row or in adjacent rows, respectively. We note that an attractive short-range interaction of $\sim$0.1 eV between two DV's along a row has been obtained also by previous first principles calculations [26], while calculations employing empirical interatomic potentials found an attractive interaction of $\sim$0.1 eV between DV's in adjacent rows and a

long-range repulsion between DV's located in the same row [27]. Thus, we conclude that available calculations of DV cluster formation energies do not provide a satisfactory explanation of the observed growth pattern of the etch pits.

As an alternative, we consider the precursor to dimer removal; i.e., we compute the $SiCl_2(a)$ formation energy on a dimer next to a DV. We find that two Cl atoms saturating the DB's of a dimer next to a single DV on a row are just as energetically stable as they would be in an undamaged region of the surface (to within a few hundredths of an eV). However, in this geometry the formation energy and barrier of the $SiCl_2(a)$ species are, respectively, lower by 0.3 eV and $\sim$0.2 eV than what they would be in the absence of the DV (see Fig. 2). Finally, the formation of a $SiCl_2(a)$ species next to a DV located on the adjacent row is more favorable by only 0.1 eV than in an undamaged region of the surface; i.e., it is 0.2 eV less favorable than in the row-pit geometry. This is consistent with CGAW's observation of preferential linear growth of etch pits along dimer rows.

In conclusion, we have presented first-principles calculations for the etching of defect-free Si(100) at low Cl coverages. Our results show that in these conditions the etching process is likely to involve the desorption of $SiCl_2$ units which are formed via an isomerization mechanism and which are subsequently stabilized by the diffusion of a neighboring Si atom over the surface. Moreover, the lowering of the activation barrier to form $SiCl_2$ species at the end of a pit is essential for explaining its growth pattern as observed in STM experiments.

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[17] We did not attempt a detailed calculation of the $SiCl_2$ desorption barrier. However, approximate calculations suggest that desorption energy and barrier have the same value. Note that an * superscript is always used to distinguish activation energies from the corresponding reaction energies.
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[24] Since the barrier for one Cl to jump *out* of a $SiCl_2'$ unit and that for a Cl to get *into* a $SiCl_2'$ temporarily occupied by a single Cl differ by $\sim$0.3–0.6 eV, at 850 K and $\theta_{Cl} \sim 0.3$ the "jump-out" rate is a factor $\sim$25 to $\sim 10^3$ smaller than that to "jump in" (assuming equal prefactors). Thus $SiCl_2'$ only rarely looses one of its Cl's. This makes the process of "pitting without etching" (in which the $SiCl_2'$ decays by loosing both Cl's to the surface while the remaining Si atom is ejected just like Si2) relatively unfrequent with respect to $SiCl_2'$ desorption.
[25] The desorption barrier for $SiCl_2'$ is $\sim$0.1 eV lower than that found for $SiCl_2(a)$. Calculations to be reported elsewhere (G. A. de Wijs *et al.,* to be published) show that the $SiCl_2$ desorption energy can be substantially lower than $\sim$3 eV in the presence of a high local concentration of adsorbed Cl atoms.
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