Surface Modification without Desorption: Recycling of Cl on Si(100)-(2 × 1)

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We demonstrate chlorine-induced modification of Si(100)-(2 × 1) under conditions where Cl is recycled rather than desorbed as $SiCl_2$. A dimer with 2 Cl atoms, 2SiCl, converts to $SiCl_2$ + Si, allowing the bare Si atom to escape onto the terrace. At temperatures below the desorption threshold, the $SiCl_2$ unit decays through Cl diffusion, allowing the second Si atom to escape. The result is a dimer vacancy, terrace regrowth structures, and Cl that is able to participate in another pitting event. Access to this unexpected roughening pathway is controlled by the Cl concentration and temperature. This previously overlooked process represents an important component of Si(100) surface processing.

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Dry etching implies the removal of material from a surface into the gas phase. While dry etching is an essential part of Si chip fabrication, the dynamics of etching are complicated, especially under processing conditions in the presence of a plasma. In the simplest case of etching, the surface is exposed to a halogen at room temperature, then heated until surface modification occurs. Even this simple, thermally activated process challenges our ability to describe the motion of Si atoms, halogen atoms, and vacancies on the surface and to follow silicon halide desorption. Previous atomic-scale studies of surface modification have attributed defect formation to desorption events [1]. Here we show that etchants like Cl can be used to create defects and pits without desorption and that this process depends in a nonintuitive way on the Cl concentration. These findings are important because they show surface roughening facilitated by recycled Cl and lead to new insight into surface modification and material removal.

In this Letter, we demonstrate the structural consequences of thermally activated reactions of Cl on Si(100)-(2 × 1). We used scanning tunneling microscopy (STM) to obtain atomic-resolution images of the surface before and after thermal processing. Temperature programmed desorption (TPD) experiments show that the desorption of $SiCl_2$ from the saturated surface peaks at 953 K [2]. Therefore, we adjusted the temperature to the point where desorption events were rare and then varied the initial Cl concentration on the surface. The resulting surface morphologies are inconsistent with the presently accepted desorption pathway. This paper establishes a new reaction pathway for pit creation and predicts its dependence on coverage, temperature, and time.

The accepted high temperature reaction pathway for Si(100)-(2 × 1) proposed by de Wijs, De Vita, and Selloni (WVS) is based on first principles local density functional calculations of the energies for different Si-Cl configurations [3,4]. The terrace sites are initially equivalent, a single monovalent Cl atom bonds to each dangling bond of a Si dimer. WVS concluded that a monochloride-dichloride isomerization that creates a precursor $SiCl_2$ and a bare Si atom was a necessary first step on a dimer site. A single atom vacancy could be formed adjacent to the $SiCl_2$ by the escape of the Si atom. Thus, vacancy formation eliminated the reverse isomerization channel and enhanced desorption [3,4]. This vacancy-assisted etching mechanism was supported by STM [5,6] and TPD experiments [2,7]. Nakayama *et al.* [5,6] showed that the etching rate increased with Cl concentration, $\theta(\mathrm{Cl})$, until $\theta(\mathrm{Cl}) \simeq 0.8$ monolayer (ML), but then it decreased sharply as Cl blocked the escape of the Si atom. Dohnálek *et al.* [2] also reported that the desorption signal of $SiCl_2$ decreased with increased $\theta(\mathrm{Cl})$ in their coverage dependent desorption spectra.

All experiments reported here were carried out in an ultrahigh vacuum system (base pressure 6×10^{-11} Torr) containing an Omicron STM (controlled by RHK electronics), an electrochemical halogen cell, and a sample heating capability. The Cl electrochemical cell and the preparation of clean Si(100) surfaces are described elsewhere [5,6]. Procedurally, we exposed clean Si(100) to accumulate a given initial Cl surface concentration. In the filled-state STM images, dimers with Cl appear darker than bare Si dimers because the density of states near the Fermi energy decreases upon adsorption (see inset of Fig. 1). This contrast allows us to both detect individual adsorption sites and quantify the Cl coverage. The sample was then heated at a rate of 2 Ks^{-1} to 775–800 K, held for a given time (10–60 min), and quenched to room temperature. The surface was then imaged again to obtain the amount of Si removal and the area of regrowth structures and to quantify the final Cl coverage.

Surface modification is facile at high temperatures if the Cl concentration is not high, as reported previously [5,6]. If the starting concentration is 0.9 ML, however, the likelihood that the first Si atom can escape is reduced and the etch rate is lowered. Figure 1(a) shows the morphology obtained when a sample with $\theta(\mathrm{Cl}) = 0.9$ ML was heated to 800 K for 10 min and then imaged at room temperature. The result is that 0.2 ML of the Cl desorbed as $SiCl_2$ in 10 min, leaving single layer deep pits, dimer vacancy lines, DV_L, that grew along dimer rows, and Si atoms that formed regrowth dimer chains on the terrace, RG. Much

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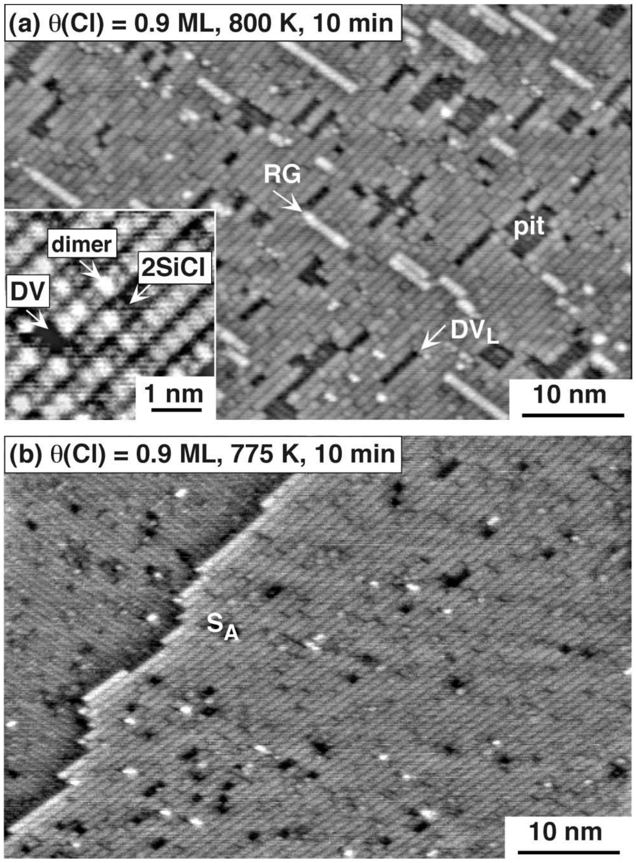

FIG. 1. Room temperature STM images of Si(100)-(2 × 1). (a) A surface with θ(Cl) = 0.9 ML was heated to 800 K for 10 min. In the inset, dimers having two protrusions correspond to 2SiCl and the Cl-free Si dimers are brighter (sample bias −2.5 V, tunneling current 30 pA). (b) An equivalent initial surface was heated to 775 K for 10 min. Etching occurs at 800 K, but it is quenched at 775 K because the temperature is too low (minimal desorption) and the surface concentration is high (frustrating the transition to the second well of Fig. 2). A dimer vacancy, DV, a dimer vacancy line, DV$_\text{L}$, a regrowth chain, RG, an S_A step, and a single-layer etch pit are labeled.

less surface modification occurs for an equivalent surface heated to 775 K, as shown in Fig. 1(b), with few dimer vacancy lines and regrowth features. Indeed, the pit density of 1.2×10^{13} cm^{-2} compares to 1.0×10^{13} cm^{-2} for typical Si(100)-(2 × 1) starting surfaces prepared by thermal treatment. Hence, surface damage is minimized by the combination of high coverage (to prevent the escape of the Si atom) and reduced thermal activation (to minimize desorption).

These results are consistent with the currently accepted model for etching, which is illustrated by the unshaded pathway in Fig. 2. The first few steps of Fig. 2 represent the monochloride-dichloride isomerization pathway from 2SiCl to $SiCl_2$ + Si. Previously, this state was thought to yield the gas product, $SiCl_2$(g), directly from the first well in the potential energy diagram [8]. WVS suggested that the desorption barrier was too high, 3.1 eV, and that $SiCl_2$ + Si would decay back to 2SiCl unless the bare Si atom escaped onto the terrace to create a single vacancy, SV, and enter the second well in Fig. 2.

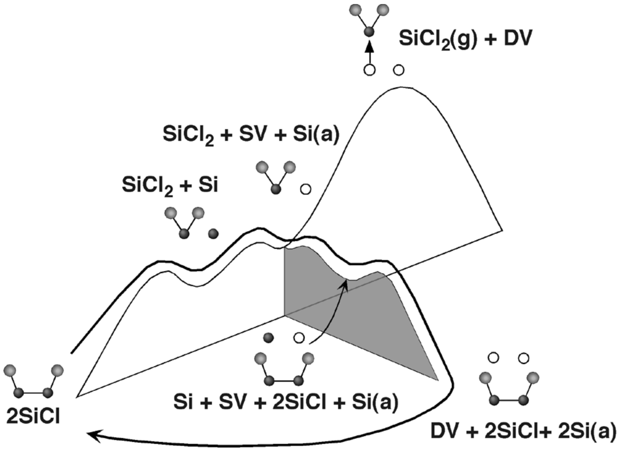

FIG. 2. Representation of the potential energy surface for thermally activated material removal and low temperature surface roughening through Cl recycling. The first step, isomerization, produces a Si atom with two dangling bonds, Si, and a Si atom with two Cl adatoms, $SiCl_2$. The second well is reached when Si transfers onto the terrace as Si(a) by overcoming a modest barrier of 0.6–1 eV [2–4,10,11]. The $SiCl_2$ unit can desorb or it can decay by Cl transfer to other active sites on the terrace, represented by the branched reaction pathway. If the latter occurs, the second Si atom is ejected. This pathway is evident at low temperature as the Cl is recycled and dimer vacancies and regrowth features appear.

The vacancy-assisted mechanism caused a paradigm shift in the way etching was envisioned because vacancy creation replaced desorption as the rate limiting step. As illustrated in Fig. 2, however, we propose an equally important process where dimer vacancies, DVs, could be produced without desorption, i.e., surface pitting without material removal. In Fig. 2, the $SiCl_2$ unit in the second well will either desorb or decay by transfer of Cl to unsaturated bonds of nearby Si dimers. If the latter occurred, the system would evolve to the third well, branching from the desorption pathway and ultimately transforming to DV + 2SiCl + 2Si(a), where Si(a) denotes the transferred Si adatom on the terrace. This last configuration differs from the starting configuration because there is a dimer vacancy and the two Si(a) atoms can form regrowth structures. The Cl atoms could start the reaction process again, and the surface quality would deteriorate. However, WVS argued that this branching pathway was negligible because the transfer of Cl from $SiCl_2$ to a nearby dimer cost ~0.3−0.6 eV and the jump-out rate of the Cl atom is smaller than the jump-in rate [3].

To test whether this new process could, in fact, occur, we dosed a sample with θ(Cl) = 0.7 ML then heated it to 775 K for 10 min. The resulting surface after thermal treatment, shown in Fig. 3(a), is inconsistent with the desorption pathway of Fig. 2. The importance of the new pathway is seen in analysis of Fig. 3(a). Counting adsorption sites yields a final Cl coverage of 0.7 ML,

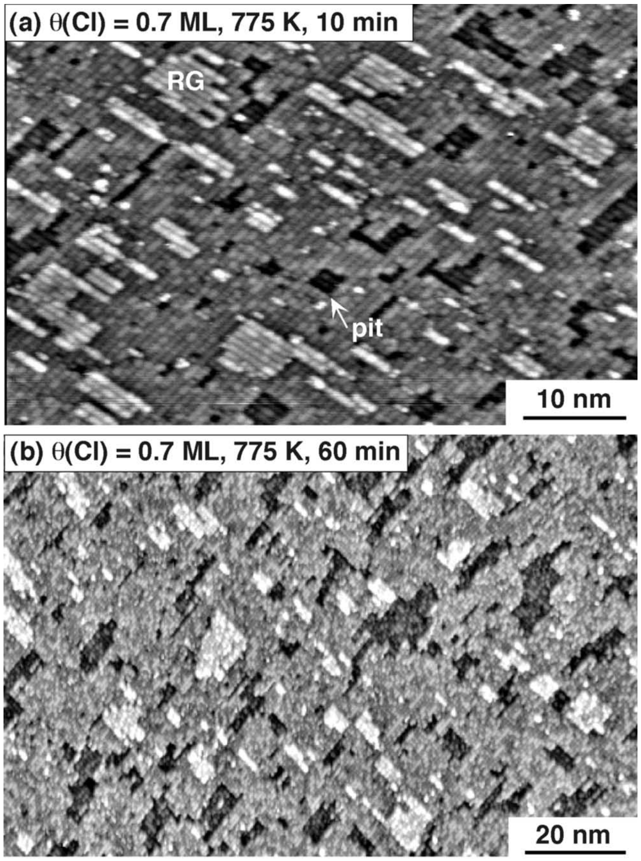

FIG. 3. (a) Filled state image after a surface with $\theta(\mathrm{Cl}) = 0.7$ ML was heated to 775 K for 10 min. The pits and the regrowth features both amount to 0.1 ML and the Cl concentration did not change. This demonstrates the recycling pathway and the accompanying surface modification. (b) Image for a surface with $\theta(\mathrm{Cl}) = 0.7$ ML that was heated for 60 min at 775 K to demonstrate that the surface roughens as pits expand and regrowth features grow, with limited $SiCl_2$ desorption.

indicating negligible $SiCl_2$ desorption, whereas heating an equivalent sample to 800 K reduced the Cl concentration to $\theta(\mathrm{Cl}) = 0.5$ ML because $SiCl_2$ desorbed. Thus, by reducing the temperature from 800 to 775 K, we have severely limited access to the desorption branch. Since desorption was negligible, the profound surface modification confirms that the low energy pathway, shaded in Fig. 2, exists and is important. With the terrace having only 0.7 ML of Cl, the $SiCl_2 + SV + Si(a)$ configuration can decay by transfer of Cl to nearby Si dangling bonds, and SV converts to a DV as the second Si atom moves onto the terrace [9]. Regrowth features up to eight rows wide formed from the large number of released Si atoms, and large pits formed because vacancy diffusion contributed to pit growth. Analysis of Fig. 3(a) shows that the total area of regrowth structures is equal to the area of single-layer-deep pits, namely 0.1 ML, further supporting the absence of desorption from the surface modification process.

A key feature of the new pathway is that Cl atoms are not lost to the gas phase. Instead, after participating in one reaction, they are relocated to another bare dimer, where another reaction occurs and Cl is recycled. Thus, while 2 Cl atoms create only a single DV through the desorption pathway, they can create many DVs through the low energy pathway. To demonstrate the effect of the recycling process, we held a surface with $\theta(\mathrm{Cl}) = 0.7$ ML at 775 K for 60 min. The resulting surface is shown in the large scan area of Fig. 3(b). Clearly, a more damaged surface was produced even though the initial Cl concentration and the sample temperature were the same as in Fig. 3(a). Even more striking is the fact that the Cl concentration remained unchanged within a few percent, indicating that indeed desorption events are rare at 775 K. This amount of surface modification without loss of Cl could be achieved only by using the Cl atoms more than once. Analysis shows that the large pit in the center of the image crosses 16 rows and is derived from 220 missing dimers, and the second layer pitting is evident. The large regrowth features are derived from ~100 Si dimers. Since the amount of regrowth was 0.11 ML and the pit area was 0.15 ML, we conclude that Si atoms can be captured at intrinsic steps like that of Fig. 1(b). Although the time of the heating process was 6 times longer than for the surface in Fig. 3(a), only 50% more pitting was observed. This indicates extensive healing as mobile Si(a) atoms were captured at steps of the evolving pits.

In this Letter, we demonstrated a new low energy pathway for the modification of Si(100) by Cl. Access to this low energy pathway is strongly dependent on the surface Cl concentration, similar to the desorption pathway. Though not previously considered, this new pathway will contribute to surface modification at higher temperatures as well. This suggests that previous studies of Cl etching of Si(100) will need to be reexamined in order to assess the impact of the low energy pathway on the resulting surface structures. Thus, similar to the discovery that higher Cl concentrations can reduce the etch rate, our results demand a rethinking of atomic scale halogen reactions on Si(100)-(2 × 1) with a full incorporation of this new low energy pathway. Furthermore, our results illustrate the importance of STM studies for surface processes since significant surface modification can occur without producing gas phase products. The ability to view the atomic structure of the surface made it possible to find this new reaction pathway.

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[1] J. J. Boland and J. H. Weaver, Phys. Today **51**, No. 8, 34 (1998).
[2] Z. Dohnálek, H. Nishino, N. Kamoshida, and J. T. Yates, Jr., J. Chem. Phys. **110**, 4009 (1999).
[3] G. A. de Wijs, A. De Vita, and A. Selloni, Phys. Rev. Lett. **78**, 4877 (1997).

[4] G. A. de Wijs, A. De Vita, and A. Selloni, Phys. Rev. B **57**, 10 021 (1998).

[5] K. Nakayama, C. M. Aldao, and J. H. Weaver, Phys. Rev. Lett. **82**, 568 (1999).

[6] K. Nakayama, C. M. Aldao, and J. H. Weaver, Phys. Rev. B **59**, 15 893 (1999).

[7] A. Szabó, P. D. Farrall, and T. Engel, Surf. Sci. **312**, 284 (1994).

[8] M. Chander, D. A. Goetsch, C. M. Aldao, and J. H. Weaver, Phys. Rev. Lett. **74**, 2014 (1995).

[9] There are actually two barriers for Cl atom decay and one barrier for each Cl atom.

[10] G. Brocks, P. J. Kelly, and R. Car, Phys. Rev. Lett. **66**, 1729 (1991).

[11] R. A. Wolkow, Phys. Rev. Lett. **74**, 4448 (1995).