

Atomistic View of the Recombinative Desorption of H₂ from H/Si(100)

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Scanning tunneling microscopy is employed to investigate the recombinative desorption of H₂ from hydrogenated Si(100) surfaces consisting of dihydride (SiH₂) and monohydride (SiH) surface species organized in (1 × 1), (3 × 1), and (2 × 1) configurations. The results show that desorption from dihydrides involves a pair of neighboring dihydrides linked along the tetrahedral bond direction. Dihydrides in (3 × 1) domains are separated in the same direction by monohydrides, and desorption from a pair is geometrically impossible. The same desorption mechanism nevertheless applies via first a position switching of dihydrides with neighboring monohydrides.

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Recombinative molecular desorption from a surface generally requires the assembly and organization of constituent atoms or molecular fragments on the surface into favorable precursor or predesorption configurations that are compatible with the free molecular shape [1,2]. Geometric constraints can play an important role in the pathway leading to a predesorption configuration, and this subject matter is of fundamental interest to surface physics and chemistry. In this Letter, we report a study with scanning tunneling microscopy (STM) of the relevant atomistic issues associated with the desorption of H₂ from hydrogenated Si(100) surfaces. Being a simple model system, H/Si(100) has attracted intense interest, both experimentally and theoretically [3–8]. A detailed understanding of this system is also important from the technological point of view, as hydrogen termination and desorption are often employed in Si device processing. The key question is how two H atoms on H/Si(100) can organize themselves into a state conducive to recombination and desorption. The underlying principles are straightforward, as we shall demonstrate: the two H atoms must move sufficiently close to each other, and subsequent desorption must not leave behind a highly unstable surface configuration. The relevant geometries are indicated schematically in Figs. 1(a)–1(c). The clean Si(100) surface forms a (2 × 1) reconstruction consisting of parallel rows of dimers. Each surface Si atom has one dangling bond, and saturation of these dangling bonds with H leads to a (2 × 1) monohydride surface. Further H adsorption breaks the dimer bond. With each Si surface atom accommodating two H atoms, a fully H-saturated surface is a (1 × 1) dihydride surface [9–11]. There also exists an intermediate (3 × 1) phase in which rows of monohydride dimers are interlaced with rows of dihydrides [9,11–14]. Theory has shown that the (3 × 1) phase is more stable than separate (1 × 1) dihydride and (2 × 1) monohydride regions or other periodic patterns, but the free energy difference is relatively modest [15]. Experimentally, antiphase domain boundaries are com-

monly found on the (3 × 1) surface, which can be in the form of two adjacent monohydride dimer rows or two adjacent dihydride rows.

To examine the desorption process in real space with atomic resolution, we employed a variable-temperature scanning tunneling microscope (STM) in a vacuum chamber with a base pressure of 1 × 10⁻¹⁰ torr. Samples of Si(100) were prepared from commercial wafers, outgassed in the vacuum chamber, and then heated by direct Joule heating to ~1400 K to create clean and well-ordered surfaces with the (2 × 1) dimer reconstruction. Atomic hydrogen was produced by backfilling the chamber in the presence of a hot tungsten filament ~5 cm away from the sample. The background hydrogen pressure is about 2 × 10⁻⁷ torr. STM was employed to check the surface reconstruction as a function of H dosage. An indirect heating stage and a thermocouple were used for sample temperature control during desorption. All STM images were taken at room temperature with a constant current mode. Various bias voltages were employed as an aid for positive identification of the different surface species. All images presented below were taken at a sample bias of +2.3 V unless otherwise stated. The size of a 1 × 1 unit cell in the image is 3.84 × 3.84 Å².

Figure 2 shows representative STM images for a (3 × 1) surface after annealing for 0, 0.5, 4.5, and 33 h, respectively, at 570 K, which is barely above the threshold for desorption. The initial (3 × 1) surface is fairly well ordered, with some randomly located antiphase domain boundaries. Figure 2(d) shows that after 33 h anneal the surface is essentially completely converted to a monohydride (2 × 1) surface. In the process, H in the amount equivalent to nominal $\frac{1}{3}$ of a Si monolayer (1 ML = 6.8 × 10¹⁴ cm⁻²) is desorbed. Since the dimer rows for the initial (3 × 1) reconstruction and the final (2 × 1) reconstruction are organized with different periodicity, the conversion must involve dimer row reorganization. A detailed examination of the STM images at intermediate stages of de-

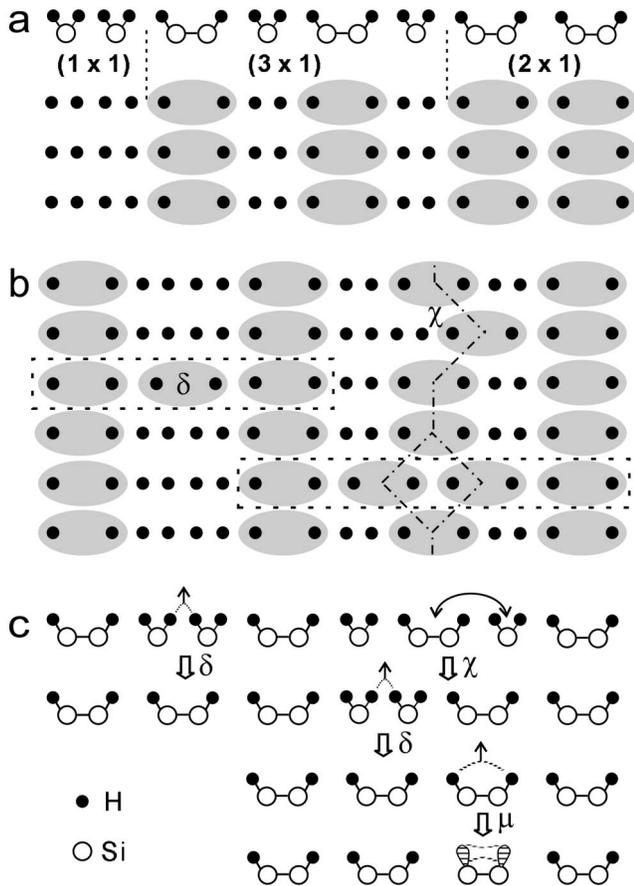


FIG. 1. Schematic diagrams showing (a) side and top views of (1×1) dihydride, (2×1) monohydride, and (3×1) mixed monohydride-dihydride phases, and (b) top and (c) side views of atomic configurations involved in χ , δ , and μ reactions as discussed in the text. Dashed rectangles indicate (6×1) and (8×1) units. Dash-dotted lines outline the V- and diamond-shaped structures.

sorption reveals that two kinds of reactions are happening as described below.

First, let us focus on a domain boundary involving a local (1×1) patch consisting of two adjacent dihydride rows, as shown in Fig. 3(a), which is an unoccupied-state image obtained after annealing for 0.5 h. Here, one can see two cases of recombinative desorption. In each case, two adjacent dihydrides donate one H each to form a desorbing H_2 molecule, leaving behind a monohydride dimer. This process, referred to as the δ process, is schematically illustrated on the left side of Figs. 1(b) and 1(c). The resulting surface structure consists of three adjacent monohydride dimers strung along the dimer bond direction. For simplicity, we shall refer to this as a (6×1) unit. Desorption from a single dihydride is never observed; the reason is that the end product would be a Si surface atom with two dangling bonds, which is energetically unfavorable. Likewise, desorption does not occur for two adjacent

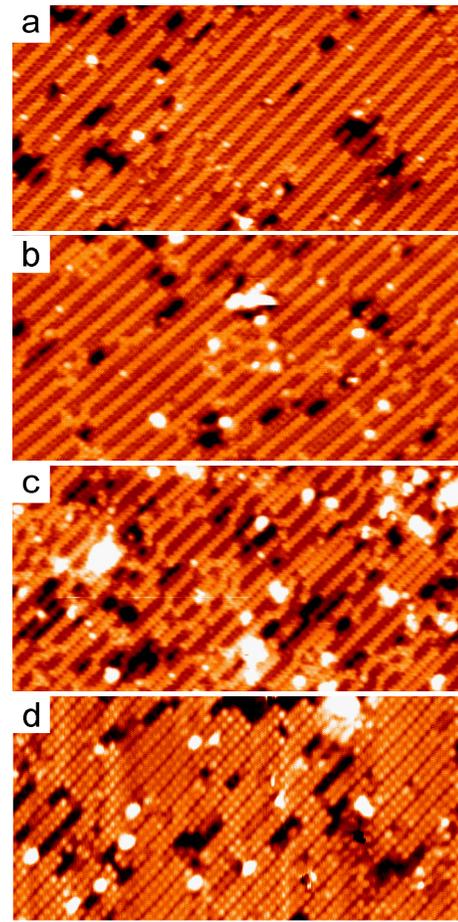


FIG. 2 (color online). STM images taken at room temperature after a (3×1) sample has been annealed at 570 K for (a) 0, (b) 0.5, (c) 4.5, and (d) 33 h. The dark pits are single or double vacancies. In (a)–(c), the brighter rows are monohydrides and the darker rows are dihydrides.

dihydrides lined up perpendicular to the dimer bond direction. This dihydride-pair desorption (δ) process accounts for the conversion of (1×1) patches into monohydrides, but is incompatible with the (3×1) geometry because the dihydrides are separated along the tetrahedral bond direction by monohydride dimer rows.

The other kind of reaction, referred to as the χ process and schematically indicated in Figs. 1(b) and 1(c), occurs in ordered (3×1) areas. An example is shown in Fig. 3(b), taken after 0.5 h of annealing. Here, a monohydride dimer is seen to switch its position with its neighboring dihydride, resulting in a V-shaped kink in an otherwise straight row. As theory indicates, the barrier involved in this switch is actually quite low [16]. The resulting configuration can be considered as a combination of two adjacent antiphase defects. This antiphase defect pair (ADP) contains two adjacent dihydrides, and can therefore desorb via the same δ process as discussed above and illustrated in Figs. 1(b) and 1(c). Indeed, STM images taken at inter-

mediate annealing times show a number of such reaction products. An example is shown in Fig. 3(c). This two-step desorption process ($\chi + \delta$) leads to a local surface geometry consisting of four monohydride dimers stringed along the dimer bond direction, resulting in an overall diamond-like shape in the image. This is referred to as an (8×1) unit in the following.

A counting of the STM images after 1.5 h of annealing shows that there are more ADPs than (8×1) units with a ratio of about two. This is consistent with the low energy barrier for the formation of ADPs (the χ process), and the rate of desorption appears to be dominated by the

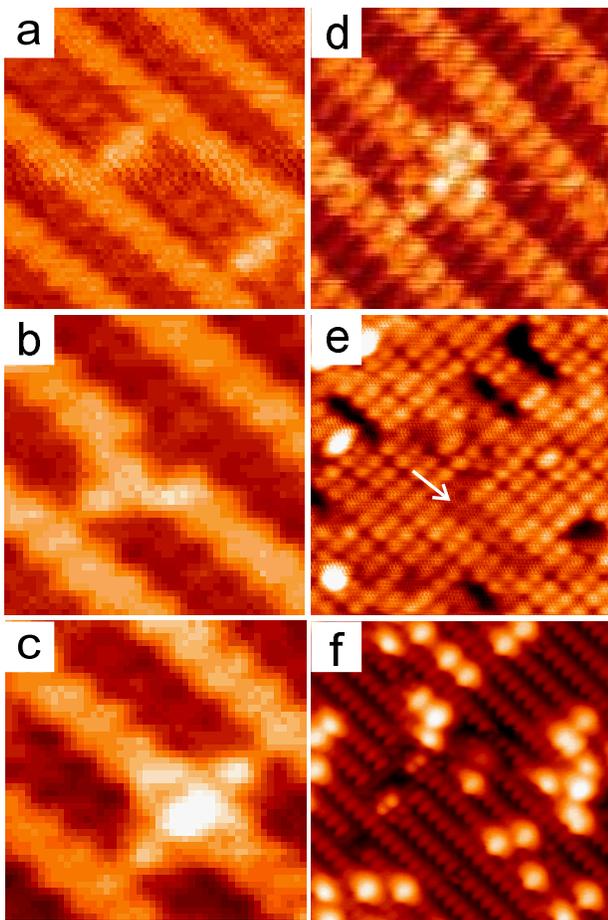


FIG. 3 (color online). Closeup images showing (a) two (6×1) units formed as a result of the δ desorption process in a two-row-wide (1×1) dihydride domain, (b) a V-shaped kink (ADP) resulting from a position-switching χ process and (c) a diamond-shaped (8×1) unit resulting from combined χ and δ processes, (d) an ADP neighboring an (8×1) unit, (e) a dihydride row trapped in a 2×1 domain, and (f) desorption (μ) events from a monohydride (2×1) phase. Image (f) was taken at a sample bias of -2.1 V, while all of the others were taken with $+2.3$ V. Images (a)–(d) were taken after annealing a (3×1) sample at 570 K for 0.5 h, while image (e) was taken after a 33 h anneal. Image (f) was taken after annealing a (2×1) monohydride surface for 1 min at 725 K.

dihydride-pair recombination (δ) process. Further evidence is provided by earlier temperature-programmed desorption (TPD) studies which have shown two desorption peaks: a β_2 peak at about 680 K (with an onset near 570 K) corresponding to the conversion of dihydrides to monohydrides, and a β_1 peak at about 790 K corresponding to the conversion of monohydrides to the clean Si(100)- (2×1) surface [10,17]. The β_2 peak appears identical for both the (1×1) and the (3×1) surfaces, suggesting that the geometrical barrier for desorption from the (3×1) surface does not play a significant role in the desorption energetics.

As the annealing progresses, further desorption appears to favor sites next to where desorption has already occurred. An example is shown in Fig. 3(d), where an (8×1) unit is neighbored by an ADP, and the resulting pattern is closely matched by a combination of the two features shown in Figs. 3(b) and 3(c). With continued desorption, (8×1) and (6×1) units tend to expand into $(8 \times n)$ and $(6 \times n)$ patches. Since the initial (3×1) surface also contains (4×1) units in antiphase domain boundaries, the overall surface structure can become fairly complicated as domains form, grow, and merge, as seen in Fig. 2(c). The complicated domain patterns eventually give way to a simple monohydride surface with an overall (2×1) reconstruction as seen in Fig. 2(d). However, cases are found where a single row of dihydrides gets trapped in large patches of (2×1) monohydrides, and an example is shown in the image in Fig. 3(e). These features are relatively rare, but are robust as desorption can no longer proceed via the same two-step mechanism.

Some prior studies have suggested recombination involving two H atoms from a single dihydride unit as an important or dominant contribution to desorption [17–19]. Such a process would lead to a bare Si atom on the surface with two dangling bonds, which is highly unstable, and our study shows that this does not occur. A single row of dihydrides trapped within a (2×1) monohydride domain can be considered as a kind of (2×1) antiphase (or twin) domain boundary. It is interesting to note that this type of antiphase domain boundary has never been observed on clean (2×1) surfaces apparently to avoid bare Si atoms with double dangling bonds. For the present system, such boundaries form due to reaction kinetics and stabilization by hydrogen termination. In Figs. 2(a)–2(d), significant numbers of single vacancies and double vacancies form short chains and/or clusters. The initial vacancies of $\sim 4\%$ of the surface area result from etching during the atomic H exposure [20]. Up to $\sim 4\%$ more vacancies could be found after annealing at 570 K. These vacancies presumably result from the formation and desorption of Si_2H_2 and SiH_4 [21,22]. These etching processes could account for some reduction of surface hydrogen during the 3×1 to 2×1 phase transformation.

Significant desorption from the monohydride phase requires a higher temperature. An example is shown in

Fig. 3(f) where a monohydride surface has undergone annealing at 725 K for a minute. This temperature falls within the width of the β_1 peak. The bright spots indicate where desorption has occurred. A careful inspection of the surface at different bias conditions reveals that the desorption involves a pair of H atoms from a single monohydride dimer. The process, referred to as the μ process and schematically indicated in Fig. 1(c), is consistent with the notion that desorption must involve two nearby H atoms which can easily move close to each other (through bond flexing in the present case). Our results for monohydride desorption are consistent with prior observations [23,24].

To summarize, we have presented a detailed atomistic view of the desorption of H_2 from H/Si(100) in terms of three processes: χ , δ , and μ . The results illustrate two basic principles relevant to recombinative desorption: the constituent atoms must be organized first on the surface into predesorption states that are compatible with the free molecular geometry, and the resulting surface structure must be energetically favorable. Specifically, desorption from dihydrides proceeds by recombination of two H atoms coming separately from two adjacent dihydrides, leaving behind after the reaction a monohydride dimer on the surface. This process is geometrically forbidden for the (3×1) surface, but becomes possible with a switch of a dihydride with a neighboring monohydride dimer to form an ADP structure. Desorption from monohydrides occurs at a higher temperature, and proceeds by recombination of the two H atoms on a given monohydride dimer. Bare Si atoms with two dangling bonds are never observed, and the allowed surface states include just dihydrides, monohydrides, and clean Si dimers.

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