

Real-space investigation of hydrogen dissociation at step sites of vicinal Si(001) surfaces

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H₂ adsorption on vicinal silicon (001) surfaces with double atomic height D_B steps has been investigated using scanning tunneling microscopy. At room temperature, the only observable reaction is dissociative adsorption at step sites. This process leads to H adsorption at pairs of adjacent step atoms aligned with the dimer rows of the upper terrace. The sticking probability is found to increase at sites next to those already occupied by adsorbed H, as manifested in a strongly nonstatistical distribution of occupied pairs of dangling bonds. At elevated surface temperature, dissociative adsorption is also observed to occur at the complementary pairs of step atoms.

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The nature of vicinal surfaces is a subject of great interest and importance because of the distinctive properties exhibited by atoms at step sites compared to those comprising the ideal surface. This difference plays a critical role, for example, in metal catalysts where the lower coordination of the step sites may significantly increase their reactivity.^{1,2} Steps also are of obvious relevance in the preparation of thin films where the step-flow mode of growth yields uniform overlayers and single-domain surfaces.³ For the case of silicon surfaces, the interaction of hydrogen at the step sites has been shown to be significant in the growth of single-crystal silicon films by gas-source molecular beam epitaxy.⁴

In addition to its technological importance, hydrogen on silicon is an intriguing system from the fundamental point of view, and has emerged as a model for interactions of adsorbates on covalently bonded surfaces. One of the striking characteristics of this system is the phenomenon of phonon-assisted sticking in which the probability for dissociative adsorption of H₂ increases dramatically with increasing surface temperature.^{5,6} This behavior may be attributed to a strong dependence of the adsorption barrier height on the coordinates of the atoms comprising the Si surface. It has further been suggested that changes in the local structure of the Si(001) surface induced either by predosed hydrogen⁷⁻⁹ or by steps¹⁰ lead to an increase by several orders of magnitude in the H₂ sticking coefficient. The latter effect may be explained in terms of a sharply reduced barrier for adsorption at the D_B step sites, as found in density-functional theory (DFT) calculations.¹⁰

In this Rapid Communication we present a real-space study of adsorption of molecular hydrogen on vicinal Si(001) surfaces by means of scanning tunneling microscopy (STM). The reaction pathway leading to the sharply enhanced probability for adsorption is identified and found to be a dissociative process leading to the production of pairs of adsorbed H atoms on adjacent rebonded Si atoms comprising the D_B step edges. From the STM observations, we are able to establish the reactivity at each of the two inequivalent pairs of step atoms and to examine the relative importance of each channel at different surface temperatures. A striking additional finding is the propensity of the adsorbed hydrogen atoms to form 1-D chains along the step edges. These experi-

mental data may be understood and modeled in terms of an increased reactivity at vacant step sites situated next to those already occupied by H atoms. The results of these investigations highlight the remarkable sensitivity of reactions on this model covalent system to the local surface structure. The findings of these experiments also cast light on the behavior for flat surfaces and thereby provide general information on the driving force for reactions on covalently-bonded surfaces.

The experiments were carried out in an ultrahigh vacuum chamber equipped with a commercial scanning tunneling microscope. The preparation of the Si(001) sample (n -type, 10 Ω cm), miscut 5.5° towards the [110] direction, was performed as described previously⁷ and yielded a defect and contamination level well below 1%. For H₂ dosing, the chamber was back-filled with gas of 99.9999% purity that was passed through a liquid-nitrogen cooled trap to freeze out residual water vapor. During exposure of H₂, all filaments were switched off to eliminate production of H atoms. The base pressure during experiments was $\leq 5 \times 10^{-11}$ mbar. With respect to the STM data, we note that the surface temperature was always maintained at a sufficiently low value so as to avoid surface diffusion of H during the course of the experiments. Thus, the STM images may be regarded as reflecting the initial adsorbate distribution on the surface.

As shown in Fig. 1, the STM images of the clean surface exhibit well-ordered 2×1 terraces of approximately seven dimers width that are separated by steps perpendicular to the dimer rows. Most of the steps can be identified as double-height rebonded D_B steps,¹¹⁻¹⁴ which are characterized by the presence of an additional trigonally bonded Si atom on the step edge that serves to minimize the number of dangling bonds (Fig. 1, inset). In addition, other types of steps are present at lower concentration. As seen in Fig. 1 (and Fig. 3), these are principally the shortest possible combination of single-height rebonded S_B^R and single-height S_A steps formed at the kinks of D_B steps to avoid energetically less favorable segments of D_A steps.^{11,12}

The result of exposing the room-temperature surface to a moderate dose of 230 L of H₂ is displayed in the occupied-state image of Fig. 2(a). It can be readily seen that reactions occur only at the step edges, where pairs of the unreacted

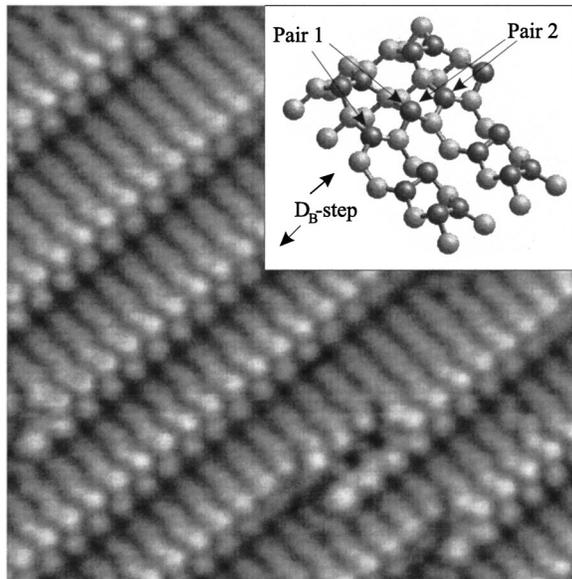


FIG. 1. Occupied-state STM image of the clean Si(001) $5.5^\circ \rightarrow [110]$ surface taken at a sample bias of $U = -2.2$ V and a tunneling current of $I = 0.7$ nA. The ends of the dimer rows perpendicular to the D_B steps appear somewhat brighter than the other terrace dimers. The bright features between the terraces correspond to two of the buckled, rebonded step atoms. A ball-and-stick model of the step is shown in the inset, with those silicon atoms having dangling bonds drawn in a darker shade. The two types of inequivalent pairs of adjacent rebonded step atoms are indicated.

dangling bonds of the buckled rebonded step atoms appear as bright features.^{12,13} The dark regions marked A, B, and C are interpreted as the result of the adsorption of one, two, and three pairs of H on the rebonded step atoms. The dimers on the upper and lower terraces remain unchanged in this image. The unoccupied state image in Fig. 2(b) provides additional information about the exact adsorption sites. In this image, pairs of dangling bonds of Si dimers at the edge of the upper terrace and from the rebonded Si atoms at the step edge appear as bright spots.¹⁴ Hydrogen adsorption simultaneously eliminates the bright features associated both with the dimers of the upper terrace adjoining the step and with rebonded step atoms themselves. Taken in combination with the occupied-state image, this behavior indicates that adsorption takes place dissociatively at two rebonded step atoms that are aligned with the dimer rows of the upper terrace (pair 1 in Fig. 1). The reduction of the unoccupied states of the first terrace dimers may be explained by charge redistribution induced by hydrogen adsorption on the step sites.

To further strengthen our interpretation of the STM images, we dosed the surface with atomic hydrogen to a coverage of about 10%. The unoccupied-state image of Fig. 2(c) indicates that single H atoms adsorbed at step sites produce only a small dark spot, distinguishable from that resulting from H_2 adsorption in part (b). We can therefore exclude the possibility that the dark feature B in Fig. 2 actually corresponds to the adsorption of a single molecule of H_2 at a pair of dangling bonds located between the dimer rows of the upper terrace (pair 2 in Fig. 1). Rather, it arises from the adsorption of two H_2 molecules at adjacent pairs of type 1 dangling bonds.

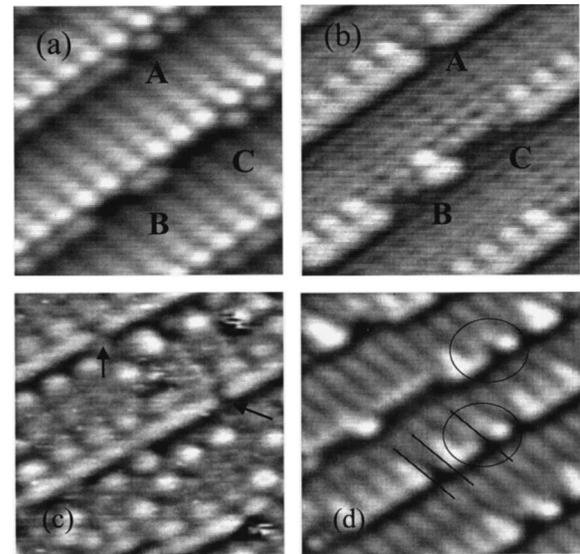


FIG. 2. (a) Occupied state image after a dose of 230 L H_2 . One, two, and three of the bright features are quenched and an elongation of the adjoining bright spots is observed. (b) Unoccupied state image [$U = +0.8$ V, $I = 0.5$ nA, also in (c) and (d)] of the same frame as in (a). The bright features correspond to the last set of terrace dimers and the rebonded atoms of the step edge. Hydrogen reacts with the step sites located in line with the dimers of the upper terrace, the brightness of the first of which is also reduced upon hydrogen adsorption. (c) Image of a silicon surface predosed with 10% atomic hydrogen. The positions marked with arrows indicate single hydrogen atoms, each saturating one dangling bond of a rebonded step atom. The adjacent step atoms are found to be uninfluenced under these tunneling conditions. The bright spots on the terraces are single dangling bonds adjacent to a hydrogen atom on the opposite side of the same dimer. (d) Adsorption of molecular hydrogen at a surface temperature $T_s = 500$ K. Circles indicate the presence of a second adsorption site at the offset pairs of step atoms (type 2).

A further interesting aspect of the experimental data concerns the observation of correlated adsorption along the step edge. This effect is apparent in the data of Fig. 3 where a higher hydrogen dose has been applied to the room-temperature surface. The correlation manifests itself in the formation of long continuous rows of adsorbed hydrogen. The effect is clear from a comparison of the experimental data (solid bars of Fig. 4) and the prediction of a purely statistical distribution of a sample Langmuir adsorption model (shaded bars in Fig. 4). The experimental ratio for the prevalence of chains of five pairs compared to that of single pairs, for example, exceeds the statistical value by a factor of six. The experimental data suggest the existence of an enhanced sticking coefficient at sites adjacent to occupied ones. Using a modified Langmuir model with two sticking coefficients, s_0^1 for adsorption sites without and $s_0^2 = 3 \times s_0^1$ for sites with occupied neighbors, we are able to reproduce the experimental distribution (open bars in Fig. 4). The experimental dependence of coverage on the hydrogen exposure shown in the inset of Fig. 4 can also be explained by this model. Both the experimental and simulated up-take curves yield an extended quasilinear behavior as a result of the competition

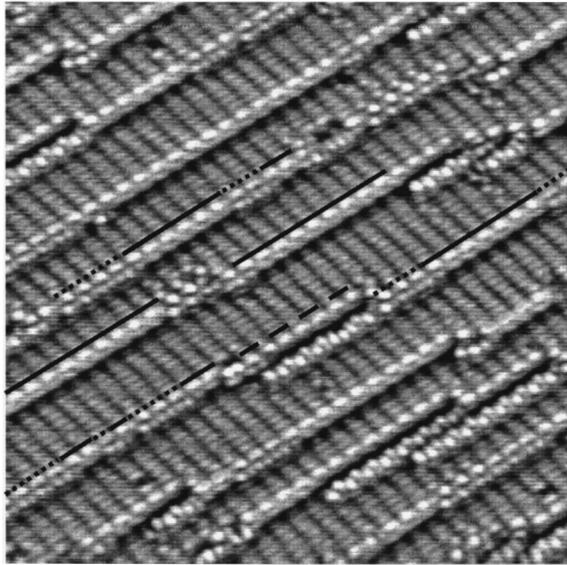


FIG. 3. $20 \times 20 \text{ nm}^2$ image at negative sample bias ($U = -2.2 \text{ V}$, $I = 0.5 \text{ nA}$) after an exposure to 450 L of H_2 . Hydrogen has adsorbed at 65% of the D_B step sites. The formation of rows of saturated (full line) and unsaturated (dotted line) dangling bonds is observable. Most of the remaining unsaturated dangling bonds appear unbuckled. All hydrogen is adsorbed at pairs of step atoms aligned with the upper dimer row. Additionally the $S_B^R \cdot S_A$ step configuration is present (dashed line, all except the two left most rebonded atoms are hydrogen terminated).

between an increasing number of sites with higher reactivity and a decrease of the overall number of available adsorption sites. From the initial slope, a sticking coefficient of $s_0 = 4 \cdot 10^{-4}$ per site is deduced, in good agreement with previously reported data.^{10,15}

For an increased surface temperature of $T_s = 500 \text{ K}$, the overall sticking coefficient increases by a factor of six. Also, as shown in Fig. 2(d), adsorption can be seen at sites consisting of the offset pairs of step atoms (pair 2 in Fig. 1). At 500 K the sticking coefficient for these sites was found to be about 10 to 20 times lower than s_0 at the step atoms aligned with the upper terrace (pair 1). The results just presented may be considered both in terms of the proposed adsorption channels at the step sites and with respect to hydrogen adsorption on clean and predosed terraces of Si(001).

The finding of a high sticking coefficient at the step sites at low surface temperatures is in good agreement with earlier second-harmonic generation measurements.¹⁰ The present data complement the earlier results by providing direct evidence that dissociative adsorption occurs on the rebonded step atoms. The role of the rebonded step atoms in the adsorption process was in fact predicted by density functional calculations.¹⁰ These calculations, performed in an adiabatic approximation that allows for full relaxation of the positions of the silicon atoms along the reaction pathway, indicated a barrierless pathway for dissociative adsorption. Indeed, the actual barrier height must be quite low since adsorption occurs readily. Recent measurements indicate, however, the presence of a finite barrier,⁹ which agrees well with the increase of the sticking probability with surface temperature

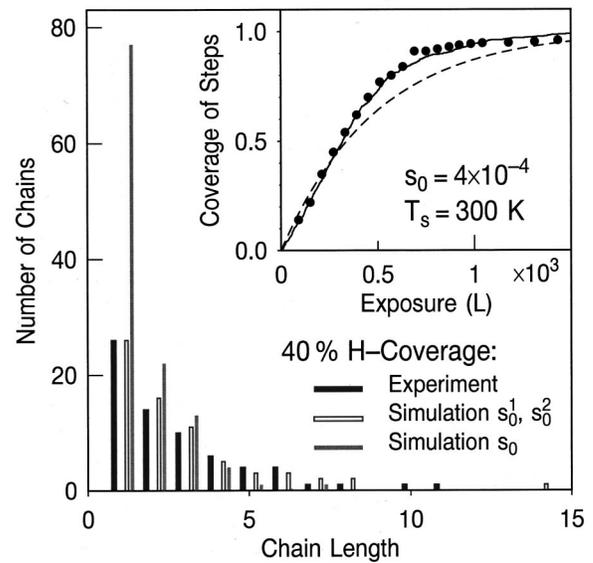


FIG. 4. Distribution of the chain length of saturated dangling-bond pairs in a $30 \times 30 \text{ nm}^2$ frame (black bars) compared to the results of Monte Carlo simulation with (i) s_0 equal for each adsorption site (shaded bars) and (ii) adsorption three times more likely on sites next to a saturated dangling-bond pair (unfilled bars). Inset: Uptake curve during hydrogen exposure at a surface temperature of $T_s = 300 \text{ K}$ (dots). The dashed curve indicates a pure Langmuir adsorption with a single initial sticking coefficient. The solid line was found using the same simulation as shown in the main figure.

from which an activation energy of $E_a = 0.1 \text{ eV}$ has been deduced.¹⁰ We interpret this behavior in terms of a phonon-assisted sticking process: For an appropriate arrangement of the silicon atoms, the adsorption barrier is assumed to be negligible, in accordance with the DFT calculations. Since the substrate atoms do not fully relax during the motion of the light hydrogen atoms, a finite barrier is still expected for a realistic trajectory. With increasing surface temperature, however, there is a greater likelihood of the Si surface atoms being in more favorable positions, hence the activation with surface temperature. The lower sticking probability at the pairs of type 2 and the stronger activation with temperature for these sites suggest that the equilibrium configuration of the Si atoms for this pathway is less favorable than for the pairs of type 1.

The influence of occupied adsorption sites on unsaturated dangling bonds and their adsorption behavior can be understood in a similar fashion. As described in Ref. 10, calculations indicate that the motion of step atoms towards a symmetric configuration favors the adsorption process. The effect can be achieved by thermal excitation, but also appears to occur at sites adjacent to H-terminated step atoms. This may be seen in Fig. 2(a) where the bright features associated with the dangling bonds of the step atoms adjacent to occupied sites assume a more elongated shape. The change, which is taken as indicative of a relaxation of the buckling of the step atoms and a charge redistribution, is also apparent at most of the unsaturated dangling bonds in Fig. 3 and illustrated in Fig. 5. This modification may be static or dynamic (flipping between two buckled configurations) in character.

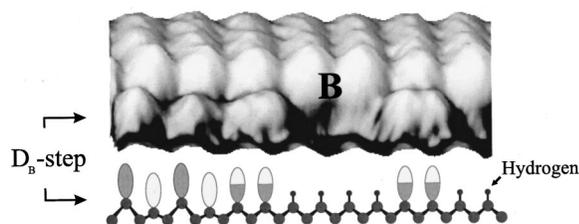


FIG. 5. Pseudo-3D rendering of one of the step edges in Fig. 2(a) and a ball-and-stick model with filled, half-filled, and empty dangling-bond states at unreacted Si atoms.

In either case, a configuration results that is easier to be brought to that of a more symmetric transition state, with a concomitant increase in adsorption probability.

The results presented above fit very well in our general picture of hydrogen adsorption on silicon surfaces:^{6,7,9,10} Activation with surface temperature indicates that distorted lattice configurations lead to a reduction of the mean barrier height. This effect is less pronounced at step sites due to the lower adsorption barrier for the equilibrium geometry. Similarly, static distortions can increase reactivity for both terrace^{7,9,16} and the step sites. In the former case, preadsorbed H atoms induce dangling-bond states (dbs) near the Fermi level, which lower the barrier for dissociation over two dimers.^{9,17} For the step sites, the enhanced reactivity induced by adsorbed H atoms described above can be attributed to a

similar electronic structure, i.e., symmetrization of the Si step atoms and a strongly reduced band splitting.¹⁰ In contrast, a different mechanism appears to be responsible for the recently reported enhancement in reactivity of single isolated, untilted dimers.⁸ The π -like bonding between the dbs should prevent any significant reduction of the band splitting in this case.⁹

In summary, we have observed directly the dissociative adsorption process of H₂ on the stepped Si(001) surface by means of STM. A low barrier pathway is found leading to adsorption of H atoms on pairs of rebonded step atoms, which are aligned with the dimer rows of the upper terrace. At a higher surface temperature, a second pathway becomes accessible involving the offset pairs of step atoms. The reactivity at the steps, already much higher than that for the flat surface, can be increased both by activation through surface temperature and through static configurational changes induced by the interaction between occupied sites and unsaturated dangling bonds. These characteristics, which resemble ones found for hydrogen on flat silicon surfaces, confirm the importance of the lattice degrees of freedom in the reaction dynamics of covalently-bonded surfaces.

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¹G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994).

²S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnquist, and J. K. Nørskov, *Phys. Rev. Lett.* **83**, 1814 (1999).

³B. Voigtländer, T. Weber, P. Smilauer, and D. E. Wolf, *Phys. Rev. Lett.* **78**, 2164 (1997).

⁴J. H. G. Owen, K. Miki, D. R. Bowler, G. M. Goringe, I. Goldfarb, and G. A. D. Briggs, *Surf. Sci.* **394**, 91 (1997).

⁵W. Brenig, A. Gross, and R. Russ, *Z. Phys. B: Condens. Matter* **96**, 231 (1994).

⁶P. Bratu and U. Höfer, *Phys. Rev. Lett.* **74**, 1625 (1995); P. Bratu, K. L. Kompa, and U. Höfer, *Chem. Phys. Lett.* **251**, 1 (1996).

⁷A. Biedermann, E. Knoesel, Z. Hu, and T. F. Heinz, *Phys. Rev. Lett.* **83**, 1810 (1999).

⁸E. J. Buehler and J. J. Boland, *Science* **290**, 506 (2000).

⁹M. Dürr, M. B. Raschke, E. Pehlke, and U. Höfer, *Phys. Rev. Lett.* **86**, 123 (2001).

¹⁰P. Kratzer, E. Pehlke, M. Scheffler, M. B. Raschke, and U. Höfer, *Phys. Rev. Lett.* **81**, 5596 (1998).

¹¹D. J. Chadi, *Phys. Rev. Lett.* **59**, 1691 (1987).

¹²P. E. Wierenga, J. A. Kubby, and J. E. Griffith, *Phys. Rev. Lett.* **59**, 2169 (1987).

¹³H. Itoh, S. Narui, Z. Zhang, and T. Ichonokawa, *Surf. Sci.* **277**, L70 (1992).

¹⁴T. Komura, T. Yao, and M. Yoshimura, *Phys. Rev. B* **56**, 3579 (1997).

¹⁵M. Dürr, M. B. Raschke, and U. Höfer, *J. Chem. Phys.* **111**, 10 411 (1999).

¹⁶F. M. Zimmermann and X. Pan, *Phys. Rev. Lett.* **85**, 618 (2000).

¹⁷E. Pehlke, *Phys. Rev. B* **62**, 12 932 (2000).