

## Real-Space Study of the Pathway for Dissociative Adsorption of H<sub>2</sub> on Si(001)

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Dissociative adsorption of molecular hydrogen on clean Si(001) surfaces has been investigated by means of scanning tunneling microscopy. The dissociated hydrogen atoms are found to occupy Si atoms of adjacent dimers. In addition to this interdimer configuration associated with the adsorption of isolated hydrogen molecules, pairs of adjacent doubly occupied dimers are readily formed. They arise from the enhanced reactivity of partially occupied dimers following the initial H<sub>2</sub> adsorption step. The results are considered in light of recent adsorption and desorption measurements.

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The system of H<sub>2</sub>/Si(001) has emerged as a prototype for understanding the dynamics of gas/surface interactions on semiconductors. Despite its relatively simple structure, the interaction of hydrogen molecules with the Si(001) surface has been found to exhibit several remarkable features. The rate of desorption of H<sub>2</sub> from Si(001), for example, varies nearly as the first power of the coverage of the adsorbed hydrogen atoms [1–3], in contrast to what is normally expected for such a recombinative process. Further, the desorbing molecules exhibit low translational energy, suggesting that they encounter almost no barrier in the exit channel [4]. Dissociative adsorption, on the other hand, is clearly activated [5,6], and the sticking coefficient for clean surfaces at room temperature is less than 10<sup>-10</sup>. The effective adsorption barrier, however, decreases sharply with increasing surface temperature [5,6], corresponding to the phenomenon of phonon-assisted sticking [7].

Microscopically these and other experimental observations have generally been considered in terms of the interaction of pairs of hydrogen atoms adsorbed on individual dimers of the reconstructed surface (the pairing model). Preparing of H<sub>2</sub> on dimers provides, for example, a natural explanation of the observed first-order desorption kinetics [2,3]. Since the dimers are tilted on the clean surface but symmetric in the presence of adsorbed hydrogen, the pairing model also seems to be a suitable starting point for explaining the dynamics of adsorption and desorption. In this picture, the dimer tilting coordinate provides the coupling between the barrier height and lattice distortions required within the model of phonon-assisted sticking to explain the adsorption and desorption characteristics in a self-consistent fashion [7]. A lowering of the barrier with decreasing dimer tilt angle has indeed been predicted [8,9]. Quantitatively, however, the calculated reduction in barrier height is insufficient to yield a nearly thermal energy distribution of the desorbing H<sub>2</sub> molecules, while the lattice distortion in the transition state is too weak to account for the large activation energy of 0.7 eV for phonon-assisted sticking [10].

Despite its popularity, no direct experimental evidence in favor or against the “pairing model” has been available.

On the one hand, the high mobility of hydrogen at the desorption temperature of 800 K prevents one from observing the desorption sites by real-space imaging of the surface immediately after desorption [11]. On the other hand, the extremely low sticking coefficients pose significant difficulties in undertaking adsorption experiments. While the focus of theoretical work has been primarily on pairing models, symmetry considerations and calculated barrier heights were put forward earlier on that argued against an intradimer transition state [12,13]. Alternatives to the pairing models were also suggested experimentally by the demonstration of highly reactive interdimer pathways on vicinal and H-precovered surfaces [14–17]. In the high-coverage regime, however, a recent study of H<sub>2</sub>/Si(001) by scanning tunneling microscopy (STM) evoked an intradimer transition state [18].

In this Letter we present the first direct, real-space observation of dissociative adsorption of hydrogen on the clean Si(001) surface. At surface temperatures below 500 K, surface diffusion is slow enough to observe the hydrogen atoms of the dissociated molecules in their original configuration by STM. At the same time, through the use of a heated hydrogen beam, the sticking coefficients are high enough to detect adsorbed hydrogen in a carefully designed experimental apparatus. The results provide clear evidence that H<sub>2</sub> reacts with two adjacent dimers of the clean Si(001) surface.

The experiments were conducted under ultrahigh vacuum (base pressure  $\leq 7 \times 10^{-11}$  mbar) with a commercial STM (Omicron STM-1). The chamber was also equipped with capabilities for Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS). Molecular hydrogen could be introduced either by simple backfilling or through a hyperthermal molecular beam [19]. In either case, we used 99.9999% pure H<sub>2</sub> gas that was further purified by a liquid nitrogen cold trap to freeze out residual H<sub>2</sub>O. During H<sub>2</sub> exposure all filaments were switched off and the pressure was monitored with a baratron gauge. The sample [*n*-doped, 10  $\Omega$  cm, oriented within 0.25° to the (001) plane] was prepared as described earlier [15] and exhibited broad 2  $\times$  1 reconstructed terraces with a defect

density  $\leq 0.5\%$ . All STM images were recorded at room temperature. The temperatures for dosing and desorption were determined to within 15 K from the current-temperature characteristics of the sample, which we calibrated with a thermocouple attached to the silicon surface after the experiments.

In Fig. 1 the Si(001) surface is shown after exposure by backfilling the chamber to  $\sim 10^6$  Langmuir of  $H_2$  (dosing time  $t = 20$  min,  $p = 10^{-3}$  mbar). For the image in Fig. 1(a), the surface was held at room temperature during exposure. No adsorption is observed to an accuracy defined by the initial defect density, implying a detection limit for the sticking coefficient of  $s_0 \approx 5 \times 10^{-10}$ . Figure 1(b) shows the surface after exposure to the same dose of hydrogen as in (a), but with the surface held at a temperature of 500 K. The dominant features seen on this surface, which appear as square dark spots, are clusters of four hydrogen atoms on two adjacent dimers. Three such features are shown in more detail in Fig. 1(c). In Fig. 1(b), the concentration of the few dark single dimers is comparable to that on the clean surface; it can be attributed primarily to initial defects. No clusters of three saturated dimers were found under these conditions. To exclude any possible influence of the adsorption of water or oxygen on

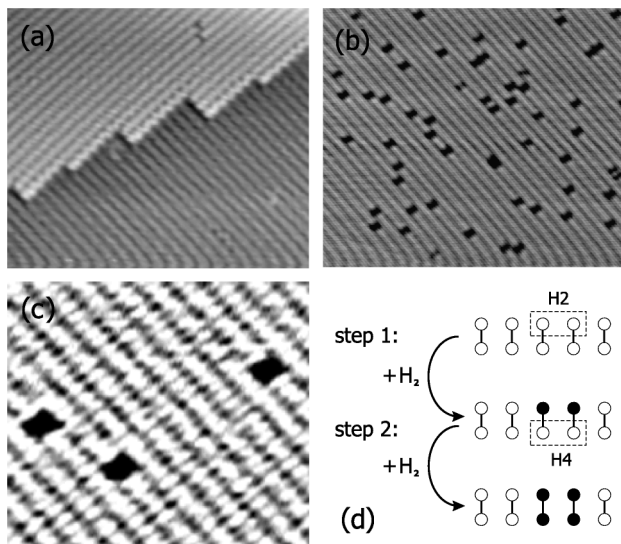


FIG. 1. Filled-state STM images ( $U = -2.2$  V,  $I = 0.7$  nA) of approximately  $25 \times 20$  nm<sup>2</sup> of a Si(001) surface [(a) and (b)]. (a) The room-temperature surface was exposed to  $10^6$  L  $H_2$  by backfilling the chamber. (b) Same exposure as in (a) for a surface temperature of  $T_s = 500$  K leads to enhanced dissociative adsorption of  $H_2$ . The dark features are mostly pairs of saturated dimers. (c) Closeup of three hydrogen clusters after exposure of  $10^6$  L  $H_2$  to a surface at a temperature comparable to that in (b). Comparison with silicon dimers in the adjacent rows clearly indicates a cluster size of two saturated dimers. (d) Schematic representation of the adsorption process. Top: clean dimer row before adsorption. Middle: after the adsorption of one  $H_2$  molecule in the interdimer configuration. Bottom: final configuration after a second  $H_2$  molecule has been dissociatively adsorbed.

these measurements, the surface was annealed for 20 s to a temperature of 850 K, just above the hydrogen desorption temperature of 800 K. This treatment resulted in a defect concentration comparable to that of the clean surface. Had a significant concentration of oxygen atoms been present, these atoms would have remained on the surface and been observed in the STM image [20]. Additionally, AES measurements performed at higher coverages did not reveal evidence of oxygen.

As adsorbed hydrogen is immobile at temperatures  $\leq 500$  K [15,21], the observed hydrogen configuration must be interpreted in terms of a two-step adsorption process. Considering an interdimer reaction pathway, a straightforward explanation of the experimental findings may be given. The initial step is the dissociative adsorption of an  $H_2$  molecule on adjacent clean dimers in a cis configuration [H2, Fig. 1(d)]. This occurs slowly with an initial sticking coefficient  $s_0 \sim 10^{-8}$ . The resulting configuration (H4) has, however, been previously shown to be highly reactive towards  $H_2$  adsorption [15] and leads to the observed presence of 4 adsorbed H atoms from the dissociative adsorption of a second  $H_2$  molecule. Since the sticking probability of the H4 sites is  $8 \times 10^{-4}$  [15], most sites react within a second for the experimental flux of  $\approx 3000$  ML/s. If contrary to the scenario above, we assume that the initial adsorption occurs through an intradimer step, the experimental findings are difficult to understand. First, no appreciable enhancement in adsorption adjacent to a doubly occupied dimer was previously observed [15,17]. Further, even if such a weak enhancement were present under some conditions, one would not expect the increased reactivity adjacent to an isolated doubly occupied dimer to be far stronger than that present, say, adjacent to a pair of doubly occupied dimers. Hence, in such a scenario, chains of doubly occupied dimers of varying lengths would be present, in contradiction to experiment.

In order to isolate the first step of hydrogen adsorption for the clean Si(001) surface experimentally, we need to increase the probability of the initial adsorption process. We were able to achieve this by means of dosing the surface with a hyperthermal beam of hydrogen molecules. For a supersonic hydrogen beam at a nozzle temperature of 1300 K, the sticking probability  $s_0$  increases from about  $10^{-8}$  to  $10^{-5}$  for the Si(001) surface at 450 K [6]. In this regime, sticking on the clean surface competes with the enhanced dissociation at H4 sites, at least at sufficiently low coverages. The corresponding STM image is shown in Fig. 2(a). In addition to the quartets of hydrogen formed by the mechanism described above, one can detect pairs of H atoms in the cis interdimer configuration (indicated as configuration C). High-resolution filled- and empty-state images of such a configuration prepared by adsorption of atomic hydrogen are displayed in Figs. 2(b) and 2(c). The presence of a pair of adsorbed H atoms is very clear in filled-state image (b), while empty-state image (c) highlights the presence of the

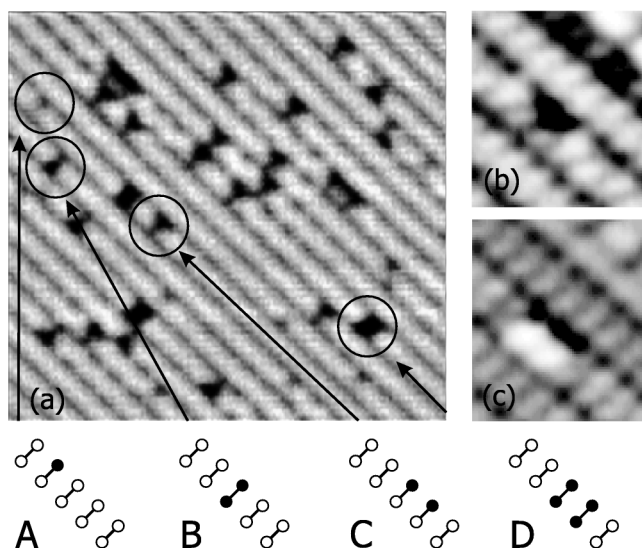


FIG. 2. (a) Filled-state STM image [ $U = -2.2$  V,  $I = 0.5$  nA, also in (b)] of approximately  $10 \times 10$  nm<sup>2</sup> of a Si(001) surface after  $\approx 10^3$  L exposure of H<sub>2</sub> through a nozzle at a temperature of 1300 K with the surface at a temperature of 450 K. Features of type: *A*: isolated singly occupied sites from the adsorption of H atoms produced by gas-phase dissociation in the 1300-K beam. *B*: intradimer sites, which are indistinguishable from surface defects. *C*: interdimer configurations from the first-step H<sub>2</sub> adsorption. *D*: two doubly occupied dimers from a 2-step H<sub>2</sub> adsorption process. (b) and (c) show, respectively, filled-state ( $U = -2.2$  V,  $I = 0.5$  nA) and empty-state ( $U = +0.7$  V,  $I = 0.5$  nA) STM images of two adjacent H atoms (configuration *C*), for comparison. The two remaining dangling bonds in (c) appear bright.

corresponding pair of unsaturated dangling bonds. Since these measurements must be carried out at low coverages of adsorbed hydrogen in order to avoid the H4 process, the presence of defect sites cannot be disregarded. Common defects, such as site *B* in Fig. 2, are difficult to distinguish from the possible presence of Si dimers saturated with two H atoms. In analyzing various images, we found that adsorption in the interdimer configuration was strongly favored over any possible intradimer pathway (ratio  $>8 : 1$ ).

The results just presented are in good quantitative agreement with the sticking probability and its surface temperature dependence obtained earlier in measurements by optical probing techniques [5,6]; the current findings also agree, in the appropriate regime, with the trend of enhanced sticking probability for surfaces covered with adsorbed hydrogen [16,17]. The new STM data provide, however, direct and previously unavailable information on the microscopic pathway of the adsorption process. We now consider briefly the implications of these findings for our picture of the dynamics and kinetics of the hydrogen/silicon interaction.

Most theoretical investigations to date have focused on the intradimer adsorption/desorption pathway. This was motivated by two facts: First, the Si-Si separation across

a dimer is much less than that for Si atoms in adjacent dimers. Intuitively, this suggests a higher dissociative adsorption probability, given the short bond length of the H<sub>2</sub> molecule. Second, an intradimer desorption process together with a pairing energy of a few tenths of an eV for hydrogen atoms on the same dimer provides a natural explanation for near first-order desorption kinetics at moderate-to-high H coverage, as well as the deviation at low coverage found experimentally [3]. In spite of these observations, comparison with theoretical investigations of an interdimer pathway [9,12,17,22] suggests that the latter is indeed the natural reaction channel.

Vittadini and Selloni [9], for example, obtained similar adsorption barriers for the interdimer and intradimer pathways. The two possible reaction channels differed, however, in terms of the energy stored in the substrate when frozen in the transition state: the lattice energy found for the interdimer transition state greatly exceeded that for the intradimer transition state. In later calculations, Pehlke arrived at qualitatively similar results. Indeed, a slightly lower adsorption barrier for the interdimer pathway was obtained (0.2 eV compared to 0.3 eV for intradimer case), while an appreciable amount of energy (0.3 eV) was stored in the substrate only for the interdimer transition state [17,22]. The issue of substrate energy storage in the transition state is of critical importance: Only when this value is significant can the model of phonon-assisted adsorption explain the strong rise in the H<sub>2</sub> sticking probability with increasing surface temperature. Thus, theoretical predictions for an interdimer adsorption pathway appear to be compatible both with the relative barrier height for the intradimer pathway and, importantly, with activation of the adsorption process with surface temperature.

An interdimer adsorption mechanism can also be related to earlier experimental observations of H<sub>2</sub> adsorption on stepped [14] and hydrogen predosed surfaces [15,17]. For the latter case in particular, a configuration equivalent to that of Fig. 1(d), middle panel, was found to exhibit a barrierless interdimer adsorption pathway. This observation in itself makes the interdimer pathway on the clean surface plausible. It further suggests that such a pathway would be strongly influenced by the configuration of the substrate atoms, since the barrier encountered on the clean surface is reduced by static lattice distortions such as those associated with preadsorbed hydrogen atoms. Appropriate thermally induced displacements of the substrate atoms on the clean surface might be expected to lead to similar low-barrier configurations, in accordance with the phonon-assisted sticking model. Such a reduction of the barrier height has been ascribed to the creation of two dangling bond states that can effectively hybridize with and fill the H<sub>2</sub> antibonding orbital [22].

The principle of detailed balance, which has been shown to be applicable to this system in Ref. [6], suggests that the same transition state is relevant for adsorption and desorption. As a consequence, one might expect that the

observed interdimer pathway would lead to second-order kinetics for desorption, in contrast to the near first-order kinetics observed experimentally at moderate to high coverages [1–3]. Considering, however, the attractive interactions between the two hydrogen atoms of a doubly occupied dimer (pairing), between hydrogen in pairs of doubly occupied dimers (clustering), and between two hydrogen atoms bonded to adjacent dimers (pairing, cis configuration), Zimmermann and Pan [16] were able to reproduce their experimental data with a purely interdimer desorption mechanism. Alternatively, a slightly higher barrier for desorption from the H4 configuration (two doubly occupied dimers, dominant at high coverages) compared to that for desorption from H2 configuration (two dimers each occupied with only one hydrogen atom, dominant at low coverages) can also explain the observed behavior, notably the shift towards second-order kinetics at low coverages [3,23]. Inherent to both models is a change in active reactive sites with coverage. As a consequence, the dynamics should change from low energy molecules desorbing out of H4 sites at high coverages [4] to a higher mean translational energy for desorption out of H2 sites at low coverages [6].

In summary, we have directly observed the initial configurations resulting from dissociative adsorption of H<sub>2</sub> on the Si(001) surface by STM. On the clean surface, the process occurs through an interdimer reaction pathway, in contrast to the widely held view that an intradimer pathway is operative. The interdimer pathway exhibits an adsorption barrier that may be strongly influenced by the local configuration of the Si atoms. This behavior is exemplified by the dramatic increase in sticking probability when hydrogen atoms are present in a cis configuration on adjacent dimers and explains the prevalence of pairs of adsorbed H<sub>2</sub> molecules on the surface at temperatures below that required for surface diffusion.

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