Dissociative Adsorption of H_2 on Si(100) Induced by Atomic H

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We report the observation of H_2 adsorption on the H/Si(100) surface using scanning tunneling microscopy. Predosing the surface by atomic H leads to the efficient adsorption of H_2 in an *interdimer* configuration of adjacent singly occupied dimers. This strong and local promotion of dissociative adsorption is explained by the noninteracting character of the relevant dangling bonds. By way of contrast, H_2 sticking is strongly inhibited on the clean Si(100)-(2×1) surface where the dangling bonds are rendered less reactive by their mutual interaction.

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The system of H and H_2 on Si(100) represents a prototype for the interaction of atoms and molecules with covalent surfaces. The motivation for this choice of system lies in its relative simplicity, from both the theoretical and the experimental standpoints, and its relevance to semiconductor technology. While the structural properties of H/Si(100) are now relatively well understood, the nature of basic dynamical processes such as recombinative desorption and dissociative adsorption of molecular hydrogen are only now being probed in detail [1–10].

One of the noteworthy characteristics of this system is the extremely low sticking coefficient for the dissociative adsorption process by which molecular H_2 is adsorbed on the silicon surface as H atoms [1–3]. This result suggests a sizable barrier to adsorption. The assumption of adsorption-desorption reciprocity then implies that desorbing molecules should experience the same barrier. Kolasinski *et al.* [8,9] demonstrated that this is not the case. Desorbing H_2 molecules do not exhibit a substantial amount of excess energy. This argument, however, assumes a unique adsorption pathway with a barrier that depends solely on the energy of the molecule. The strong variation of the sticking coefficient of H_2 on Si(100) [1–3] and Si(111) [11] with surface temperature reported by Bratu *et al.* demonstrates, however, the importance of surface excitation in the adsorption process. This finding led to the introduction of the notion of phonon-assisted sticking [1,3] in which the thermal excursions of the surface atoms from their equilibrium positions create atomic configurations with low or vanishing barrier heights [4–6].

One important missing piece in this puzzle is direct real-space information on the adsorption process, which might provide insight into how dissociation occurs and by what factors it is promoted. On the clean surface, adsorption events are so rare that it is virtually impossible to detect except at elevated temperatures. At temperatures below 450 K, where diffusion does not immediately obliterate the initial configuration of the adsorbed H atoms, the estimated sticking coefficient according to the published Arrhenius form [1–3] is less than 10^{-10}, and only $\approx 2 \times 10^{-14}$ at 300 K. The observation of H_2 adsorption activated by surface temperature already, however, suggests the existence of surface-bound adsorption promoters.

In this Letter, we report that predosing the Si(100)-(2×1) surface with atomic hydrogen creates active sites with a high probability for dissociative adsorption of H_2 molecules. Through scanning tunneling microscopy (STM), we are able to see directly the final state and to identify the final sites of the two adsorbed H atoms. Adsorption is found to take place next to an interdimer pair of preadsorbed H atoms with a sticking probability roughly 10 orders of magnitude above that estimated for the clean surface at room temperature [1–3].

These observations have two important implications. (1) The local structure of the active sites is found to be capable of dramatically altering the sticking probability. The effect is interpreted in terms of the presence of reactive isolated dangling bonds on the dimers occupied by a single H atom. This leads to the hypothesis that the dependence of the sticking coefficient of the clean surface on temperature may be understood as a weakening of the intradimer interaction of the dangling bonds by thermally induced changes in the dimer geometry. (2) The measurements provide the first direct evidence of an interdimer adsorption pathway, a channel that has been ignored in most experimental and theoretical work to date. The observed interdimer adsorption configuration reveals the possibility of a corresponding desorption pathway proceeding through pairs of doubly occupied dimers.

The experiments were carried out in an ultrahigh vacuum chamber equipped with a scanning tunneling microscope (Omicron STM-1) and capabilities for Auger-electron spectroscopy and thermal desorption spectroscopy (TDS). The Si(100) samples (P doped, 10 Ω cm; B doped, 2 Ω cm) were prepared by direct current heating to temperatures above the SiC desorption temperature ($\approx$1400 K), as indicated by the complete disappearance of the weak C peak at 273 eV in the Auger-electron spectra. The samples were cooled at a rate of 1 K/s to minimize surface defect formation. Atomic hydrogen for predosing the sample was obtained by dissociation of H_2 with a hot tungsten filament ($\approx$2000 K, sample distance 20 mm).

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Molecular H_2 and D_2 were dosed simply by backfilling the chamber with all filaments switched off.

Dosing molecular H_2 on the clean Si(100)-(2×1) surface at room temperature does not lead to measurable hydrogen adsorption. Presently, the background of water vapor limits our sensitivity to sticking coefficients exceeding 5×10^{-7}. After preadsorption of H, however, exposures to H_2 at doses as low as 100 L yield a significant effect. Figure 1 shows STM images of the Si(100) surface obtained before and after exposure to 280 L of H_2. The initial surface was prepared by dosing with atomic hydrogen to a coverage of 0.05 ML.

In the STM images of Fig. 1, the small circular bright spots arise from electrons tunneling into isolated dangling bonds. These are produced by the presence of a single adsorbed H atom on the opposite side of the Si dimer [12,13]. The larger oval spots, marked by circles in the figure, correspond to adjacent pairs of such singly occupied dimers. Once both dangling bonds of a dimer are saturated with H atoms, i.e., a doubly occupied dimer is formed, the site appears dark.

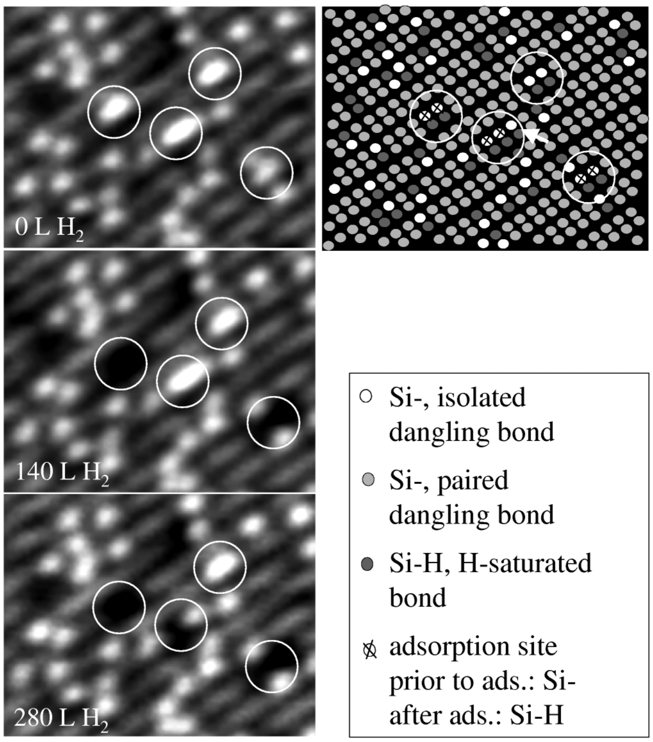

FIG. 1. STM images of Si(100) predosed with 5% atomic H before and after dosing with 140 and 280 Langmuir molecular H_2, respectively. The gray stripes in the STM images are rows of Si dimers. The bright spots are single dangling bonds and indicate an H atom on the opposite side of the dimer. The larger oval bright spots (circled) are adjacent dangling bonds (H atoms) on the same side of the dimer row. The only visible difference between the images is the disappearance of the larger bright spots, which indicates the saturation of the two corresponding adjacent, isolated dangling bonds (circled). In the case of three dangling bonds (H atoms) in a row, the third one remains unoccupied (arrow). The tunneling conditions were sample voltage +0.8 V and tunneling current 0.5 nA.

With increasing exposure to H_2 the large bright features, consisting of two isolated dangling bonds, turn dark, indicating their saturation. In the case of chains of three H atoms, we invariably see that only two become dark and one dangling bond remains (arrow in Fig. 1). In the full STM images of 30×30 nm^2 size, no further changes are perceivable on the terraces. The simultaneous saturation of two and only two dangling bonds corresponds perfectly to the dissociative adsorption of H_2, as depicted in Fig. 2.

To provide more quantitative information, we can determine the sticking probability at the active sites by counting the reacted sites as a function of H_2 exposure. For convenience, we define a local sticking coefficient S_{act} as the average sticking coefficient divided by the fractional area of active sites, with an active site (a pair of isolated dangling bonds) being considered to occupy the area of a (2×1) unit cell. S_{act} can be viewed as the probability for an H_2 molecule to stick if its initial trajectory ends on either of the two active dangling bonds. We find in this fashion a value of $S_{\mathrm{act}} = (8 \pm 2) \times 10^{-4}$ for a surface temperature of 300 K; a comparable or slightly smaller S_{act} is obtained for a surface temperature of 400 K.

A direct confirmation of the chemical identity of the adsorbed atoms observed in the STM images was obtained from measurements of TDS. In these experiments, we exposed the surface to D_2 after predosing with atomic H. Since diffusional intermixing of the adsorbed species occurs prior to the thermally induced recombinative desorption process, we observed the desorption of H_2, HD, and D_2 species. Given the preponderance of H on the surface, we typically followed the HD desorption yield to determine the amount of dissociative adsorption of D_2 at the active sites. We examined the role of the active adsorption sites by altering their concentration through thermal annealing of the predosed sample. At temperatures below ≈450 K, no diffusion of the preadsorbed H atoms occurs. At higher temperatures, however, surface diffusion of the adsorbed H drastically alters the density of active sites: active sites composed of two adjacent singly occupied dimers convert into inactive sites with one empty and one doubly occupied dimer. The driving force for this

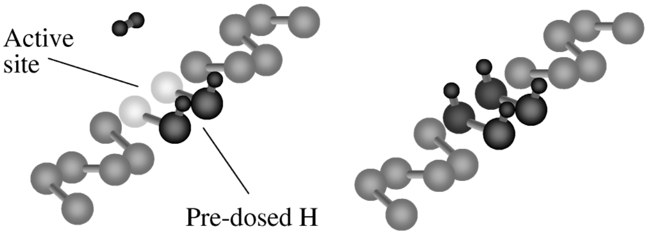

FIG. 2. Schematic of observed H_2 adsorption. The two H atoms initially on the surface were adsorbed atomically. The dimers forming the active adsorption site are in almost a symmetric configuration due to the two preadsorbed H atoms.

process is the effective pairing energy of 0.3 eV associated with the creation of a dimer π bond in this transformation [3,14–16]. Figure 3 illustrates the marked influence of this reduction in the density of active sites on the dissociative adsorption of D_2. Both the TDS peak and the density of active sites measured by STM drop sharply and in tandem for annealing temperatures above 450 K.

Parallel to our investigations, Raschke and colleagues [17,18] have examined dissociative adsorption of H_2 on vicinal Si(100) surfaces with double-height steps. The step sites are believed to exhibit a local structure similar to that relevant in our scenario, i.e., neighboring dangling bonds on Si atoms separated by the interdimer distance of 0.384 nm. Just as for the active sites discussed here, dissociative adsorption of H_2 at these step sites was found to occur with high efficiency. In a first-principles molecular dynamics calculation, Kratzer *et al.* [18] have identified a corresponding barrier-free adsorption pathway.

We may compare the sticking probability S_{act} in our experiment with that obtained [1–3] for clean surfaces at elevated temperatures [$S = 0.1\ \exp(-kT/0.75\ \mathrm{eV})$]. Upon extrapolation to room temperature, we find that the active sites on our surface increase the sticking coefficient by approximately 10 orders of magnitude. Further, the absence of any increase in sticking with increasing surface temperature in our case indicates that the local structure is already in a favorable configuration for dissociative adsorption.

How do we account for this dramatic increase in sticking probability? From the experimental data provided by the STM studies, we may immediately conclude that the process must be highly local in character: The H_2 molecules adsorb at the activated sites and nowhere else. This observation then leads us to consider the characteristics of the active sites and, in particular, why singly occupied dimers prove to be so effective in promoting adsorption. To provide at least a qualitative answer to this question, we shall briefly discuss the local electronic structure of the Si dimers and how it is altered in the presence of a single adsorbed H atom.

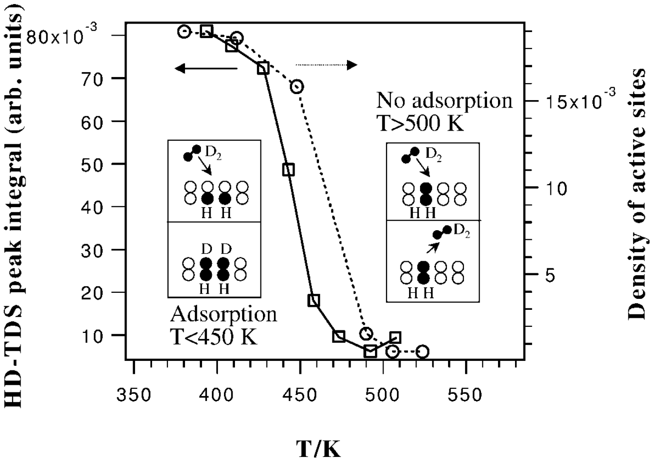

FIG. 3. Adsorption of D_2 on H predosed Si(100) as a function of annealing temperature. The TDS signal for HD is taken as a measure of the dissociative adsorption of D_2. Also plotted as a function of annealing temperature is the density of active sites (see Fig. 2) obtained from STM images. Above ≈450 K, H diffusion converts the active sites to empty and doubly occupied dimers, thereby eliminating the dissociative adsorption channel. To correct for the presence of residual HD gas during the preadsorption step, we determined the baseline TDS signal by reversing the order of dosing with D_2 and atomic H.

On the clean surface, the dimers undergo a strong relaxation, leading to asymmetric, tilted (or buckled) dimers. This changes both the energy levels of the dangling bonds and their orbital character [19–21]. One of the Si atoms moves upwards into a more tetragonal, bulklike coordination and its dangling bond becomes completely filled; the other Si atom of the dimer moves downward into a more graphitelike planar coordination with an empty dangling bond. The hypothetical, metallic surface structure of weakly interacting dangling bonds becomes semiconducting with completely filled and completely empty surface-state bands. This tendency towards the formation of a surface band gap is common on the surfaces of semiconductors, e.g., by buckling transitions on the Si(100)-(2 × 1) and Ge(100)-(2 × 1) surfaces [19,20] or by the π-bonded chain structure of the metastable Si(111)-(2 × 1) and Ge(111)-(2 × 1) surfaces [20].

The adsorption of a single H atom has a significant impact on both the geometric and the electronic structures of the dimer. One of the dimer's dangling bonds is now saturated by the H atom. In the absence of the π-bonding interaction of this bond with the other dangling bond, the latter moves close to the Fermi edge in energy. This behavior is clear from the STM data of Fig. 1 in which the isolated dangling bonds stand out as bright spots even at very low tunneling voltages. Scanning tunneling spectroscopy measurements [22] also demonstrate the dominance of these states around the Fermi level. For the case of a periodic arrangement of isolated dangling bonds (a dangling-bond wire), calculations [23] and experimental realizations [24] exhibit a single surface-state band around the Fermi level. The calculations also show that the H induced change in the electronic structure is accompanied by a return to a symmetric, untilted dimer. A single H atom is predicted to reduce the tilting angle from 19° to below 4° [15].

These geometric and electronic changes upon adsorption of a single H atom on a Si dimer reflect the formation of partially filled quasifree dangling bonds, which, as just discussed, do not exist in the ground state of the surface because of mutual interaction of the dangling bonds. The essential element for a low barrier pathway for dissociative adsorption of H_2 thus appears to be the availability of two of these quasifree dangling bonds on adjacent Si dimers. The changes in geometrical structure of the surface are not in and of themselves thought to be of importance for promoting dissociative adsorption: The separation of the dangling bonds on a single dimer (0.23 nm), where desorption does not occur at room temperature, would be more favorable than the 0.384 nm separation between the adjacent dimers of the active sites. Within the picture of the phonon-induced sticking introduced in [1] the generic vibrational degree of freedom assumed in this model might be identified, on the basis of our results, as a mode capable of decoupling the two dangling bonds of a dimer sufficiently. Such a motion would probably involve the dimer-rocking mode, as proposed in Refs. [1,4]. To disrupt the remaining π-interaction, dimer-stretching phonon modes might be of importance as well. On the other hand, the thermal excitation of electrons from the lower surface state band to the upper surface state band might have a similar effect, since lattice distortions of the Si(100) surface are closely tied to the electronic Fermi level structure.

To date, most experimental studies have been interpreted in terms of an *intradimer* adsorption/desorption pathway [14,25]. Theoretical studies, however, do not exclude *a priori* an interdimer channel [10,26]. Indeed, it has been pointed out [1] that the interdimer pathway [10] might fit the model potential used in the phonon-assisted sticking model [1] better than an intradimer reaction pathway. The present studies offer clear experimental justification for the consideration of interdimer reaction pathways. In particular, our experiments demonstrate that there exists an interdimer adsorption pathway with a very low barrier leading to a Si(100) surface with pairs of doubly occupied dimers. Since such a configuration may readily exist under desorption conditions, it is natural to assume the existence of a similar low-barrier interdimer desorption pathway. Further investigations will be required to determine the relative significance of this desorption channel.

In summary, we have observed the dissociative adsorption of H_2 on active sites of the H/Si(100) surface by STM and TDS. The adsorption process at these sites, which consist of two adjacent dimers each occupied by a single H atom, is found to be local in character and to occur with a high sticking coefficient. The results may be explained by the availability of adjacent, quasifree dangling bonds produced by saturation of one of each dimer's dangling bonds by the adsorbed H atom. Our studies also suggest that the low sticking coefficient for dissociative adsorption of H_2 on the clean surface is a consequence of the strong interaction of the dangling bonds; the observed thermal activation of the dissociation channel may then be viewed as proceeding from a phonon-induced weakening of these interactions. The present investigations also demonstrate directly the possibility of an interdimer adsorption channel and point to the existence of a similar low-barrier desorption channel.

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[1] P. Bratu, W. Brenig, A. Groβ, M. Hartmann, U. Höfer, P. Kratzer, and R. Russ, Phys. Rev. B **54**, 5978 (1996).

[2] P. Bratu, K.L. Kompa, and U. Höfer, Chem. Phys. Lett. **251**, 1 (1996).

[3] U. Höfer, Appl. Phys. A **63**, 533 (1996).

[4] P. Kratzer, B. Hammer, and J.K. Nørskov, Chem. Phys. Lett. **229**, 645 (1994).

[5] E. Pehlke and M. Scheffler, Phys. Rev. Lett. **74**, 952 (1995).

[6] A. Groβ, M. Bockstedte, and M. Scheffler, Phys. Rev. Lett. **79**, 701 (1997).

[7] A.J.R. da Silva, M.R. Radeke, and E.A. Carter, Surf. Sci. **381**, L628 (1997).

[8] K.W. Kolasinski, Int. J. Mod. Phys. B **9**, 2753 (1995).

[9] K.W. Kolasinski, W. Nessler, A. de Meijere, and E. Hasselbrink, Phys. Rev. Lett. **72**, 1356 (1994).

[10] A. Vittadini and A. Selloni, Chem. Phys. Lett. **235**, 334 (1995).

[11] P. Bratu and U. Höfer, Phys. Rev. Lett. **74**, 1625 (1995).

[12] T. Uchiyama and M. Tsukada, Surf. Sci. **295**, L1037 (1993).

[13] J.J. Boland, Adv. Phys. **42**, 129 (1993).

[14] U. Höfer, L. Li, and T.F. Heinz, Phys. Rev. B **45**, 9485 (1992).

[15] A. Vittadini, A. Selloni, and M. Casarin, Phys. Rev. B **49**, 11 191 (1994).

[16] J.E. Northrup, Phys. Rev. B **51**, 2218 (1995).

[17] M.B. Raschke and U. Höfer, Phys. Rev. B **59**, 2783 (1999).

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

[19] P. Krüger and J. Pollmann, Phys. Rev. Lett. **74**, 1155 (1995).

[20] J.A. Kubby and J.J. Boland, Surf. Sci. Rep. **26**, 61 (1996).

[21] A. Ramstad, G. Brocks, and P.J. Kelly, Phys. Rev. B **51**, 14 504 (1995).

[22] J.J. Boland, Phys. Rev. Lett. **67**, 1539 (1991).

[23] S. Watanabe, Y.A. Ono, T. Hashizume, and Y. Wada, Phys. Rev. B **54**, R17 308 (1996).

[24] T. Hitosugi, T. Hashizume, S. Heike, Y. Wada, S. Watanabe, T. Hasegawa, and K. Kitazawa, Appl. Phys. A **66**, 695 (1998).

[25] M.L. Wise, B.G. Koehler, P. Gupta, P.A. Coon, and S.M. George, Surf. Sci. **258**, 166 (1991).

[26] C.J. Wu, I.V. Ionova, and E.A. Carter, Surf. Sci. **295**, 64 (1993).