Structure Sensitive Reaction Channels of Molecular Hydrogen on Silicon Surfaces

M. Dürr,[1] M. B. Raschke,[1] E. Pehlke,[2] and U. Höfer[1,3]
[1]*Max-Planck-Institut für Quantenoptik, D-85740 Garching, Germany*
[2]*Fachbereich Physik, Universität Essen, D-45117 Essen, Germany*
[3]*Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, D-35032 Marburg, Germany*
(Received 4 August 2000)

The ability of the Si(001) surface to adsorb H_2 molecules dissociatively increases by orders of magnitude when appropriate surface dangling bonds are terminated by H atoms. Through molecular beam techniques the energy dependent sticking probability at different adsorption sites on H-precovered and stepped surfaces is measured to obtain information about the barriers to adsorption, which decrease systematically with an increase in coadsorbed H atoms. With the help of density functional calculations for interdimer adsorption pathways, this effect is traced back to the electronic structure of the different adsorption sites and its interplay with local lattice distortions.

DOI: 10.1103/PhysRevLett.86.123 PACS numbers: 68.35.Ja, 42.65.Ky, 71.15.Mb, 82.30.Lp

The relation between surface electronic structure and chemical reactivity is of great fundamental and technological importance [1]. In the case of semiconductor surfaces chemical reactivity is generally correlated with the presence of dangling bond states (dbs). However, it is not simply the concentration of dbs that determines reactivity. The electronic properties of the dbs are also important. It has been shown, for example, that the different charge density of dbs on Si(111)-(7×7) leads to site selectivity for reactions with certain adsorbates [2]. Here we demonstrate for a very fundamental reaction, the dissociative adsorption of H_2 on Si(001) surfaces, how the reactivity is governed by the interplay between lattice distortion and surface electronic structure.

A prominent feature of the H_2/Si system is the low sticking probability for dissociative adsorption at room temperature ($<10^{-11}$) and its increase by many orders of magnitude when the surface is heated [3]. Just as vibrationally excited molecules are able to overcome (late) dissociation barriers more easily according to the Polanyi rules, phononic excitations of the substrate are believed to promote the reaction of H_2/Si [4–8]. Whereas detailed dynamical information about vibrationally assisted sticking of molecules at metal surfaces has been obtained by state-selective molecular beam experiments for several systems [9], the microscopic mechanism of phonon-assisted sticking remains poorly understood. An important experimental difficulty in examining phonon-assisted sticking lies in the fact that thermal activation of the substrate leads to statistical excitation of many different surface modes, rather than to the controlled excitation of the relevant mode or modes. Consequently, it is difficult to correlate the observed enhancement in reactivity with any specific atomic-scale motion.

In this Letter, static distortions of the Si(001) surface are introduced by precoverage with atomic hydrogen or by steps. The measurement of site-specific sticking coefficients as a function of the kinetic energy of the incident hydrogen molecules then yields adsorption barriers for the corresponding, highly activated reaction channels. These local distortions and the changes in reactivity that they induce may be regarded as a more precisely defined analog of the thermally induced perturbations responsible for the strong increase in reactivity with increasing surface temperature. Density-functional calculations are presented to corroborate the interpretation of the experimental barrier heights in terms of the local distortion of the adsorption sites.

The experiments were performed under ultrahigh vacuum conditions with a base pressure of 5×10^{-11} mbar. Clean, well-ordered Si(001) surfaces were prepared and characterized as described previously [3]. For exposure of the Si(001) surface with H_2, a supersonic beam with translational energies between 20 and 350 meV and a flux Φ up to 2×10^{16} cm^{-2} s^{-1} [10] as well as background dosing was employed. The amount of adsorbed hydrogen was monitored *in situ* using optical second-harmonic generation (SHG). Sticking coefficients, $s_0 = \Delta\theta/\Delta t \Phi^{-1}$, were deduced from the decrease of the calibrated nonlinear susceptibility exploiting its linear dependence on hydrogen coverage θ [3]. To facilitate comparison, the results are given in terms of site-specific reactivities $\hat{s}$ that are obtained by normalizing initial sticking coefficients s_0 to a corresponding number of sites. Various initial distributions of adsorbed H atoms on the surface were created by adsorbing 0.15–0.25 ML of atomic hydrogen followed by different annealing cycles. The required H atoms were produced by dissociation of H_2 molecules on a hot tungsten filament in the chamber backfilled with gas (Fig. 1 inset). For surface temperatures $T_s < 350$ K, the adsorbed H atoms are immobile [11] and occupy dangling-bond sites in a largely random fashion.

The dimers of the reconstructed Si(001) surface are shown schematically in the right panel of Fig. 1. At low coverages θ of the predosed H atoms, very few sites [$\approx 2 \times \theta^2(1-\theta)^2 = 3\%$ for $\theta = 0.15$] are expected to form half-occupied pairs of adjacent dimers in which the two unreacted dangling bonds are aligned in a row. Recent

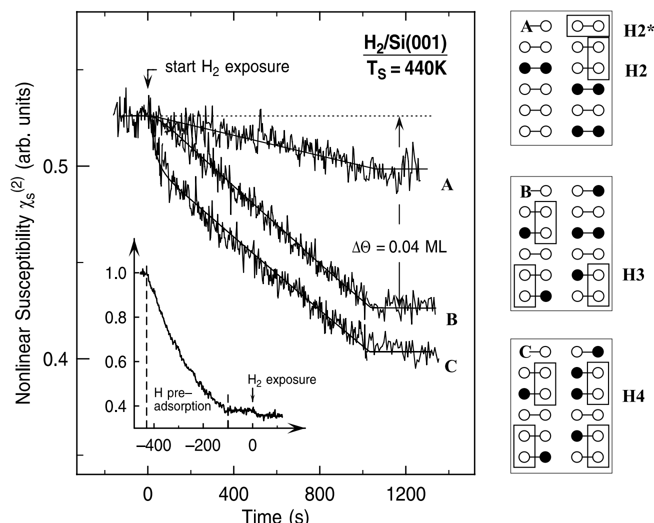

FIG. 1. SH response of Si(001) kept at $T_s = 440$ K during adsorption of thermal H_2 ($T_{gas} = 300$ K). For preparation 0.15 ML atomic hydrogen was preadsorbed at 300 K and followed by annealing cycles for 400 s at 500 K for trace B and 600 K for trace A. The corresponding surface precoverages are shown schematically on the right. Some of the dangling bonds (open circles) are quenched with hydrogen (filled circles). The respective reaction sites are labeled by rectangles. The inset shows the preparation of 0.2 ML H precoverage and the following saturation of the H4 sites with H_2.

experiments by Biedermann *et al.* [12] have, however, demonstrated that these minority sites lead to efficient dissociation of H_2. The reaction at these sites produces adjacent pairs of doubly-occupied dimers and is referred to here as the H4 reaction channel. This adsorption process may be identified in the SH adsorption data of trace C of Fig. 1 as the rapid initial drop in the SH signal.

When the hydrogen precovered surface is annealed at a temperature of 600 K for 400 s, its reactivity to H_2 molecules is greatly reduced (Fig. 1, trace A). The response is clearly characterized by a single sticking probability of $s_0 = 1.5 \times 10^{-9}$. At 600 K, the adsorbed hydrogen is mobile enough to reach thermodynamic equilibrium on the surface [11]. The equilibrium distribution for $\theta = 0.15$ monolayer (ML) consists almost entirely of doubly occupied dimers [13]. From the fact that the sticking coefficient of these hydrogen covered and annealed surfaces agrees well with that of clean Si(001) [3], we conclude that a small concentration of doubly occupied dimers has little influence on the reactivity of the surface. Annealing at 500 K for 400 s quenches the most reactive H4 channel by transformation of the H4 sites to a paired dimer [12]. However, the H_2 reaction proceeds considerably faster than on the fully annealed surface (Fig. 1, trace B). The sticking coefficient is identical to that one observed without annealing but after the initial saturation of the H4 sites. We assign this sticking coefficient to dissociation at adsorption sites labeled H3. These sites involve isolated adsorbed H atoms producing one half-filled dimer. They are the only sites of enhanced reactivity that are present on the surface after this treatment and which are quenched by annealing at 600 K.

To investigate the dynamics of adsorption, sticking coefficients were measured as a function of the kinetic energy of the incident hydrogen molecules for each of the arrangements described above. In addition the dynamics at D_B-step sites of vicinal Si(001) surfaces were investigated as well. Here Si instead of H atoms terminate one end of the dimers of a H4-like configuration, which have been shown to have an increased reactivity, too [14]. The sticking coefficient for the H4 sites was found to be the highest for low kinetic energies but to decrease slightly with increasing beam energy [Fig. 2(a)]. This behavior is characteristic for a barrierless reaction pathway [15]. In contrast, H_2 dissociation at the rebonded D_B steps is clearly activated [Fig. 2(b)]. The reactivity $\hat{s}(E)$ increases strongly as a function of beam energy until it saturates for

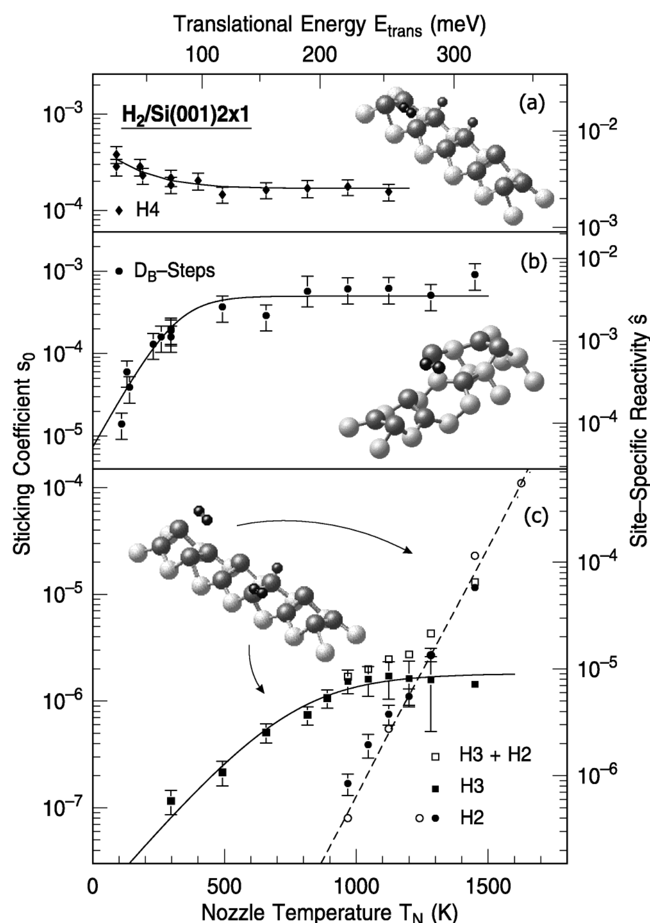

FIG. 2. Energy dependent sticking coefficients for the four main reaction channels: (a) H4 at $T_s = 350$ K, (b) D_B steps at $T_s = 540$ K, (c) H3 at $T_s = 350$ K (filled squares) and H2 at $T_s = 350$ K (filled circles) and $T_s = 90$ K (open circles). The open squares are the superposition of adsorption at the H2 and H3 sites at $T_s = 350$ K as determined in the experiment. The solid lines in (b) and (c) are fits to $\hat{s}(E) = \hat{A}/2[1 + \tanh(E - E_0)/W]$, whereas the other lines are guides to the eye. Also shown as ball and stick models are the corresponding reaction sites with Si atoms comprising the top (lower) layer denoted as large dark (bright) balls. H atoms are small balls.

$E \simeq 100$ meV. We can fit the empirical s-shaped adsorption energy function $\hat{s}(E) = \hat{A}/2[1 + \tanh(E - E_0)/W]$ [9] to our data which can be interpreted as a barrier distribution of the width W around a mean adsorption barrier E_0 due to thermally activated configurational changes. The reaction at the H3 and H2 sites is also activated [Fig. 2(c)]. The mean adsorption barrier associated with the H3 mechanism is $E_0 = 0.19 \pm 0.03$ eV, about twice the value for the steps ($E_0 = 0.08 \pm 0.02$ eV). $\hat{s}(E)$ shows a rather gradual increase for low beam energies, indicative of a wide distribution of barriers ($W = 76$ meV). The H2 channel is associated with the strongest activation; the sticking coefficient $s_0(E)$ does not saturate within the range of available beam energies which translates into a barrier $E_0 \geq 0.6$ eV, in agreement with results obtained for the clean Si(001) surface [10].

To shed light on the physical mechanism governing these processes, we have performed density-functional total-energy calculations [16] for the different reaction pathways. The generalized gradient approximation by Perdew *et al.* [17] (PW91-GGA) has been applied to the spin-unpolarized exchange-correlation functional. The substrate is simulated by a five atomic-layer thick slab of which the topmost three layers are fully relaxed, while the Si atoms in the bottom two layers are fixed at their bulk positions, and the dangling bonds on the bottom surface are terminated with hydrogen atoms. The supercells are one dimer wide and contain three or four Si dimers. The silicon atoms are represented by a Hamann pseudopotential constructed consistently within the PW91-GGA [18], while the unmodified $1/r$ Coulomb potential is taken for the hydrogen atoms. The energy differences given below refer to the potential-energy surface. We neglect zero-point energies, which does not alter any physical conclusions.

For the H4 configuration, we have found an interdimer reaction pathway in which the hydrogen molecule approaches the surface with its H-H bond perpendicular to the Si-dimer bond and undergoes dissociative adsorption without encountering any energy barrier. In further calculations the dangling bonds of the Si dimers are seen to become progressively less reactive if fewer preadsorbed H atoms are present. Removal of one of the initially two preadsorbed hydrogen atoms leads to an energy barrier for adsorption of about 0.06 eV at the so-formed H3 site. A further increase of the barrier to about 0.2 eV is found for adsorption without preadsorbed hydrogen, i.e., the interdimer adsorption path on the clean surface, H2 [19–21], in which the hydrogen molecule dissociates over two Si atoms of two adjacent, clean dimers. In principle, on the clean surface an alternative reaction pathway exists. This previously discussed intradimer path H2* [6,7] with the molecule dissociating over one silicon dimer yields the highest adsorption barrier of 0.35 eV. For this reason it does not contribute noticeably to the reactivity on the clean surface. For each of the reaction mechanisms, the elastic energy stored in the silicon substrate in the geometry of the transition state can be calculated. For the interdimer pathways it increases as the adsorption barrier increases (Table I).

All the calculated adsorption barriers are lower than the experimental activation energies. We attribute this situation to the inaccuracy of the GGA for the exchange-correlation functional, as the GGA tends to underestimate the adsorption-energy barrier up to a few hundred meV [22], as well as to dynamical effects, i.e., the inability of the silicon atoms to follow the optimum reaction pathway assumed in the calculation because of the large mass mismatch between these species. The trend of increasing barriers for the sequence H4-H3-H2-H2* has, however, been correctly predicted by the calculation.

Inspection of the Kohn-Sham orbitals and eigenenergies in the transition state supports the following explanation: To dissociate the hydrogen molecule, the H-H bond must be weakened. This is accomplished by hybridizing the antibonding $1s\Sigma_u^*$ H-H molecular orbital with two surface dangling-bond orbitals, which enter the hybrid orbital with opposite phases. The adsorption site shows a highly reactive character whenever the participating dangling-bond states lie close to the Fermi level: In this case the hybrid orbital may readily drop below the Fermi level and be filled with electrons. For the relaxed surface configurations the energy separation between the dangling-bond states is not particularly small because of the Jahn-Teller splitting. To obtain high reactivity, however, it is sufficient for the energy gap between the dangling-bond states to become small when the substrate is distorted towards the transition geometry—provided that not too much energy has to be expended in distorting the lattice. This reasoning explains the high reactivity of the two dangling bonds at the H4 site analogous to the mechanism suggested by Kratzer *et al.* [14] for the high reactivity at the D_B-step edge. It is supported by previous STM work that has revealed a reduced energy gap prior to the dissociation process [12,13]. The electronic states relevant for hydrogen adsorption at the H3 site are displayed in Fig. 3. Again, the dangling bond orbitals at -0.52 eV and at the Fermi level hybridize effectively with the antibonding molecular orbital. In this case, however, there is an extra electron that has to be transferred into the energetically unfavorable and previously unoccupied Si dangling bond, which renders this site less reactive. For the H2 configuration the same

TABLE I. Comparison of experimental and theoretical barrier heights E_0, calculated elastic energies in the transition state, and energy splitting of the dangling-bond states in an unbuckled surface configuration for the different reaction pathways of H_2/Si(001), if applicable.

	H2*	H2	H3	D_B	H4
$E_{0,\mathrm{exp}}$ (eV)	⋯	≥0.6	0.19	0.08	0
$E_{0,\mathrm{theory}}$ (eV)	0.35	0.20	0.06	⋯	⋯
Elastic energy (eV)	0.15	0.33	0.08	⋯	⋯
Energy splitting (eV)	0.7	0.7	⋯	0.4	0.35

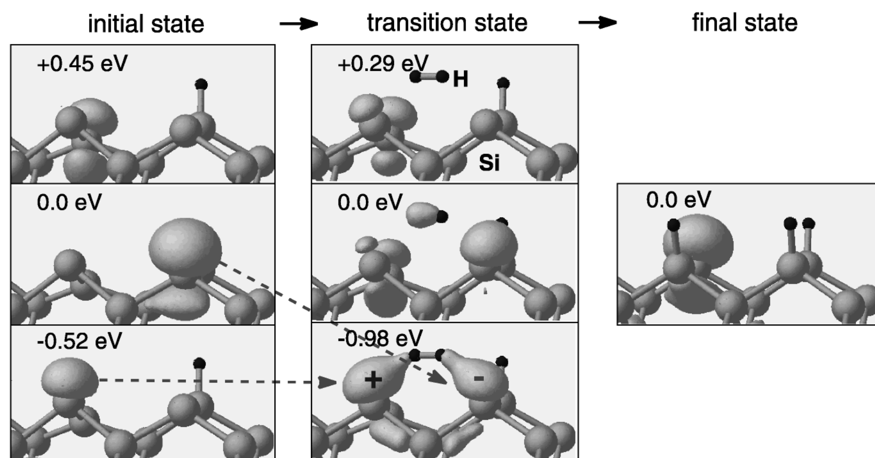

FIG. 3. Contour surfaces of constant charge density ($\rho = 0.005\ e^-/\mathrm{bohr}^3$) at the H3 site. Left hand side: electronic structure before H_2 dissociation. Because of the single preadsorbed H atom, the dangling-bond orbital at the opposite side of the Si dimer is located at the Fermi energy and occupied by one electron. The orbitals relevant for the hybridization with the H_2 molecule and their development during adsorption are indicated by arrows to the transition geometry shown in the middle panel. Right hand side: dangling bond at the Fermi level, occupied by a single electron, after dissociative H_2 adsorption. The orbitals are labeled by their Kohn-Sham eigenvalues relative to the Fermi energy.

electronic bond-breaking mechanism is still active. However, due to the interplay between the sp-rehybridization at large buckling angle and the π-bond formation at the small buckling angle of the Si dimers there is no low-energy distortion that results in a small energy gap between the dangling-bond states. Hence the elastic energy needed to distort the substrate is comparatively large. This diminishes the reactivity of the H2 site and explains the strong activation with surface temperature.

In conclusion, by combining density-functional calculations with direct measurements of the sticking coefficient we have identified three different interdimer reaction pathways for the dissociative adsorption of H_2 molecules on H-precovered Si(001) surfaces. The systematic increase of the reactivity with the number of coadsorbed hydrogen atoms in the sequence H2-H3-H4 arises from the interplay between the electronic structure of these sites and lattice distortions. Whenever the energy splitting between the dangling-bond states may be reduced by a low-energy distortion of the silicon lattice, the adsorption barrier is found to be low. On the clean Si(001) surface H_2 adsorption is thermally activated by lattice distortions that reduce the energy barrier for dissociation by means of a similar coupling between the energy of the Si dangling bonds and the dynamic lattice distortions.

The authors are grateful to A. Biedermann, W. Brenig, A. Gross, T. F. Heinz, K. L. Kompa, and P. Kratzer for helpful discussions and acknowledge support by the SFB 338 of the Deutsche Forschungsgemeinschaft.

Note added.—After submission of this work, Buehler and Boland reported the presence of a low-barrier H_2 dissociation path at untilted dimers of Si(001) [23]. Their results disagree with the conclusions of the present work and were not reproduced in related STM experiments [21].

[1] B. Hammer and J. K. Nørskov, Nature (London) **376**, 238 (1995); F. Besenbacher *et al.,* Science **279**, 1913 (1998).
[2] P. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989).
[3] P. Bratu and U. Höfer, Phys. Rev. Lett. **74**, 1625 (1995); P. Bratu, K. L. Kompa, and U. Höfer, Chem. Phys. Lett. **251**, 1 (1996).
[4] K. W. Kolasinski, W. Nessler, A. D. Meijere, and E. Hasselbrink, Phys. Rev. Lett. **72**, 1356 (1994).
[5] W. Brenig, A. Gross, and R. Russ, Z. Phys. B **96**, 231 (1994).
[6] P. Kratzer, B. Hammer, and J. K. Nørskov, Chem. Phys. Lett. **229**, 645 (1994); E. Pehlke and M. Scheffler, Phys. Rev. Lett. **74**, 952 (1995); A. Gross, M. Bockstedte, and M. Scheffler, Phys. Rev. Lett. **79**, 701 (1997).
[7] D. J. Doren, Adv. Chem. Phys. **95**, 1 (1996).
[8] A. Vittadini and A. Selloni, Surf. Sci. **383**, L779 (1997); K. Cho, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. Lett. **79**, 5078 (1997).
[9] C. T. Rettner, D. J. Auerbach, and H. A. Michelsen, Phys. Rev. Lett. **68**, 1164 (1992); M. Gostein, H. Parhikhteh, and G. O. Sitz, Phys. Rev. Lett. **75**, 342 (1995); H. Hou *et al.,* Science **284**, 1647 (1999).
[10] M. Dürr, M. B. Raschke, and U. Höfer, J. Chem. Phys. **111**, 10 411 (1999).
[11] J. H. G. Owen *et al.,* Phys. Rev. B **54**, 14 153 (1996); M. McEllistrem, M. Allgeier, and J. J. Boland, Science **279**, 545 (1998).
[12] A. Beidermann, E. Knoesel, Z. Hu, and T. F. Heinz, Phys. Rev. Lett. **83**, 1810 (1999).
[13] J. J. Boland, Phys. Rev. Lett. **67**, 1539 (1991); U. Höfer, L. Li, and T. F. Heinz, Phys. Rev. B **45**, 9485 (1992).
[14] P. Kratzer *et al.,* Phys. Rev. Lett. **81**, 5596 (1998).
[15] A. Gross, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **75**, 2718 (1995).
[16] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).
[17] J. P. Perdew *et al.,* Phys. Rev. B **46**, 6671 (1992).
[18] M. Fuchs and M. Scheffler, Comput. Phys. Commun. **116**, 1 (1999).
[19] C. J. Wu and E. A. Carter, Chem. Phys. Lett. **185**, 172 (1991).
[20] A. Vittadini and A. Selloni, Chem. Phys. Lett. **235**, 334 (1995).
[21] Recently the interdimer adsorption pathway has been identified as the relevant one by means of STM [M. Dürr *et al.* (to be published)].
[22] B. S. Jursic, Chem. Phys. Lett. **256**, 603 (1996).
[23] E. J. Buehler and J. J. Boland, Science **290**, 506 (2000).