

Stereochemistry on Si(001): Angular Dependence of H₂ Dissociation

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The angular dependence of the dissociative adsorption of molecular hydrogen at terrace and step sites of vicinal single-domain Si(001) surfaces was investigated by means of molecular beam techniques and optical second-harmonic generation. A strongly anisotropic behavior was observed for terrace adsorption with polar distributions of $\cos^3\vartheta$ and $\cos^{12}\vartheta$ parallel and perpendicular to the dimer, respectively. The D_B -steps show enhanced reactivity under glancing incidence in the upwards direction. The results are traced back to the directionality of the covalent surface bonds.

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The stereodynamic control of chemical reactions is part of the enforced effort of the last decades to understand the driving forces behind bond breaking and bond formation and to use the obtained knowledge to enhance or suppress certain reaction channels [1]. The classical experimental setup of crossed molecular beams employs electrical fields to obtain the necessary orientation of the molecules in one of the beams. An alternative approach, first suggested by Polanyi and co-workers, is to replace the second beam by well prepared single-crystal surfaces where one of the reaction partners is naturally aligned [2]. Angular dependent investigations of sticking coefficients and desorption rates have indeed provided considerable insight into the reaction dynamics of small molecules with surfaces [3–6]. Besides the kinetic energy and internal degrees of freedom of the reacting molecules also surface properties such as corrugation and temperature were shown to have a pronounced influence on the width of measured angular distributions. However, the directional dependence of an adsorption reaction on a surface due to the chemical properties of the reacting subunit, rather than simply the geometric order, has not been demonstrated yet. Corresponding stereochemical effects are expected to be important for molecular reactions at surfaces of semiconductors with covalent chemical bonds, rather than of metals where most of the previous experiments have been conducted.

In this Letter, we present measurements of the sticking probability for dissociative adsorption of H₂ on Si(001) as a function of both polar and azimuthal angles of incidence. The system H₂/Si(001) has been studied intensively as a model system for gas-semiconductor interaction [7–19]. It is characterized by small sticking coefficients [8,13,16] and a large adsorption barrier >0.6 eV [13]. Two distinct features of vicinal Si(001) surfaces are exploited for the present experiments. First, for miscut angles $>2^\circ$, double atomic height D_B steps are energetically favored with the dimer rows perpendicular to the step edges on all terraces [20]. Second, the D_B -step sites can be passivated exclusively by hydrogen because their ability to dissociate H₂ is orders of magnitude higher than that of the terrace sites

[12]. In this way, it is possible to prepare single-domain Si(001) surfaces with unreacted dangling bonds only on the terraces. We observe a strong anisotropy for the azimuthal distribution of the initial sticking coefficient on the terraces which manifests itself in a very sharp polar distribution perpendicular and a broad one parallel to the dimer. The distributions at the step sites show a less pronounced behavior with an enhanced sticking probability for molecules hitting the steps from the lower terrace side. The results suggest that the reactivity of the surface is highest for molecules incident in the direction of the dangling bonds of the silicon substrate.

For an accurate experimental determination of the initial sticking probabilities it is necessary to monitor small coverage changes on the terraces in the presence of saturated steps. This was accomplished by monitoring the hydrogen adsorption processes in real time by means of optical second-harmonic generation (SHG) as discussed previously [8,12]. The experiments were performed in ultrahigh vacuum with a base pressure $<5 \times 10^{-11}$ mbar. H₂ of 99.9999% purity (additionally cleaned in a liquid nitrogen trap) was exposed through a supersonic beam [13]. The Si(001) samples were mounted on a LN₂ cooled holder and could be rotated in the surface plane and azimuthally around the surface normal. Resistive heating up to 1300 K led to clean well-ordered surfaces with double-height atomic steps and one predominant domain ($>90\%$) as verified by low energy electron diffraction.

Typical data used to determine the sticking probabilities of H₂ adsorption on the terraces are shown in Fig. 1. For preparation, the clean surface, held at a temperature of 500 K, is exposed to a cold H₂ beam (nozzle temperature $T_N = 300$ K) under normal incidence. Under these conditions adsorption takes place only at the highly reactive step sites causing the fast signal drop and subsequent saturation [12,13]. The sample is then oriented for the desired angle of incidence of the H₂ beam. Adsorption on the terraces is indicated by the slow, monotone decrease of the non-linear susceptibility $\chi_s^{(2)}$. All sticking coefficients for terrace adsorption were determined for a kinetic energy of the

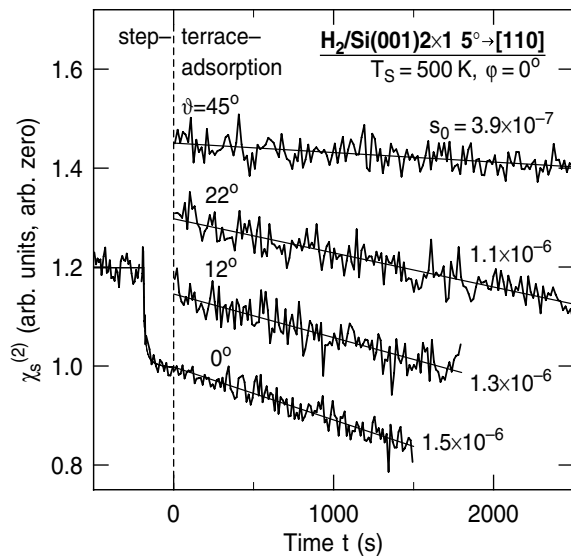


FIG. 1. Determination of the sticking coefficients s_0 for the terraces of vicinal Si(001) from the slope of the nonlinear susceptibility $\chi_s^{(2)}$ when the surface is exposed to a 250-meV supersonic H_2 beam under different angles of incidence ($t > 0$). Prior to terrace adsorption the step sites are saturated ($t < 0$). Absolute values of s_0 are obtained using the relationship $\chi_s^{(2)}(\theta) = \chi_{s,0}^{(2)} \times (1 - \alpha\theta)$, with $\alpha = 3.1$ and the hydrogen coverage $\theta \ll 1$ ML [8]. The hydrogen flux was 23 ML/s under normal incidence.

H_2 molecules of 250 meV ($T_N = 1100$ K). The particular values for surface temperature ($T_s = 500$ K) and beam energy are chosen to suppress H diffusion from the steps to the terraces [21], to maximize H_2 dissociation at the terrace sites and to avoid a significant influence of atomic H created in the heated nozzle. The relative initial sticking coefficients s_0 can be deduced directly from the ratio of the slopes of the signal corrected by the geometrical reduction factor of the hydrogen flux which was kept constant as a function of time.

The results for the adsorption on the terraces are collected in the form of polar plots in Fig. 2 together with sketches of surface geometry, respectively. Two silicon

atoms form dimers via a σ bond and are shown as black bars. In the case of the H_2 beam incident parallel to those dimers, the angular distribution is broad and has its maximum at the surface normal. Perpendicular to the dimers, in contrast, the distribution is sharply peaked and tilted by about 5° . This tilt is simply a consequence of the particular geometry of the vicinal surfaces, it directly reflects the incline of the terraces with respect to the optical surface. For a more quantitative discussion, cosine distributions are fitted to the data. One obtains $\cos^3(\vartheta)$ and $\cos^{12}(\vartheta + 5.5^\circ)$ parallel and perpendicular to the dimers, respectively. The strong anisotropy is also clearly apparent in Fig. 2(c) where the azimuthal dependence of s_0 is plotted for a beam incident under a polar angle $\vartheta' = 45^\circ$ with respect to the (001) direction.

Before we discuss the observed striking directionality in terms of the orientation of the involved Si dangling bonds we present the measured angular distribution for adsorption at the D_B step sites consisting of single silicon atoms rebonded to the upper terrace, i.e., no dimers are formed. The results, plotted in Fig. 3, show a forward-peaked symmetric distribution proportional to $\cos^{4,6}(\vartheta)$ for the beam incident parallel to the step edges. In the direction perpendicular to the steps, the sticking coefficient is asymmetric and exhibits a clear preference for the adsorption of molecules incident from the direction of the lower terrace. The best fit to the data with a distribution similar to that one parallel to the steps, $\cos^{4,6}(\vartheta - \vartheta_0)$, is obtained for a tilt angle $\vartheta_0 = 6^\circ$, i.e., $\vartheta'_0 = 11.5^\circ$ against the (001) direction.

In order to check the overall consistency of our experiment we also performed measurements of the sticking coefficient as a function of polar angle for flat, two-domain surfaces. The angular distribution was found to be proportional to $\cos^{6 \text{ to } 7}(\vartheta)$ at $T_s = 600$ K and $T_N = 815$ K. It showed no pronounced dependence on surface temperature and beam energy for $600 < T_s < 670$ K and $500 < T_N < 1100$ K. Since the superposition of the two distributions determined for the single domain surface yields a

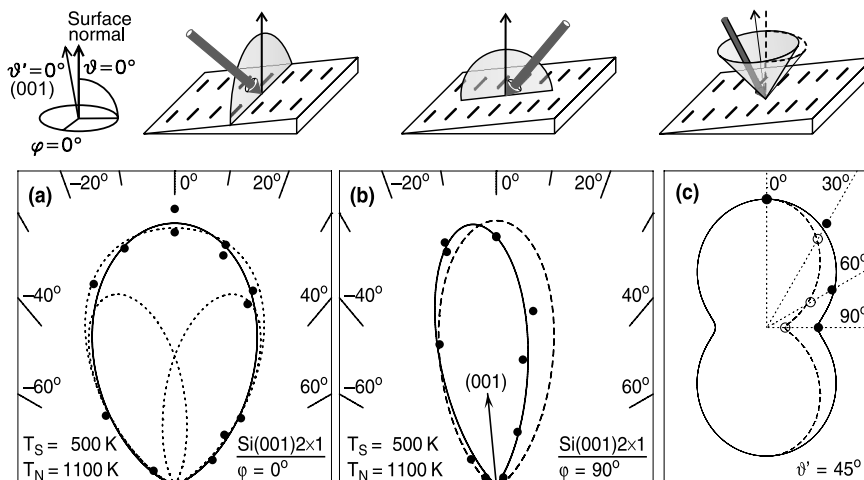


FIG. 2. Polar plots of the relative initial sticking coefficients s_0 on the terraces as a function of incident polar angle ϑ and azimuthal angle φ . (a) Parallel to the dimers ($\varphi = 0^\circ$), the solid line represents $\cos^{3.2}\vartheta$, dotted lines indicate $\cos^8(\vartheta \pm 19^\circ)$ and the superposition of these curves. (b) Perpendicular to the dimers, the solid line describes $\cos^{11.6}(\vartheta + 5.5^\circ)$, the dashed line indicates the distribution expected from normal energy scaling of the values from Ref. [13]. (c) Azimuthal dependence obtained by rotating the sample around the normal of the terraces at $\vartheta' = 45^\circ$, i.e., $\vartheta = 39.5^\circ$ for $\varphi = 90^\circ$ (filled dots); open circles show the variation of s_0 for rotation around the optical surface normal; lines are guides to the eye.

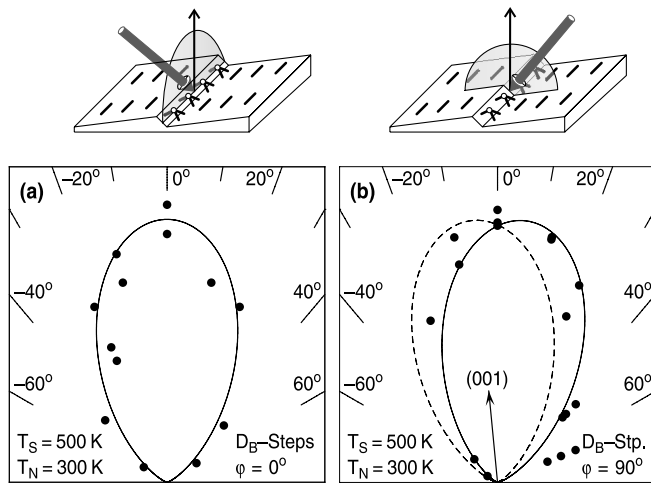


FIG. 3. Initial sticking coefficients s_0 on the steps as a function of incident polar angle ϑ at two different azimuthal positions. (a) Parallel to the step edges ($\varphi = 0^\circ$), (b) perpendicular to the step edges ($\varphi = 90^\circ$). The solid lines indicate $s_0(\vartheta) \propto \cos^{4.6}\vartheta$ and $s_0(\vartheta) \propto \cos^{4.6}(\vartheta - 6^\circ)$, respectively. The dashed line shows a distribution peaked along the (001) direction, $\cos^{4.6}(\vartheta + 5.5^\circ)$, for better comparison.

distribution very close to $\cos^7(\vartheta)$, we can exclude a major influence of the step geometry on the angular distributions of the terrace adsorption in Fig. 2. The measurements on the two-domain surface simply represent an average over the contributions of the two domains. It can directly be compared with the distribution found for the reverse reaction, recombinative desorption of H_2 . Park *et al.* [22] investigated thermal desorption of $\text{H}_2/\text{Si}(001)$ in the coverage regime $\theta = 1$ to 0.6 and reported $\cos^n(\vartheta)$ distributions with $n = 3.9$ to 5.2. As detailed balance requires for the desorption flux $\Phi_{\text{des}}(\vartheta) \propto \cos(\vartheta) \times \Phi_{\text{ads}}(\vartheta)$ our data translate into distribution $\Phi_{\text{des}} \propto \cos^7$ to $^8(\vartheta)$ for desorption in the limit of low coverages ($\theta \leq 0.1$). The larger exponent resulting from our experiments thus confirms the trend towards a sharpening of the distribution with reduced coverages that is apparent in the desorption experiments of Ref. [22].

In the case of activated adsorption of H_2 on metal surfaces, sharply forward-peaked angular distributions of sticking coefficients can sometimes be explained as a consequence of normal energy scaling [4]. If only the component of the translational energy normal to the surface is relevant for overcoming the barrier, molecules hitting the surface under an angle have a smaller chance to stick. In this sense, the observation of broader distributions for step as compared to terrace adsorption is consistent with the lower barrier associated with the step sites. However, already the observed azimuthal anisotropy excludes normal energy scaling to hold for $\text{H}_2/\text{Si}(001)$. It is, nevertheless, instructive to apply it and convert the energy dependent sticking coefficients for terrace adsorption from Ref. [13] into an angular distribution. The result [dashed line Fig. 2(b)] is only slightly broader than the observed

angular dependence parallel to the dimer rows. This can be understood in terms of a lateral corrugation of the barrier height along the rows which narrows the impact area and causes focusing of the distribution along the surface normal of the terraces [8]. In the direction perpendicular to the dimer rows, however, the measured angular dependence is considerably broader than the distribution expected for normal energy scaling. The origin for this broadening must be due to strong geometric effects.

In the following, we propose that these geometric effects are a consequence of the directionality of the dangling bonds of the silicon atoms involved in the dissociation reaction and that the most efficient pathway of H_2 molecules to overcome the dissociation barrier is the movement in the direction of these dangling bonds. This intuitive model will provide a straightforward explanation for the observed anisotropy of the sticking coefficient with respect to dimer orientation. It is fully consistent with the current microscopic understanding of hydrogen adsorption on $\text{Si}(001)$.

Theoretical studies of H_2 adsorption via defect sites as well as dissociation involving only one dimer (intradimer transition state) predict a strong enhancement of sticking under glancing incidence [9–11]. Since this is in marked contrast to the sharply forward-peaked distribution of Fig. 2(b), the present results add to the strong evidence of other recent experimental and theoretical work that H_2 dissociates over two adjacent silicon atoms of two different dimers [14,18,23]. This so-called interdimer pathway is depicted schematically in Fig. 4. On two adjacent dimers, we find two equivalent reactive interdimer subunits. They resemble the configuration at the D_B steps [compare side view of the unbuckled dimer in the inset of Fig. 4(b)] and lead to H-Si bonds that are tilted with respect to surface normal. Despite the relatively small dissociation barrier at the step sites we observed a clear preference for the adsorption of molecules incident from the direction of the lower terrace, i.e., for molecules incident in the direction of the dangling bonds. The tilt of

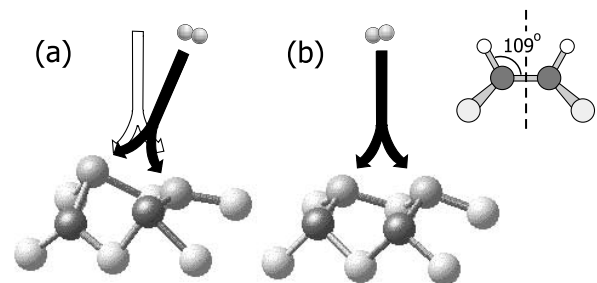


FIG. 4. Ball-and-stick model of a reactive subunit of the silicon dimer row. (a) An asymmetric transition state could lead to the expectation of enhanced sticking under glancing incidence (dark arrow). The proposed directionality of the dangling bonds favors normal incidence (white arrow) (b) A symmetric transition state also favors a forward-peaked angular distribution of s_0 . Inset: side view of one hydrogen saturated silicon dimer.

the H-Si bond with respect to the (001) direction, which is a measure for the direction of the dangling bonds, calculates within density functional theory to about 18° [18] and compares well with the center of mass of the distribution in Fig. 3(b). In analogy, one expects asymmetric distributions at the reactive subunits on terraces as well. In a first approximation, we again assume their tilt to correspond to the H-Si-Si angle of the adsorbed hydrogen, i.e., close to the 109° of a tetrahedron [24]. The superposition of the two distributions, each tilted by 19° , is in very good agreement with the data points [Fig. 2(a)].

The dimers of clean Si(001) are buckled by $\approx 19^\circ$ with a direction of buckling that alternates along the dimer rows [25]. Therefore, the Si-Si axis of the two atoms involved in the adsorption process is also tilted considerably ($\approx 11^\circ$) with respect to the surface plane. From this situation, depicted in Fig. 4(a), one might expect a superposition of two asymmetric angular distributions parallel to the dimer rows, in contrast to the observed sharply peaked distribution. However, the dangling bonds themselves are likely not to be tilted in this direction. Applying the argumentation from above, i.e., highest reactivity along the direction of the dangling bonds, a sharp distribution as observed follows naturally, at least for small buckling angles. This effect could be enhanced by a transition state that is more symmetric with respect to the surface plane [Fig. 4(b)]. Such a symmetric transition state becomes rather plausible from recent investigations of H_2 adsorption both on flat and vicinal surfaces [12,18,19], which have shown that the adsorption barrier can be effectively reduced by lattice distortions along this coordinate.

Based on our model, we expect hydrogen molecules incident under glancing angle with the plane of incidence parallel to the dimer bond to stick on the whole surface preferentially at one side of the dimer row, e.g., with a ratio of 6:1 for $\vartheta = 20^\circ$ (compare with Fig. 2). In general, it is difficult to detect this anisotropy in coverage, as to higher coverages the enhanced reactivity of the half-saturated silicon dimers [14,18] leads to a compensation of this effect. Only to low coverages, detection is possible, e.g., with a microscopic probe [26].

In summary, we have shown that the sticking probability for H_2 on single-domain Si(001) depends strongly on the polar and azimuthal angles of incidence. The results could be explained consistently by assuming that the adsorption barrier can be overcome most efficiently by molecules incident along the direction of the Si dangling bonds. The sharp angular distributions observed here suggest that adsorption of molecules from directed beams offers interesting possibilities for stereochemical control of chemical reactions on covalent surfaces.

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