Effect of beam energy and surface temperature on the dissociative adsorption of H_2 on Si(001)

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Dissociative adsorption of H_2 from a high-flux supersonic molecular beam on flat and vicinal Si(001) surfaces was investigated by means of optical second harmonic generation (SHG). The initial sticking coefficients for terrace adsorption varied between 10^{-8} and 10^{-4}. They revealed a strongly activated dissociation process, both with respect to the kinetic energy of the incident molecules ($70\,\mathrm{meV} \leqslant E_{\mathrm{kin}} \leqslant 380\,\mathrm{meV}$) and the surface temperature ($440\,\mathrm{K} \leqslant T_s \leqslant 670\,\mathrm{K}$). The results indicate that dynamical distortions of Si surface atoms can lower the effective adsorption barriers from $0.8 \pm 0.2\,\mathrm{eV}$ to almost negligible values. Previously proposed defect-mediated processes can be ruled out as a major adsorption channel. © *1999 American Institute of Physics.* [S0021-9606(99)70747-6]

Hydrogen on silicon is a good model to study fundamental aspects of the reaction dynamics on the surfaces of covalent solids for both experimental and theoretical reasons.[1–3] The reaction of molecular hydrogen with silicon surfaces is characterized by sticking probabilities for dissociative adsorption that are extremely small at room temperature ($<10^{-10}$) but increase by many orders of magnitude at elevated surface temperatures.[4,5] It has been proposed that the temperature dependence arises from strong distortions of the silicon lattice in the transition state as predicted theoretically.[6] Molecules impinging on the cold surface encounter the Si atoms in a configuration that is unfavorable for dissociation and experience a high adsorption barrier. At elevated temperature the incident molecules have a chance to hit a rearranged surface and dissociate more easily. Similarly, most of the excess barrier energy can be released into silicon phonons during the reverse reaction of recombinative hydrogen desorption. This mechanism explains the puzzling experimental observation that the mean translational energy of the H_2 molecules desorbing at $T_s > 700\,\mathrm{K}$ is almost thermal as if they encountered no barrier.[7]

Although a strong dependence of the dissociation barrier on the configuration of surface atoms is not unexpected for covalent solids like silicon, the model of *phonon-assisted sticking* has not been generally accepted. One reason for this is the lack of a consistent microscopic model for the most intensively studied Si(001) surface. Calculations using density functional theory found a coupling of the dissociation barrier with the buckling of Si dimers[8–10] but not to the extent suggested by the experimental data.[5,11] Alternatively, various defect models have been discussed in the literature.[12–14] Progress has also been slow because of contradicting experimental results. Prior to the adsorption experiments with thermal H_2 and D_2 gases that were able to measure sticking coefficients as low as 10^{-8} by means of optical second-harmonic generation (SHG),[5] supersonic molecular beam studies had reported three orders of magnitude higher values for the adsorption of D_2 on Si(001).[15] The beam data showed a weaker influence of surface temperature and a small dependence on translational energy

The intention of this Communication is to clarify the unsatisfactory situation experimentally. With a new supersonic beam experiment that combines high gas fluxes and detection of the accumulated hydrogen coverage in real time with SHG we achieve a sensitivity that exceeds that of previous beam investigations by more than two orders of magnitude. We find pronounced activation of H_2 dissociation, both in terms of translational energy and surface temperature. Experiments with misoriented samples suggest that the results reported in Ref. 15 may have been affected by minority sites and are not typical for well-prepared Si(001) surfaces. The new results for flat surfaces strongly suggest that activation in the lattice and molecular degrees of freedom is dynamically interconnected and cannot be reconciled with reaction mechanisms mediated by transient defects.

The experiments were performed in a four-stage molecular beam apparatus with a base pressure in the sample chamber of 5×10^{-11} mbar. A continuous, normally incident supersonic beam with a nozzle-sample distance of 30 cm provided a high flux of up to 2×10^{16} H_2 molecules $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ while maintaining a background pressure of $\leqslant 1 \times 10^{-7}$ mbar. The H_2 gas of 99.9999% purity was supplied from a liquid–nitrogen-cooled reservoir to freeze out residual H_2O. The nozzle, a molybdenum tube with a 30 μm diameter hole, could be heated resistively up to 1800 K. For a typical backing pressure of 11 bar and a nozzle temperature of $T_{\mathrm{N}} = 300\,\mathrm{K}$ a mean translational energy of $5.5kT_{\mathrm{N}}/2$ and a velocity ratio $v/\Delta v \simeq 10$ was established by time-of-flight measurements. The absolute H_2 flux was determined with an accuracy of 40% by referencing the quadrupole mass spectrometer signal to a calibrated ion gauge. Preparation of the Si(001) samples and the experimental

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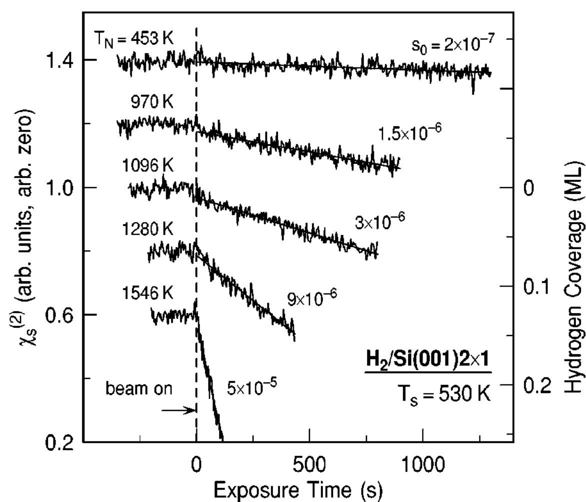

FIG. 1. Determination of the sticking coefficients s_0 for nominally flat Si(001) from the slope of the nonlinear susceptibility $\chi_s^{(2)}$ when the surface is exposed to a supersonic H_2 beam created at various nozzle temperatures T_N. The coverage scale corresponds to the measurement for $T_N = 1096$ K, an offset was added to the other data. The gas flux at this temperature was 8×10^{15} molecules $cm^{-2}\,s^{-1} = 23$ ML/s.

setup for determination of hydrogen coverages have been described previously.[5,16]

Figure 1 displays experimental results for H_2 adsorption on flat Si(001) obtained at a surface temperature of $T_s = 530$ K. The initial sticking coefficients s_0 were deduced from the decrease of the SHG signal during dosing with constant gas flux using the relationship between the nonlinear susceptibility $\chi_s^{(2)}$ and the hydrogen coverage $\theta \ll 1$ ML, $\chi_s^{(2)}(\theta) = \chi_{s,0}^{(2)}(1-\alpha\theta)$, with a proportionality factor $\alpha = 3.1$.[5] The data indicate the presence of one dissociation channel characterized by a sticking probability that increases strongly as a function of nozzle temperature.

A reaction characterized by the same sticking probabilities is observed for a vicinal surface with a miscut angle of 5.5° towards the [110] direction (Fig. 2). It becomes visible after an additional, more reactive dissociation channel, causing a fast initial signal drop, has saturated. Experiments with reduced gas exposures show that the fast initial signal change exhibits only little dependence on nozzle temperatures $T_N > 300$ K. As discussed previously in connection with the adsorption of thermal gas we attribute the fast channel to adsorption at the dangling bonds of rebonded D_B steps whereas the slow channel is characteristic for adsorption at terrace sites.[17] The fast adsorption channel was also observed for samples mounted under tension and for other less well prepared surfaces that contained more than 0.01 ML of minority sites.[18]

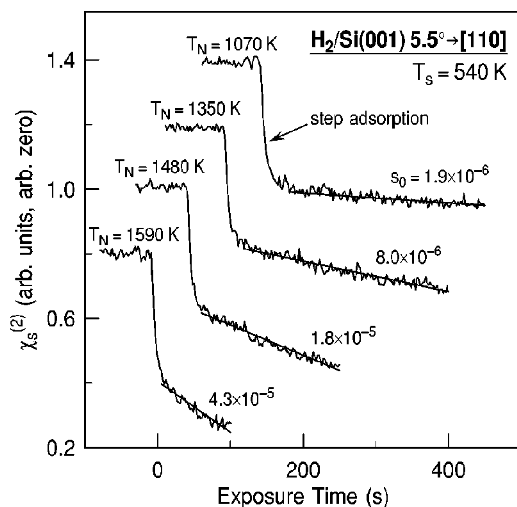

FIG. 2. H_2 adsorption on a vicinal surface with double-height steps that provide 12% of adsorption sites that are more reactive (Ref. 17).

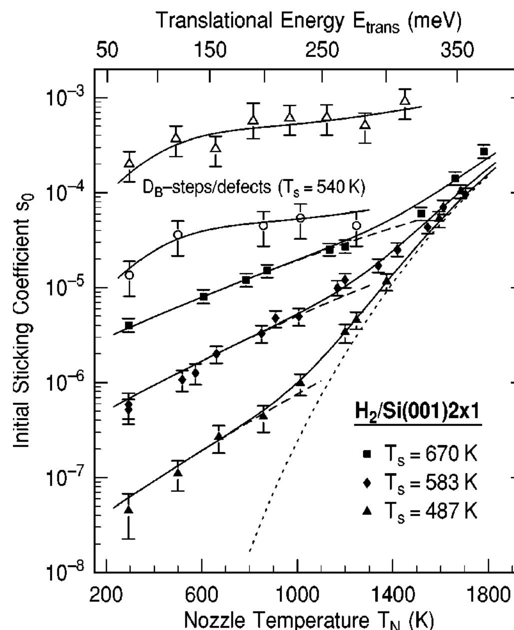

FIG. 3. Initial sticking coefficients s_0 as a function of nozzle temperature T_N (translational energy) for various surface temperatures T_s on the terraces and at steps–defects of Si(001)2×1. Dashed lines are the results of best fits to Eq. (1), the dotted line indicates the estimated contribution from vibrationally excited H_2, solid lines are guides to the eye as a combination of both of them.

The sticking coefficients for terrace adsorption could be determined for surface temperatures between 440 and 670 K and for nozzle temperatures ranging from 300 to 1800 K (Figs. 3 and 4). For the lower surface temperatures s_0 changes by almost three orders of magnitude in the investigated range of beam energies (Fig. 3). For molecules with small translational energies a similarly strong dependence on surface temperature is obtained (Fig. 4), in agreement with the behavior observed previously for a thermal gas at room temperature.[5,19] High beam energies are seen to reduce the effect of surface temperature and vice versa.

The results presented above for H_2 adsorption on flat Si(001) disagree with those of earlier beam experiments.[15] The higher absolute values of the sticking coefficients, the relatively moderate dependence on nozzle and surface temperature, and the low saturation coverage of ~0.1 ML reported in Ref. 15 reveals an adsorption behavior similar to that observed here for steps and defects. It is thus tempting to attribute the differences to our results to adsorption at minority sites. It should also be noted that the earlier experiment lacked the sensitivity to measure sticking coefficients s_0

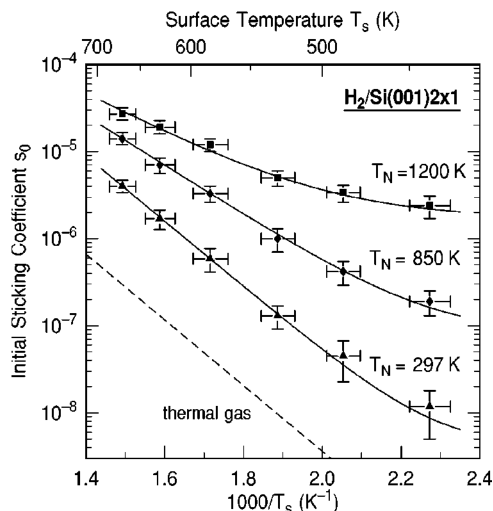

FIG. 4. Arrhenius plot of the initial sticking coefficients s_0 for various nozzle temperatures T_N. The dashed line represents the results obtained with thermal gas dosing (Refs. 5 and 19).

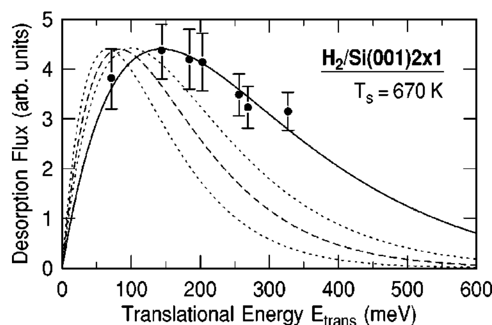

FIG. 5. Desorption flux along the surface normal calculated from the measured initial sticking coefficients s_0 for $T_s = 670\,K$ via detailed balance (dots). The converted s-shaped adsorption curve (1) for $W(T_s) = 193$ meV and $E_0 = 820$ meV has a mean energy of $\langle E \rangle = 270$ meV (solid line). The Maxwell–Boltzmann distribution fitted to the desorption experiments at $T_s \simeq 920$ K (Ref. 7) is centered at $\langle E \rangle = 170$ meV (dashed line, dotted lines indicate experimental uncertainties).

$\leqslant 10^{-5}$, which we find characteristic for terrace adsorption.

Figures 3 and 4 clearly demonstrate that hydrogen dissociation on the terraces of Si(001) is a strongly activated process, both in terms of surface temperature and in terms of beam energy. The data are incompatible with all defect models for H_2 interaction with Si surfaces proposed in the literature.[12–14] First of all, the observed activation with beam energy excludes the presence of a significant amount of highly reactive minority sites with negligible barriers for hydrogen dissociation. More sophisticated mechanisms concern short lived defect sites which are produced thermally activated, e.g., with the activation energy E_A at step sites, and possess a small but finite adsorption barrier E_0.[14] The sticking coefficients would then depend multiplicatively $[s_0(E,T_s) = n(T_s)\hat{s}(E-E_0)]$, on the defect concentration of the surface, $n(T_s) \propto \exp(-E_A/kT_s)$ and on the energy dependent reactivity of these sites, $\hat{s}_0(E-E_0)$. Consequently, the activation with surface temperature should be independent of the beam energy (leading to parallel lines in the Arrhenius plot Fig. 4) in marked contrast to the experimental findings. In addition, sticking via two separate channels, one dependent on surface temperature and the other on translational energy, does not fit the data and can be ruled out.

The measured sticking coefficients require that both Si lattice and H_2 molecular excitation can *directly* activate adsorption, as in the model of phonon-assisted sticking.[6] A detailed comparison with potential energy surface for this process can only be made on the basis of dynamical calculations. Here, we restrict ourselves to a simple parameterization using the commonly employed s-shaped adsorption energy function[20,21]

$$s_0(E,T_s) = \frac{A}{2}\left[1 + \tanh\frac{E-E_0}{W(T_s)}\right]. \qquad (1)$$

Since the saturation value A is not reached experimentally, the mean energy barrier E_0 that is obtained from best fits of Eq. (1) to the data has a relatively high uncertainty of ± 0.2 eV. We find $E_0 = 0.82(0.65,1.0)$ eV for reasonable choices of $A = 0.01(0.001,0.1)$. Prefactors $A < 0.001$ would not be compatible with our data. Since A is *not* the maximum achievable sticking probability but an effective saturation value for those channels with the most favorable molecular orientation and impact parameter, it is expected not to exceed 0.1.[16]

The width $W(T_s)$ is insensitive to a change of A and E_0. It increases slightly superlinear as a function of T_s from 113 meV at 440 K to 193 meV at 670 K.[22] Both the absolute value of the width parameter and its dependence on surface temperature are considerably higher than observed for H_2/Cu(111) where the mean barrier height E_0 is comparable.[21,23] The pronounced increase of the measured $s_0(E)$ for high beam energies E which deviates from the functional form (1) are likely to be caused by vibrationally excited molecules that are more efficient in crossing the dissociation barrier. A significant influence of atomic hydrogen produced in the heated nozzle can be excluded.

To a large extent, the current interest in the dynamics of H_2/Si has been prompted by the desorption experiments of Kolasinski *et al.*[7] The observed mean translational energies between 0.15 and 0.2 eV were considerably below the estimated adsorption barriers and the question was raised, how this could be reconciled with the principle of detailed balance. In Fig. 5 we show sticking coefficients $s_0(E)$ obtained at the highest surface temperature $T_s = 670$ K converted to desorption flux along the surface normal via $\Phi(E) \propto E \times \exp(-E/kT_s)s_0(E)$ as required by detailed balance. The result is a mean translational energy of the desorbing H_2 molecules of $\langle E \rangle = 0.27$ eV, slightly higher than the value reported in Ref. 7 for $T_s \simeq 900$ K but considerably lower than the derived adsorption barrier of $E_0 \simeq 0.8$ eV. The small quantitative differences between the reversed adsorption data and the experimental energy distribution of desorbing molecules could be a result of different coverages of both experiments or the fast heating rate employed in laser-induced desorption. Recent scanning tunneling microscope experiments have indeed shown that pre-coverage of Si(001) surfaces with atomic hydrogen in nonequilibrium distributions can lead to reaction channels with lower adsorption barriers.[24]

The desorption experiments of Ref. 7 and the present

adsorption experiments are thus seen to be closely related by detailed balance and result in a consistent picture of the reaction dynamics of H_2/Si(001). The covalent character of the Si surface bonds causes strong coupling of adsorption barrier and lattice configuration which (neglecting the dynamics of the lattice) results in a wide distribution of barriers when silicon vibrations are excited. The increased availability of low barrier pathways at high surface temperatures then enables dissociative adsorption of relatively slow H_2 molecules. In desorption, this shifts the mean translational energy to values that are considerably lower than the mean barrier height.

The experimental data suggest that Si lattice excitations are equally efficient in promoting dissociation than an increased H_2 energy. For this reason, the inclusion of lattice degrees of freedom are already important for the most basic microscopic models of the reaction dynamics of H_2/Si. *Ab initio* calculations for Si(111)7×7 have identified the dominant surface excitation as a strong distortion of adatom back bonds.[25,26] We hope that the presence of a consistent data set will lead to renewed theoretical efforts also for the H_2–Si(001) system which is considered to be prototypical for our understanding of the reaction dynamics on semiconductor surfaces.

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