Phonon-Assisted Sticking of Molecular Hydrogen on Si(111)-(7 × 7)

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The initial sticking probability for dissociative adsorption of molecular hydrogen on Si(111)-(7 × 7) was measured as a function of substrate temperature. By monitoring the hydrogen coverage of the surface in an H_2 atmosphere with optical second-harmonic generation we find a sticking coefficient that increases from 2×10^{-9} at 580 K to 5×10^{-6} at 1050 K. An effective barrier to dissociative adsorption of 0.87 ± 0.1 eV via a substrate-phonon-assisted process is deduced. The results reveal a new type of adsorption dynamics where the lattice distortions play a major role.

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Hydrogen on silicon is an important model system for chemisorption on semiconductor surfaces that, in addition, is of considerable technological relevance [1]. For many years it has been well known that only atomic hydrogen adsorbs readily on single crystal silicon surfaces and saturates the dangling bonds, whereas the sticking coefficient for dissociative adsorption of molecular hydrogen is less than 10^{-6} at room temperature [2]. Recent experiments on the kinetics and dynamics of the reverse reaction, the recombinative desorption of hydrogen [3–8], have now raised the question about the origin of this low sticking probability [8–10]. In the case of metal surfaces, the dynamics of interaction with molecular H_2 has been successfully modeled using two-dimensional potential energy surfaces that depend on the H-H and the H_2-surface distance and relating adsorption and desorption via the principle of detailed balance [11]. A barrier present in the entrance channel of the bent potential leads to a low probability for dissociative adsorption and at the same time to translational and vibrational excitation of the desorbing molecules. As discussed in detail by Kolasinski *et al.* [8] such a model fails in the case of the H_2/Si system. H_2 desorbed from Si(100) and Si(111) surfaces at ~800 K displays some superthermal vibrational distribution [7]. However, substantial translational heating was neither observed experimentally [8] nor would it be compatible with the energetics of a conventional thermally activated desorption reaction [6,12,13].

In this Letter we report the first quantitative experimental results on the sticking coefficient of molecular hydrogen on a silicon surface. It is observed that H_2, kept at a gas temperature of 300 K, adsorbs dissociatively on Si(111)-(7 × 7) at elevated substrate temperatures. The initial sticking probability is found to increase from 2×10^{-9} at 580 K to 5×10^{-6} at 1050 K. It obeys an Arrhenius law with an activation energy of 0.87 eV. This strong temperature dependence clearly shows that the lattice degrees of freedom play an essential role in the dynamics of hydrogen interaction with Si(111) surfaces. Combined with the previous results on recombinative desorption this finding reveals that the interaction of H_2 with silicon surfaces is distinctively different to that of H_2 with metals [11,14]. It indicates that the more localized nature of semiconductor bonds may lead to a new kind of dynamics for adsorbate reactions. The results appear to be compatible with a model potential for the adsorption and desorption of H_2/Si suggested recently by Brenig, Gross, and Russ [10].

Experimentally we have overcome the difficulty of measuring extremely small sticking probabilities under conditions of low residence times of the adsorbates with a novel approach based on optical second-harmonic generation (SHG). For appropriate pump wavelengths SHG is very sensitive to the number of unreacted dangling bonds and allows accurate measurements of hydrogen coverages of less than 1% of a monolayer [5,6]. In addition, SHG may be applied at any gas pressure or substrate temperature. Thus, by monitoring the SH signal while exposing the sample to a high flux of molecular hydrogen, it is possible to detect dissociative adsorption for substrate temperatures at which the rate for recombinative desorption is already substantial.

The experiments were performed in an UHV chamber, equipped with capabilities for Auger electron spectroscopy, low-energy electron diffraction (LEED), and quadrupole mass spectrometry. The Si(111) sample was cut from a 10 Ω cm *n*-type wafer and mounted on a liquid-nitrogen-cooled cryostat. After thoroughly outgassing the sample and holder at 900 K, resistive heating of the crystal did not increase the background pressure above $\sim 6 \times 10^{-11}$ mbar. Clean, well-ordered 7 × 7 surfaces were prepared by removing the oxide layer at 1300 K. The sample temperature was determined within ±15 K by means of a thermocouple glued on the back of the crystal and with the help of a spectral pyrometer. For hydrogen exposure all filaments were turned off and the UHV chamber was backfilled with 10^{-4}–10^{-1} mbar H_2, while recording the pressure with a spinning rotor gauge (MKS instruments, absolute error <10%). The H_2 gas of 99.999% purity was kept in a liquid-nitrogen-cooled reservoir to freeze out residual H_2O and O_2.

For the SHG measurements we employed *p*-polarized 1064 nm radiation from a *Q*-switched Nd:YAG laser, incident at 45° (pulse duration 8 ns, repetition rate 10 Hz, flu-

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ence ≤ 50 mJ/cm^2) and detected the reflected s-polarized SH signal. Calibration of the SH response of Si(111)-(7 × 7) as a function of the hydrogen coverage θ was accomplished in two steps. The nonlinear susceptibility $\chi_s^{(2)}$ as a function of exposure was obtained by exposing the sample to a constant flux of *atomic* hydrogen while recording the SH signal proportional to $|E(2\omega)|^2 = |\chi_s^{(2)}E^2(\omega)|^2$. The exposure scale was then converted to hydrogen coverages θ with the help of a series of temperature programmed desorption (TPD) experiments and by identifying the saturation coverage with $\theta_{\max} = 0.8 \times 10^{15}$ cm^{-2} [1,2]. The resulting calibration curve for $\chi_s^{(2)}(\theta)$ at a surface temperature of $T_s = 600$ K is displayed in Fig. 1. For low coverages $\chi_s^{(2)}$ decreases linearly with the number of adsorbed hydrogen atoms:

$$\chi_s^{(2)}(\theta) \simeq \chi_{s,0}^{(2)}[1 - \alpha\theta], \qquad \theta < 0.4 \tag{1}$$

with $\alpha = 1.3$ ML^{-1} and one monolayer (ML) referred to the density of dangling bonds of the 7 × 7 reconstructed surface (1 ML = 0.30×10^{-15} cm^{-2}). We note that in the temperature range of interest ($T_s = 580-1050$ K) the decrease of $\chi_s^{(2)}$ by a factor of 8–10 due to hydrogen adsorption far exceeds the temperature induced change of <50% [15]. The thermal influence on the proportionality constant α is estimated to be less than 30% and thus negligible for the purposes of the present work.

Experimental data on the dissociative adsorption of molecular hydrogen are displayed in Fig. 2. For these measurements the initially clean surface was kept at a certain temperature T_s and the SH signal was recorded as a function of time t. At $t = 0$ the H$_2$ pressure P in the UHV chamber is increased to a value high enough to cause a detectable decrease of the SH signal due to adsorbed hydrogen. At any given time the H coverage $\theta(t)$ of the surface is determined by the rates of adsorption k_{ads} and desorption k_{des},

$$\theta(t) = \int_0^t [k_{\text{ads}}(\theta, t') - k_{\text{des}}(\theta)]dt', \tag{2}$$

with

$$k_{\text{ads}}(\theta, t) = \Phi(t)s_0(T_s)f(\theta), \tag{3a}$$

$$k_{\text{des}}(\theta) = \nu_d(T_s)\theta^m. \tag{3b}$$

Here $\Phi = P(2\pi m_{\text{H}_2}kT_g)^{-1/2}$ is the flux of H$_2$ molecules impinging on the surface (gas temperature $T_g = 300$ K), $s_0(T_s)f(\theta)$ denotes the sticking coefficient, m is the order of the desorption kinetics [16], and $\nu_d(T_s) = \nu_d^0 \exp(-E_d/kT_s)$ describes the thermally activated desorption probability. The solid lines through the data points of Fig. 2 are the result of a numerical evaluation of Eqs. (1)–(3) with the initial sticking coefficient s_0 treated as a variable parameter to get the best fit to the experimental results. For the coverage dependence of the sticking coefficient $f(\theta)$ we assumed a Langmuir adsorption model with $f(\theta) = (1 - \theta)^2$. As most measurements were done for $\theta \leq 0.1$ ML, this assumption has only little influence on the deduced values of s_0.

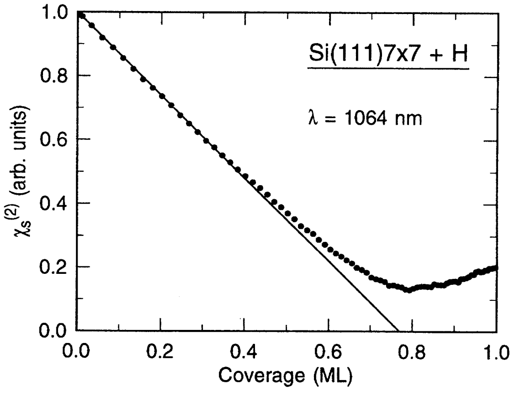

FIG. 1. Dependence of the second-order nonlinear susceptibility $\chi_s^{(2)}$ of Si(111)-(7 × 7) on the coverage with atomic hydrogen for a surface temperature of $T_s = 600$ K. 1 ML corresponds to 0.30×10^{15} H atoms/cm^2.

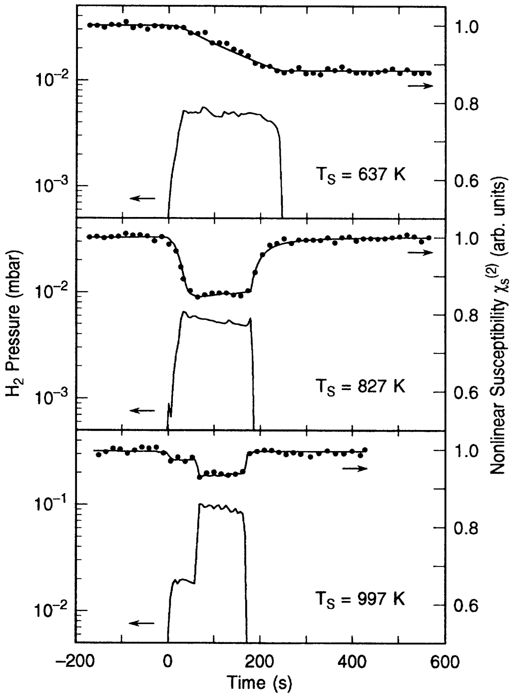

FIG. 2. H$_2$ pressure in the UHV chamber and nonlinear response of Si(111) during adsorption experiments at three different substrate temperatures T_s. The symbols of the upper traces indicate the measured nonlinear susceptibility $\chi_s^{(2)}$; the lines are the results of a numerical evaluation of Eqs. (1)–(3) using the recorded H$_2$ pressure P shown below and a sticking probability s_0 that best fits the experiment.

The treatment of desorption in the numerical fit depends on the substrate temperature. For $T_s < 700$ K, desorption is negligible on the time scale of our experiment and $\theta(t)$ is solely determined by sticking of molecular hydrogen [Fig. 2(a)]. For $700 \leq T_s \leq 850$ K desorption occurs on a time scale of $1-10^3$ s. Because of the θ dependence of k_{des}, the hydrogen uptake slows down with time until an equilibrium between adsorption and desorption is established. If the H_2 exposure is stopped, the coverage decreases [Fig. 2(b)]. In this temperature range both the sticking coefficient and the desorption rate may accurately be extracted from the measurement. For $T_s > 850$ K desorption is too fast to be followed in the experiment. The measured hydrogen coverage of the sample is thus governed by the equilibrium $k_{\mathrm{ads}}(\theta) = k_{\mathrm{des}}(\theta)$ [Fig. 2(c)] and depends on the ratio $\Phi s_0/\nu_d$. In order to deduce $s_0(T_s > 850\ \mathrm{K})$ from the equilibrium coverage we use the parameters for the desorption kinetics determined earlier from SHG measurements [5].

The inferred values for the initial sticking coefficient are displayed in Fig. 3 as a function of the inverse substrate temperature. The sticking probability of the clean surface shows a thermally activated behavior, $s_0 = A \exp(-E_a/kT_s)$ with $E_a = 0.87 \pm 0.1$ eV and $A = 7 \times 10^{-2.0\pm0.5}$. With $580 \leq T_s \leq 1050$ K the temperature range over which we were able to observe adsorption is quite large. It corresponds to a variation of s_0 by more than 3 orders of magnitude. The lowest still detectable sticking probability was $\sim 2 \times 10^{-9}$ for $T_s = 580$ K.

The accuracy of our measurements in the regime of lower temperatures is limited by the presence of small amounts of contaminants in the dosing gas which also quench the Si dangling bonds upon adsorption. For $T_s > 650$ K we can exclude a significant amount of adsorbates other than H, because the parameters of the desorption kinetics deduced from the current measurements agree well with those obtained from surfaces exposed to atomic hydrogen [5]. For $T_s > 850$ K the error bars mainly arise from the necessity to extrapolate the desorption rate over several orders of magnitude.

The observed steep increase of the adsorption probability with substrate temperature T_s is a striking and unusual effect. It cannot be caused by equilibration of the gas with the surface in a precursor as commonly assumed whenever s_0 shows a dependence on T_s [14], because the very shallow physisorption well of H_2 is negligibly small compared to the large dissociation barrier. Instead, the observed effect must be caused by temperature-induced static or dynamical distortions of the silicon surface.

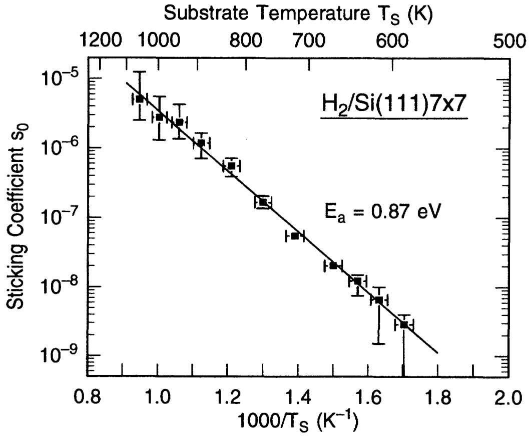

FIG. 3. Arrhenius plot of the initial sticking coefficient for dissociative adsorption of molecular H_2 on Si(111)-(7 × 7).

Although Si(111)-(7 × 7) is the most stable and well defined of all semiconductor surfaces, inspired by the low overall values of $s_0 < 10^{-5}$, one might suspect that minority sites, such as steps or defects, could be important for the dissociative adsorption of H_2. The temperature dependence of s_0 could then arise from the subsequent diffusion of atomic hydrogen to the majority sites and/or from an increased number of defects at high surface temperatures. Such a model with a vanishing adsorption barrier at the defects [13] would also be compatible with the lack of translational heating upon desorption [8]. However, a defect model is unlikely for the following reasons: First, the adsorption process cannot be diffusion limited because the measured activation energy of $E_a = 0.87 \pm 0.1$ eV is significantly different from the known barrier for thermally activated diffusion of H/Si(111) of $E_{\mathrm{diff}} = 1.5 \pm 0.2$ eV [17]. Second, high temperature scanning tunneling microscopy experiments [18] indicate that the Si(111)-(7 × 7) surface is thermally stable up to $T_s \simeq 1100$ K. There is some migration of the adatoms of the 7 × 7 unit cell at elevated temperatures but no fluctuation of step edges, etc., as observed on Si(100)-(2 × 1) [18]. Third, the desorption kinetics of H_2/Si(111) at low coverages indicate that for $T_s = 700-800$ K the number of reactive sites is larger than 5% of a monolayer and thus by far exceeds the defect density of well-prepared Si(111) surfaces [5]. We conclude that the temperature-induced changes of the surface morphology are weak and do not have a dominant influence on the interaction of H_2 with Si(111)-(7 × 7). Rather the observed behavior of s_0 is related to phononic excitations.

A well-known system where the initial sticking probability also rises with T_s is the dissociative adsorption of methane on metal surfaces [19]. There, the temperature dependence is believed to arise from coupling of a tunneling barrier to the thermal motion of the surface atoms [19]. A similar mechanism could be effective in the case of H_2/Si, especially since tunneling can, in principle, account for the observed vibrational excitation in the absence of translational heating upon desorption [9]. However, the required barrier would have to be unrealistically narrow [9]. This and the lack of any unusual isotope effects [3,7] in the energetics and dynamics of desorption make a reaction dominated by tunneling less likely.

A simple model that consistently explains *all* existing experimental data has recently been proposed by Brenig, Gross, and Russ [10]. It assumes a considerable increase of the Si-Si bond length upon adsorption of hydrogen. The potential energy surface essentially consists of two displaced Morse potentials for the Si-Si surface oscillations which are smoothly interconnected as a function of the

Si-H_2 distance. The incoming H_2 molecule experiences a large barrier to adsorption as the system is brought into the repulsive part of the Si-Si Morse potential. Upon desorption, the reaction starts with an increased Si-Si spacing. With an appropriate choice of parameters, the potential energy surface has only a very small gradient along the reaction path for the desorbing particle, since the potential with the smaller Si-Si equilibrium position is deeper. This way, the Si-Si oscillator is left in an excited state upon desorption, whereas the H_2 molecules do not gain substantial kinetic energy.

According to this model, the sticking probability is expected to increase not only with the incident energy of the H_2 molecules, but also with the excitation of Si-Si vibrations at elevated surface temperatures [10]. The activation energy of 0.87 eV measured in our experiment is related to the relative displacement of the ground states and the equilibrium spacing of the two Si-Si oscillators. It is already quite close to the 0.75 eV predicted from Fig. 4 of Ref. [10] for a gas temperature of 300 K. The prefactor $A = 7 \times 10^{-2}\ \mathrm{s}^{-1}$ contains information on molecular orientation and impact parameters that are required for sticking. Further information on the details of the potential energy surface could be gained from future measurements of the sticking probability as a function of translational energy. We emphasize that the experimental approach used in the present work could easily be combined with molecular beam dosing. This would allow the simultaneous variation of gas and surface temperatures over a wide range.

In conclusion, the present investigations of dissociative adsorption of H_2 on Si(111)-(7×7) with optical second-harmonic generation reveal a sticking probability that strongly increases as a function of surface temperature. The apparent activation barrier for a gas temperature of 300 K is 0.87 ± 0.1 eV. The results demonstrate that the excitation of lattice vibrations plays a decisive role in the dynamics of hydrogen interaction with Si(111) and probably all semiconductor surfaces. This behavior is distinctively different from that commonly observed for H_2 interaction with metal surfaces and results in a new adsorption-desorption dynamics.

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[16] In Ref. [5] it was shown that H_2 desorption from Si(111)-(7×7) does not obey simple second-order kinetics ($m = 2$) due to the presence of different H adsorption sites. In agreement with the present desorption data, the coverage dependence of k_{des} for $\theta < 0.3$ ML could be described phenomenologically by $m = 1.5$ in Eq. (3b).

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