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Optical second-harmonic investigations of H_2 and D_2 adsorption on Si(100)2×1: the surface temperature dependence of the sticking coefficient

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Abstract

Optical second-harmonic generation has been used to determine the sticking probability for dissociative adsorption of H_2 and D_2 on Si(100)2×1 as a function of surface temperature. The initial sticking coefficient increases from 10^{-8} at 550 K to 10^{-5} at 1000 K. It shows an activated behaviour as a function of the surface temperature with an activation energy of 0.70 ± 0.1 eV for H_2 and 0.75 ± 0.1 eV for D_2. The results demonstrate that lattice distortions play a significantly stronger role in the adsorption process than would be expected solely from the tilting of Si–Si dimers.

1. Introduction

The sticking probability for dissociative adsorption of molecular hydrogen on silicon surfaces is extremely low. Already from early flash desorption data [1] one may deduce that the room temperature sticking coefficient of H_2 on the terraces of single-crystal filaments is less than 10^{-8}, and similarly small upper bounds were subsequently obtained for H_2 or D_2 adsorption on the (111) and (100) surfaces of silicon [2,3]. While the low sticking probability indicates the presence of a high adsorption barrier ($E_{ads} > 0.5$ eV), it was recently observed that the D_2 molecules desorbing recombinatively from Si(111) and Si(100) surfaces have little excess energy [4]. This implies the presence of a negligible barrier in the reverse reaction ($E_{ads} < 0.1$ eV), seemingly in contradiction to the principle of detailed balance [4]. One possibility to reconcile the adsorption and desorption behaviour of H_2/Si is provided by the model of Brenig, Gross and Russ [5]. With a sufficiently strong dependence of the potential energy surface on the structure of the silicon lattice, it is possible that the incident H_2 molecules experience a large adsorption barrier, whereas most of the excess energy upon desorption is transferred to Si phonons [5]. In such a situation, the principle of detailed balance is not applicable to the H_2 degrees of freedom alone. The lattice degrees of freedom are of equal importance for the reaction path. One may then expect that phonon excitations would lead to a significantly enhanced sticking probability at elevated surface temperatures [5].

For H_2 adsorption on Si(111)7×7 we have already reported a strong effect of surface temperature [6]. Sticking coefficients as low as 2×10^{-9} could be measured with a new experimental approach based on optical second-harmonic generation (SHG). This method provides a sensitive monitor of the hydrogen coverage of the surface *during* exposure to a high flux of molecular hydrogen because it is (a) sensitive to the

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number of Si dangling bonds and (b) applicable at any gas pressure. The measurements revealed a sticking probability of H_2 on Si(111)7×7 that increased by more than three orders of magnitude ($s_0 = 2 \times 10^{-9}$–5×10^{-6}) when the surface temperature T_s was raised from 580 to 1050 K [6]. In contrast to these results, Kolasinski et al. [7] reported only a rather mild T_s dependence based on a beam investigation of D_2 adsorption on Si(100)2×1. The sticking coefficient was observed to vary only from $s_0 = (0.5\text{–}1.5) \times 10^{-5}$ in the temperature range T_s = 300–650 K [7].

In this Letter, we present SHG results for the sticking of H_2 and D_2 on Si(100)2×1 as a function of surface temperature, obtained with a sensitivity that is 500 times higher than that of the beam experiment of Ref. [7]. Our results are qualitatively similar to those obtained previously for H_2/Si(111)7×7. The absolute values of the measured sticking probabilities range from 10^{-8} to 10^{-5} and exhibit only a weak isotope effect. With an Arrhenius energy for phonon-assisted sticking of E_a = 0.70–0.75 eV the effect of surface temperature is only a little weaker than in the case of H_2/Si(111)7×7 ($E_a \approx 0.85$ eV [6]). Our new results are of particular interest for the comparison with theoretical works on H_2/Si which have largely concentrated on the Si(100)2×1 surface [8–18]. Both, the high activation energy and the analogy of the present results to H_2/Si(111)7×7 indicate that the tilting of the Si(100) dimers considered in recent ab initio calculations [14–16] can only account for part of the asymmetry between the reaction path for adsorption and desorption of H_2/Si(100)2×1. Additional excitations of the silicon lattice must be important in the H_2/Si interaction.

2. Experiment

The experimental apparatus and procedures were similar to those described previously for H_2/Si(111)7×7 [6]. Briefly, the Si(100) samples were cut from 10 Ω cm n-type wafers with a miscut < 1/4° and mounted on a liquid-nitrogen-cooled cryostat in a small UHV chamber with a base pressure of $p < 3 \times 10^{-11}$ mbar. They showed sharp two-domain 2×1 low energy electron diffraction patterns after the oxide layer had been removed by resistive heating to 1300 K. A thermocouple glued on the back

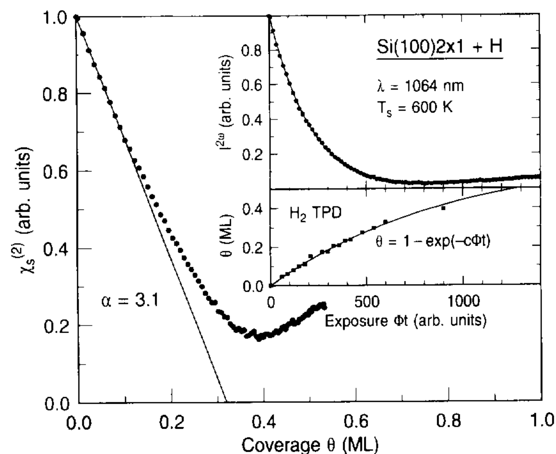

Fig. 1. Calibration of the SH response of Si(100)2×1 as a function of the hydrogen coverage θ. Inset, top: SH signal $I^{2\omega}(\Phi t)$ recorded during continuous exposure of an initially clean surface kept at T_s = 600 K to a constant flux Φ of atomic hydrogen which was created by H_2 dissociation at a hot W filament. Inset, bottom: hydrogen coverage $\theta(\Phi t)$ as obtained from the relative areas of the monohydride TPD peaks (1 ML = 0.68×10^{15} atoms/cm^2) for discrete exposures (squares) and a numerical fit to first-order Langmuir adsorption kinetics (line). Main panel: resulting calibration curve $\chi_s^{(2)}(\theta)$ for the second-order nonlinear susceptibility $\chi_s^{(2)} \propto (I^{2\omega})^{1/2}$.

of the crystal and an infrared pyrometer were used to measure the sample temperature with an absolute accuracy of ±15 K. The 1064 nm pump radiation for SHG was provided by a 10 Hz Q-switched Nd:YAG laser with a pulse duration of 8 ns. It was incident at 45° with respect to the surface normal and linearly polarized with s- and p-components chosen to maximize the SH signal and the sensitivity to adsorbed hydrogen. The pump fluence was kept below 50 mJ/cm^2 and did not influence the reactivity of the surface.

The calibration of the SH response as a function of hydrogen coverage is illustrated in Fig. 1. It is obtained by combining the measured SH signal as a function of exposure to atomic hydrogen with a series of temperature programmed desorption (TPD) experiments. The coverage of the saturated monohydride desorption peak (1 ML) is identified with the density of dangling bonds of the 2×1 reconstructed surface (0.68×10^{15} cm^{-2}). The high sensitivity of SHG to the dangling bonds of Si(100)2×1 leads to a decrease in the measured signal $I^{2\omega}$ by a factor of 50 upon hydrogen adsorption. For $\theta < 0.15$ ML the magnitude of

the nonlinear susceptibility $\chi_s^{(2)}$, which is proportional to $(I^{2\omega})^{1/2}$, has an approximately linear coverage dependence, $\chi_s^{(2)}(\theta) \approx \chi_{s,0}^{(2)}[1-\alpha\theta]$, with a slope $\alpha = 3.1\,\mathrm{ML}^{-1}$. In most data used to derive sticking coefficients, the hydrogen coverage was $\theta < 0.1$ ML so that the linear dependence of $\chi_s^{(2)}(\theta)$ holds [1].

3. Results and discussion

Typical data used to derive the sticking coefficient for H_2 and D_2 on Si(100)2×1 are collected in Fig. 2. For these measurements the initially clean surface was kept at the desired temperature T_s and the SH response was recorded as a function of time. At $t = 0$ the UHV chamber was backfilled with typically $p = 10^{-4}$–10^{-3} mbar of purified H_2 or D_2 from a liquid-nitrogen-cooled reservoir. For some measurements gas pressures up to $p = 10^{-1}$ mbar were used. The resulting flux of molecules impinging on the sample, $\Phi = p[2\pi m_{H_2} kT_{gas}]^{-1/2}$ varied between 10^3 and 10^6 ML/s. The gas temperature in the chamber was $T_{gas} = 300$ K. During exposure, the ion-gauge was turned off and the chamber pressure p was recorded with a spinning rotor gauge. After H_2 exposure at $t = 0$, dissociative H adsorption reduces the nonlinear response of the surface until either the H_2 flux is turned off (Figs. 2a–2c) or an equilibrium between adsorption and desorption is established (Figs. 2d and 2e). For sufficiently high temperatures ($T_s > 700$ K) hydrogen desorbs recombinatively and $\chi_s^{(2)}$ goes back to its initial value after adsorption has stopped (Figs. 2c–2f).

As described in Ref. [6], the initial sticking coefficient s_0 may be derived from these and similar data by numerically integrating the equation

$$\theta(t) = \int_0^t [k_{ads}(\theta, T_s, t') - k_{des}(\theta, T_s)]\,dt'. \qquad (1)$$

[1] The calibration curve of Fig. 1 is exactly valid only for a surface temperature $T_s = 600$ K. From the temperature dependence of the spectroscopic SHG measurements of Si(100)2×1 [19] we estimate a 50% variation in the initial slope α in the temperature range 550–1000K. This uncertainty in the calibration is negligible compared to the three orders of magnitude variation in s_0 observed in the present experiment.

The rate of adsorption k_{ads} is assumed to obey Langmuir kinetics

$$k_{ads}(\theta, T_s, t) = \Phi(t)s_0(T_s)(1-\theta)^2. \qquad (2)$$

The coverage and temperature dependence of the desorption rate $k_{des}(\theta, T_s)$ is taken from Ref. [20]. The solid lines through the data points of Fig. 2 are the result of best fits of Eq. (1) with the sticking coefficient s_0 treated as a variable parameter. The accuracy of this procedure varied between ±20% for intermediate temperatures (Figs. 2a, 2c, 2d) and up to ±50% at the extremes (Figs. 2b, 2f).

The experimentally accessible temperature range was $T_s = 550$–1000 K limited on both ends by small amounts of water contamination ($\ll 1$ ppm) in the dosing gas of the UHV chamber. Water has a high sticking coefficient for dissociative adsorption on Si(100) (unity at $T_s = 300$ K) [21]. If the gas flux or the total exposure is extended in order to compete against desorption at high temperatures, or against the lower sticking coefficient at low temperatures, then H_2O adsorption starts to dominate over H_2 adsorption. The effect of H_2O contamination is illustrated in Fig. 3. It may be effectively distinguished from H_2 adsorption, because the adsorbed oxygen desorbs in the form of SiO, which leads to a slower recovery of $\chi_s^{(2)}$ at $T_s = 900$ K than the desorption of H_2 [22]. Detectable amounts of water (or oxygen) were not present in the data shown in Fig. 2 or the other data used to derive $s_0(T_s)$. Compared to Ref. [7], wherein a detection sensitivity of $s_0 > 3 \times 10^{-6}$ due to water contamination in the molecular beam was given, the corresponding detection limit was $s_0 > 5 \times 10^{-9}$ in the present work.

The inferred values for the initial sticking coefficient s_0 for dissociative adsorption of H_2 and D_2 on Si(100)2×1 are displayed in Fig. 4 as a function of the inverse surface temperature (full symbols). s_0 increases dramatically as a function of the surface temperature, from $s_0 \approx 10^{-8}$ at $T_s = 550$ K to $s_0 \approx 10^{-5}$ at $T_s = 1000$ K. For both isotopes the sticking coefficient shows a similar thermally activated behaviour, $s_0 = A\exp(-E_a/kT_s)$. The activation energies and prefactors are $E_a = 0.75 \pm 0.1$ eV, $A = 1 \times 10^{-1\pm0.5}$ for H_2 and $E_a = 0.70 \pm 0.1$ eV, $A = 4 \times 10^{-2\pm0.5}$ for D_2 adsorption.

The small sticking probabilities that we observe are in agreement with the earlier literature [1–3], but not

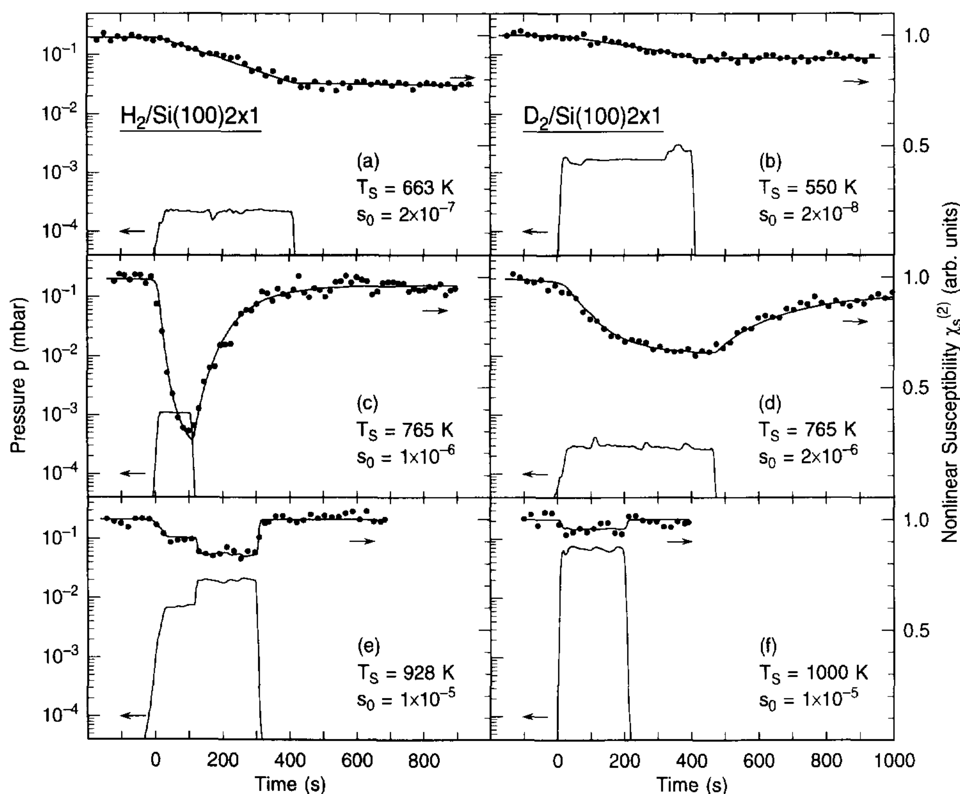

Fig. 2. H_2 or D_2 pressure p in the UHV chamber (lower traces) and nonlinear response $\chi_s^{(2)}$ (upper traces) of Si(100)2×1 during adsorption experiments at different substrate temperatures T_s. The dots in the upper trace represent the measured time dependence of $\chi_s^{(2)}(t)$, the solid lines through the data points are the result of the numerical fit described in the text using the indicated values for the sticking coefficient s_0 and the measured pressure $p(t)$.

with the results of Kolasinski et al. [7], who exposed the Si(100)2×1 surface to a supersonic molecular D_2 beam and subsequently determined the coverage with TPD. The results of Ref. [7] corresponding to a nozzle temperature of 300 K are also shown in Fig. 4 for comparison (open triangles). The discrepancy between these and our data in the same range of surface temperatures is striking. The absolute value of the sticking coefficient is 2–3 orders of magnitude higher than ours and the temperature dependence is much weaker (Arrhenius energy $E_a < 0.07$ eV). This disagreement cannot be caused by the different mean translational energies of the gas molecules in the two experiments (quasi monoenergetic beam with $\langle E_z \rangle \approx 2.5kT \approx$ 65 meV in Ref. [7]; Boltzmann distributed gas with $\langle E_z \rangle = 0.5kT = 13$ meV in this work) because the dependence on nozzle temperature reported in Ref. [7] is similarly weak as the dependence on surface temperature. In the presence of a high adsorption barrier ($E_{ads} \gg kT_{gas}$) one should, in general, even expect the Maxwell distributed gas with its broad high energy tail to exhibit the larger sticking probability than the almost monoenergetic gas in the supersonic beam.

At present, the discrepancy between our results and those of Ref. [7] has not been resolved. It could, in principle, be caused by a strong enhancement of the sticking probability for normally versus randomly incident molecules. However, in order to explain the three orders of magnitude difference, the directionality would have to be considerably stronger than the $\cos^5\theta$ distribution observed for recombinative desorption [23]. Another somewhat speculative explanation for the higher sticking probability found in Ref. [7] would be that the high dopand concentration

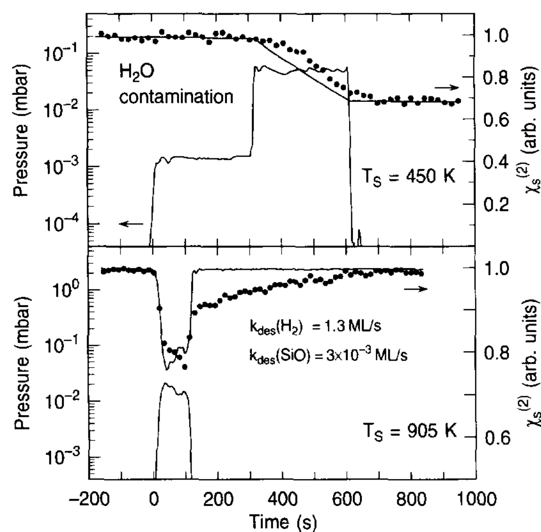

Fig. 3. Effect of water contamination in the dosing gas on the measured SH response. Top: if the H_2 pressure is increased in an attempt to determine sticking coefficents $s_0 < 10^{-9}$, water contamination builds up in the UHV chamber, dissociative H_2O adsorption on Si(100)2×1 quenches the dangling bonds [21] and causes the measured nonlinear susceptibility $\chi_s^{(2)}$ to decrease. Bottom: H_2O adsorption may be distinguished form H_2 adsorption by the different desorption behaviour. After the gas flux with H_2O contamination is turned off at T_s = 905 K, $\chi_s^{(2)}$ increases rapidly due to recombinative desorption of H_2, followed by a slower recovery due to desorption of SiO (t = 100–800s). The amount of oxygen present in this example was $\theta \approx 0.03$ ML.

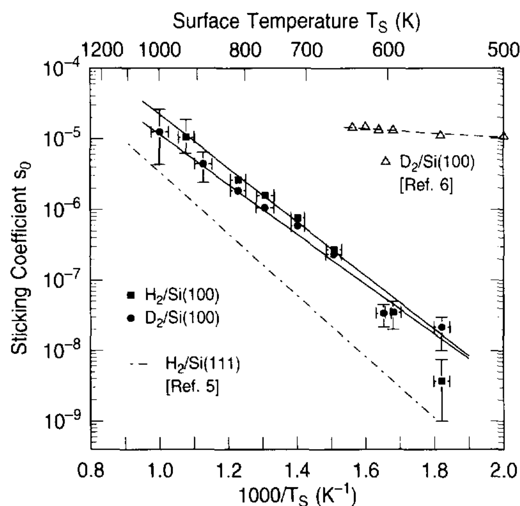

Fig. 4. Arrhenius plot of the initial sticking coefficients for dissociative adsorption of molecular hydrogen on silicon surfaces. The full symbols indicate the values derived in this study for H_2 and D_2 on Si(100)2×1. The solid lines are the result of a fit to an exponential temperature dependence, $s_0 = A\exp(-E_a/kT_s)$ with $A = 1 \times 10^{-1\pm0.5}$ ($4 \times 10^{-2\pm0.5}$) and $E_a = 0.75 \pm 0.1$ (0.70 ± 0.1) eV for H_2 and (D_2), respectively. The open triangles are values determined in Ref. [7] for D_2/Si(100)2×1. The dot-dashed line shows the behaviour we determined previously for H_2/Si(111)7×7 [6].

of $n \sim 10^{19}\,cm^{-3}$ of the utilized wafers (resistivity of 0.005 Ω cm) slightly alters the electronic structure of the surface and reduces the H_2 adsorption barrier compared to a weakly doped sample ($n \sim 5 \times 10^{14}\,cm^{-3}$ in our case).

We now compare our results to recent theoretical work on the interaction of molecular hydrogen with silicon surfaces. Four important results of our experiments should be pointed out for this discussion: (1) the weak isotope effect between H_2 and D_2 adsorption, (2) the low overall sticking probability, (3) its strong dependence on the surface temperature, and (4) the similar behaviour of Si(100)2×1 and Si(111)7×7.

The weak isotope effect between H_2 and D_2 observed here for dissociative adsorption and in other experiments for recombinative desorption [24–26] makes a reaction dominated by tunnelling through a narrow barrier rather unlikely [27]. Likewise, one should expect a significant isotope effect if the observed temperature dependence of the sticking probability resulted from a phonon-gain process of the incident molecules as described by the model of Luntz and Harris [28]. Since D_2 and H_2 are observed to react similarly within experimental error these effects are likely to be unimportant for the reaction.

Both, the absolute values of the sticking probability and the strength of the temperature dependence are in good agreement with the model of Brenig, Gross and Russ wherein the coupling between the lattice configuration and the adsorption barrier is strong [5]. In a somewhat simplified interpretation, our measured activation energy of E_a = 0.70–0.75 eV corresponds to the excitation energy of the silicon surface required to enable the incoming (cold) H_2 molecule to adsorb without experiencing a large barrier. For this highly excited surface the reaction path of the adsorbing molecule becomes almost identical to the reverse of the desorption path. A more detailed comparison of our experimental results with this model will be given elsewhere [26].

Ab initio density functional calculations by Kratzer, Hammer and Nørskov [14], Pehlke and Scheffler

[15], and Vittadini and Selloni [16] have related the asymmetry between adsorption and desorption with the tilting of Si(100) dimers. While the Si-Si dimers of the clean Si(100) surface are known to be asymmetric [29], a symmetric configuration with an altered adsorption barrier is likely to be present if hydrogen is adsorbed. In contrast to earlier theoretical work [8-10] these new slab calculations give absolute values for the activation energy for the recombinative desorption of two H atoms from one dimer that are in good agreement with experiment [20,31]. Also the adsorption barriers given in Refs. [14,16] are compatible with the low value of the sticking coefficient found in the present work. However, the surface temperature dependence of the sticking probability predicted in Refs. [14-16] is considerably weaker than found here experimentally, because the energy required to flip an asymmetric dimer on the Si(100) surface is only of the order of $E_a \approx 0.1$ eV. Likewise, the calculated energy contained in the Si substrate at the transition state geometry is quite small [14-16]. The translational heating expected from these calculations is thus substantial, again in contrast to experimental observations [4]. Therefore, we conclude, that *additional* substrate excitations must be involved in the interaction of H_2 with Si(100)2×1.

These additional excitations could in principle be electronic in nature. The excitation of low lying surface states in the Si band-gap may either directly [18] or via local band-bending effects [33] reduce the adsorption barrier and add to the observed Arrhenius behaviour of the sticking probability. For several reasons, we believe, however, that the lattice undergoes a stronger distortion in the transition state than predicted by the aforementioned theoretical work. One reason is the success of the model potential by Brenig, Gross and Russ [5] which accurately reproduces all currently available experimental results [26]. Second, there are several ab intio investigations of H/Si(100)2×1 which show that surface relaxation may strongly affect reaction barriers. Compared to hydrogen diffusion on a rigid surface, e.g., diffusion barriers are found to be reduced by as much as 1 eV on a moveable substrate [32]. Similarly, the activation energies for recombinative desorption from Si_9H_{14} clusters without geometrical constraints were found to be considerably smaller and in much better agreement with experiment [18] than if such constraints were present [8-10]. Finally, it is the surprisingly similar behaviour of Si(100)2×1 and Si(111)7×7 which indicates that the lattice is distorted substantially during the interaction with molecular hydrogen.

While the specific reconstruction of each surface leads to characteristic desorption kinetics [20,30], the energetics and dynamics of desorption were found to be surprisingly alike in all previous experiments. The activation energies for recombinative desorption differ by less than 0.1 eV [26,31]; the kinetic and internal energy distribution of the desorbing H_2 molecules are almost identical [4,34]. The same striking similarity appears to be present in adsorption, with activation energies E_a for phonon-assisted sticking that differ only by ~ 0.1 eV between Si(111) and Si(100) (compare Fig. 4). This close resemblance indicates that both, the geometry of the transition state and the Si lattice distortions near the saddle point, are similar for Si(111) and Si(100). Since the large distance of ~ 4 Å between two hydrogen adsorption sites on Si(111)7×7 [35] dictates a significant bond stretching during recombinative desorption and dissociative adsorption of H_2 it seems likely that also in the case of Si(100)2×1, Si-Si bonds are distorted more strongly than predicted by the present state of microscopic theory.

We currently do not known what the exact geometry of the transition state of H_2 adsorption on Si(100)2×1 is and where the necessary lattice distortions are located. However, should recent calculations correctly predict that the dimer bond-length has only a moderate influence on the adsorption barrier [14], then interaction mechanisms of H_2 with Si(100)2×1 that go beyond a single Si-Si dimer must be considered. For the interdimer recombination, initially proposed by Wu and Carter [8], e.g., a substrate energy of 0.8 eV in the transistion state was calculated by Vittadini and Selloni [16]. This value is in close agreement to the present experimental finding of an activation energy for the activated adsorption in the surface coordinates of $E_a = 0.70$-0.75 eV. Alternatively, it is conceivable that the H_2 reaction on Si(100)2×1 takes place at single-atom defects, similar to the adatoms of Si(111)7×7, as proposed by several theoretical groups [11-13]. If these active sites are created transiently from distorted dimers at steps, this process becomes compatible with our observation of strong phonon-assisted sticking [26].

4. Conclusions

In conclusion, we have used optical second-harmonic generation to determine the sticking probability for dissociative adsorption of H_2 and D_2 on Si(100)2×1. The sticking coefficient s_0 exhibits a strong dependence on surface temperature with s_0 increasing exponentially with $1/T_s$ from $s_0 = 10^{-8}$ at $T_s = 550\,K$ to $s_0 = 10^{-5}$ at $T_s = 1000\,K$. The activation energy for phonon-assisted sticking is $E_a = 0.70 \pm 0.1\,eV$ for H_2 and $E_a = 0.75 \pm 0.1\,eV$ for D_2. The results reveal a qualitatively similar adsorption behaviour of the Si(100)2×1 surface as previously discovered for H_2/Si(111)7×7. The strong effect of surface temperature on the adsorption probability and the close similarity of both surfaces indicate that lattice excitations other than the tilting of Si–Si dimers play an important role in the interaction of Si(100) surfaces with molecular hydrogen.

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