Appl. Phys. B 68, 649–655 (1999)

Applied Physics B
Lasers
and Optics
© Springer-Verlag 1999

Influence of steps and defects on the dissociative adsorption of molecular hydrogen on silicon surfaces

M.B. Raschke, U. Höfer

Max-Planck-Institut für Quantenoptik, D-85740 Garching, Germany;
Physik Department, Technische Universität München, D-85747 Garching, Germany
(Fax: +49-89/32905-200, E-mail: Hoefer@mpq.mpg.de)

Received: 3 November 1998

Abstract. The dissociative adsorption of molecular hydrogen on vicinal Si(001) and Si(111) surfaces was investigated by means of optical second-harmonic generation (SHG). For temperatures up to 600 K the measured initial sticking coefficients could be decomposed into contributions from step/defect and terrace sites. Whereas the presence of steps on Si(111) leads only to a moderate increase of reactivity, the sticking coefficients for step adsorption on misoriented Si(001) are many orders of magnitude higher than for terrace adsorption and reach values up to 10^{-4}. Neither the absolute values nor the temperature dependence of adsorption on the terraces are affected by the misorientation.

PACS: 42.65.Ky; 68.35.Ja; 82.65.My

The interaction of molecular hydrogen with silicon surfaces has attracted considerable attention as a model for reaction dynamics on semiconductor surfaces [1–3]. The sticking probability for dissociative adsorption of H_2 on well-prepared Si surfaces is less than 10^{-10} at room temperature but increases to values as high as 10^{-5} when the substrate temperature is raised to 1000 K [4, 5]. This striking temperature dependence and the lack of translational heating during recombinative desorption [6] indicate that the rearrangement of substrate atoms from their ideal lattice positions plays a crucial role in the underlying reaction mechanism.

In the model of phonon-assisted sticking, proposed by Brenig and co-workers [7, 8], the excitation of lattice vibrations at elevated temperature decreases the effective dissociation barrier for the incident H_2 molecule, whereas upon desorption the excess barrier energy is to a large extent released to silicon phonons. Such a scenario is supported by slab-type ab initio calculations that have found substantial coupling of the dissociation barrier with the dimer buckling of Si(001)2×1 [9–11] and with the adatom position of Si(111)7×7 [12, 13]. Alternatively, as a result of cluster calculations, it was suggested that single-atom defects mediate H_2 adsorption and desorption [14–16]. These defects would facilitate the creation of dihydride intermediates without an appreciable adsorption barrier. The presence of such sites would thus not lead to translational heating in desorption whereas the sticking probabilities would be determined by their temperature-dependent concentration and hydrogen diffusion to normal adsorption sites.

On the basis of the published experimental and theoretical work it is currently not possible to give a definite answer as to which mechanism is in operation. There are still unresolved quantitative discrepancies between the results of dynamical studies based on *ab initio* potential-energy surfaces for Si(001)2×1 and the experiments [8, 17–19]. A problem of the defect-mediated mechanism is obtaining reaction rates that are consistent with both the small sticking probabilities and the high pre-factors for thermally activated desorption [2, 20]. The experimental difficulties in measuring small sticking coefficients further complicate matters. Whereas our values obtained for the adsorption of thermal H_2 agree with the limits put forward by earlier investigations [21, 22], experiments with a supersonic molecular beam resulted in remarkably high values for the sticking probability of H_2/Si(001) and suggested only a weak effect of surface temperature [23]. Moreover, reports of H_2 sticking at minority sites with a probability of almost unity have appeared in the literature [24, 25].

In this paper, we report on systematic investigations of H_2 adsorption on misoriented Si(001) and Si(111) surfaces with a reproducible amount of minority sites. The high sensitivity and in-situ applicability of optical second-harmonic generation (SHG) makes this technique an ideal real-time monitor for the kinetics of the competing reaction channels associated with step/defect and terrace sites on these surfaces. Sticking at the steps is observed to occur at a rate that is up to five orders of magnitude higher than the rate of adsorption on the terraces. Step adsorption shows little temperature dependence, whereas the activation-energy results for phonon-assisted sticking on the terrace sites are found to be identical to results reported previously for flat surfaces [4, 5, 8]. The results suggest that on well-prepared silicon surfaces the dissociative adsorption of H_2 is not mediated by static defects.

1 Experiment

The experimental procedures used to measure small sticking coefficients were similar to our earlier works [3]. The set-up was somewhat modified in order to improve gas handling and SHG sensitivity as described elsewhere [26]. The prominent feature of the ultrahigh vacuum (UHV) system is a multi-stage pumping unit with various pumps separated from the chamber via gate valves. This set-up ensured we reached a working pressure of $\leq 6\times10^{-11}$ mbar within about 30 s after dosing hydrogen by backfilling the chamber with typically 10^{-4}–10^{-3} mbar of purified H_2 from a liquid-nitrogen-cooled reservoir.

Different types of silicon samples were used: Si(001) nominally flat oriented to within 1/4°, Si(001) with miscuts of 2.5°, 5.5°, 10° towards the [110], Si(001) misoriented by 3° towards the [010] direction and Si(111) misoriented by 5.0° towards $[1\bar{1}0]$. These samples were cut from commercial (Virginia Semiconductor) n-type 2–10 Ω cm wafers. In addition, a highly As-doped ($n = 2.5\times10^{19}\,\mathrm{cm^{-3}}$) 0.003 Ω cm sample was prepared that was misoriented by approximately 1° towards [010]. It was self-cut, polished, and chemically treated [27] prior to mounting in UHV. In-situ removal of the oxide layers by repetitive heating to 1250 K resulted in clean well-ordered surfaces as verified by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES).

For the SHG measurements, 1064-nm pump radiation with a fluence of about $\sim 30\,\mathrm{mJ/cm^2}$ incident at 45° with respect to the surface normal was provided by a Q-switched Nd:YAG laser (Coherent, Infinity) with a pulse duration of 3.5 ns and operating at a repetition rate of 30 Hz. Improved beam profile and pulse-to-pulse stability lead to a gain in adsorbate sensitivity compared to that in our previous studies. The polarization was chosen to obtain similar sensitivity for adsorption at the terrace and step/defect sites. The square root of the measured SH signal, which is proportional to the surface nonlinear susceptibility $\chi_s^{(2)}$ [28], will be shown throughout.

At the fundamental wavelength of 1064 nm $\chi_s^{(2)}$ is proportional to the concentration of unreacted surface dangling bonds for low hydrogen coverage θ_H, [3]. The coverage dependence is well described by the simple linear relationship

$$\chi_s^{(2)}(\theta_H) = \chi_{s,0}^{(2)}[1-\alpha\theta_H]. \tag{1}$$

The proportionality factor α has been calibrated by means of temperature-programmed desorption (TPD) experiments [5]. It is $\alpha = 3.1\,\mathrm{ML^{-1}}$ and $\alpha = 1.3\,\mathrm{ML^{-1}}$ for Si(001)2×1 and Si(111)7×7, respectively and $\alpha \simeq 1\,\mathrm{ML^{-1}}$ in the case of the steps. The sticking coefficient s, defined as the probability that an incident H_2 molecule dissociatively adsorbs on the surface, is determined by keeping the sample at constant temperature and measuring its SH response as a function of time, t, during exposure to a gas flux, Φ, determined from the recorded background pressure, p ($\Phi = p[2\pi m_{H_2} kT_{gas}]^{-1/2}$). In case of constant Φ and negligible desorption, the adsorption rate

$$\frac{d\theta_H}{dt} = s(\theta_H)\Phi \tag{2}$$

and thus the sticking coefficient $s(\theta_H)$ is proportional to the slope of $\chi_s^{(2)}(t)$. In practice, both the hydrogen pressure and the SH signal are recorded as a function of time and $s(\theta_H)$ is deduced with a numerical fitting procedure [4]. All the values given below are initial sticking probabilities $s_0 \equiv s(\theta_H = 0)$.

2 Results and discussion

2.1 Vicinal Si(001) 2 × 1

The adsorption behavior of the highly doped and misoriented Si(001) surface and that of the orientationally flat sample with low doping concentration are compared in Fig. 1. At a surface temperature of 575 K the sticking probability of the 10-Ω cm sample is found to be 3×10^{-8}, in perfect agreement with earlier results [5]. The adsorption reaction of the 0.003-Ω cm sample is characterized by two time constants. The fast initial drop of the SH response right after the beginning of the hydrogen exposure corresponds to a sticking probability of 8×10^{-6}. This adsorption channel quickly saturates and further hydrogen uptake occurs at a rate that is more than two orders of magnitude lower and is comparable to that determined for the flat 10-Ω cm sample.

The fast adsorption process observed for the 0.003-Ω cm sample is not specific to the high doping concentration. Very similar behavior could be observed for the surface of the 10-Ω cm sample after several cycles of oxygen adsorption and subsequent SiO desorption at ~ 950 K without further annealing. Such oxygen treatment is known to lead to the formation of steps and defects via inhomogeneous etching of the topmost surface layers [29]. We therefore attribute the fast adsorption process to the reaction with minority sites such as steps and other kinds of defects present on the surface of the misoriented 0.003-Ω cm as well as on the etched 10-Ω cm sample.

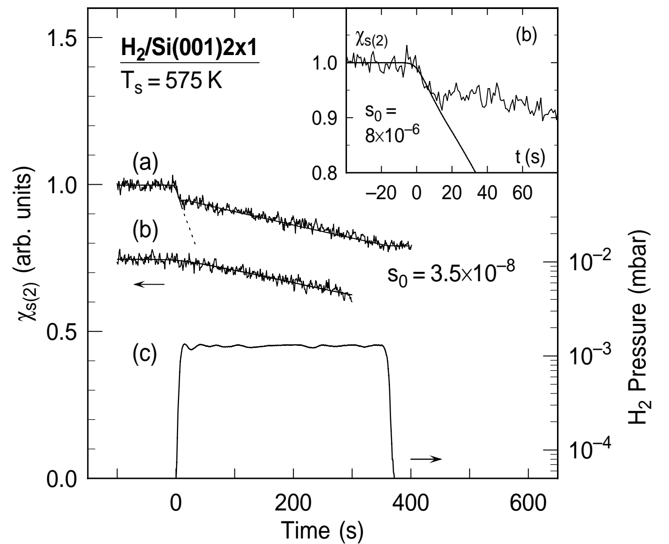

Fig. 1. Nonlinear response $\chi_s^{(2)}$ of two different Si(001)2×1 surfaces kept at $T_s = 575$ K during H_2 exposure ($T_{gas} = 300$ K): (a) 0.003-Ω cm sample misoriented by about 1° towards [010], (b) 10-Ω cm orientationally flat sample, vertically offset by −0.25. The H_2 pressure (c) during exposure, shown for trace (a), corresponds to a flux of about 3×10^3 ML/s in both cases (1 ML = 0.68×10^{15} atoms/cm²). Inset: Adsorption at the minority sites magnified from trace (a). The fast hydrogen uptake corresponding to an initial sticking probability $s_0 = 8\times10^{-6}$ saturates at a coverage of 0.03 ML

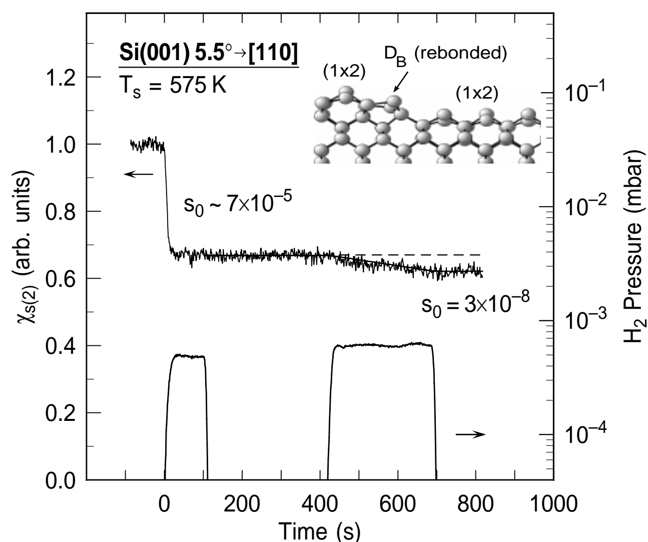

Fig. 2. Nonlinear response $\chi_s^{(2)}$ of Si(001) miscut at an angle of 5.5° towards [110] during H_2 exposure. The fast signal drop at $t = 0$ corresponds to hydrogen adsorption at the rebonded D_B steps with an initial sticking coefficient of 7×10^{-5}; the slow decrease at $t > 400$ s indicates sticking on the terraces ($s_0 = 3 \times 10^{-8}$). There is negligible hydrogen diffusion from the step sites at the surface temperature of 575 K, as indicated by the constant $\chi_s^{(2)}$ upon interruption of the H_2 exposure and because further exposure does not cause another fast signal drop that would indicate partial depletion of the step sites. Inset: Ball-and-stick model of the structure of D_B steps from [30]

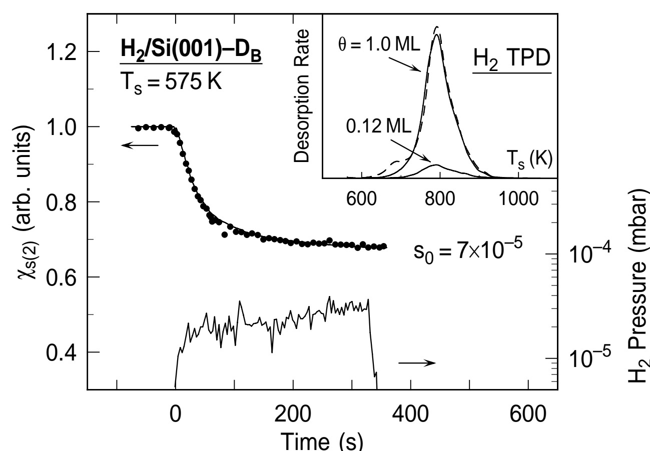

Fig. 3. Determination of the saturation coverage and sticking coefficient of H_2 adsorption at the steps of Si(001) 5.5° → [110] at a surface temperature of $T_s = 575$ K. Main panel: H_2 pressure and measured SH response during exposure. The *solid line* through the data points of the nonlinear susceptibility is the result of a numerical fit assuming Langmuir adsorption kinetics at the steps and a linear relationship between $\chi_s^{(2)}$ and θ. Inset: Temperature-programmed desorption (TPD) of H_2 from the fully monohydride and partially dihydride covered surface in comparison with the step-saturated surface.

The slow adsorption process with an apparent sticking coefficient of 3×10^{-8} could in principle be caused by hydrogen diffusion and rapid re-filling of minority sites. Experiments with interrupted gas exposure (compare Fig. 2) show that this is not the case for temperatures below 600 K, but that the slow process must be due to a separate reaction channel. The corresponding sticking probabilities are very similar for all Si(001) surfaces studied. It is thus characteristic for the reaction on the well-ordered terraces.

The motivation to explore H_2 adsorption on the (001) surface of highly As-doped silicon is provided by the experiments by Kolasinski and co-workers [6, 23]. It has been speculated that the high sticking coefficients ($s_0 \simeq 10^{-5}$ for $T_s = 600$ K) reported by these authors [23] might be due to their use of samples with a high doping concentration [5]. An enrichment of As on the surface could in principle alter the charge distribution of the dangling bonds and reduce the dissociation barrier. This would explain not only the higher sticking coefficients but also the discrepancies between calculated [17–19] and measured translational energy distributions of the desorbing H_2 molecules. The present experiments now suggest that, at least up to doping concentrations of $n \sim 10^{19}\,\text{cm}^{-3}$, no influence on surface reactivity is detectable.

To gain insight into the mechanisms of H_2 interaction with special surface sites it is necessary that these sites are characterized. This is the case for vicinal Si(001) surfaces misoriented towards the [110] direction. It is well known that for miscut angles greater than 2° and upon proper preparation, these surfaces form straight double-atomic height steps separated by terraces with the dimers oriented parallel to the step edges [31–33]. These so-called rebonded D_B steps are characterized by threefold coordinated silicon atoms that form one bond to the step and have one free dangling bond [34–36]. In the case of the miscut angle of 5.5° used here, the D_B steps are expected to account for 14.6% of the number of surface dangling bonds and the average terrace size is 5.8 dimers [30].

As shown in Fig. 2, the steps lead to rapid hydrogen adsorption when the surface, again kept at $T_s = 575$ K, is exposed to a flux of about $5 \times 10^{17}\ H_2\text{molecules/cm}^2\,\text{s}$. The fast reaction saturates long before monolayer coverage is reached. Further hydrogen uptake proceeds with the sticking coefficient of the flat surface at that temperature. In order to determine the saturation coverage and accurate sticking coefficients of the reaction with the step sites, the adsorption experiments were performed with the lowest pressure that could be monitored with the spinning rotor gauge (Fig. 3). The area of the TPD peak obtained after saturation of the fast adsorption channel amounts to 12% of that obtained from a fully monohydride terminated surface which was prepared by dosing atomic hydrogen created at a hot tungsten filament. The resulting hydrogen coverage of 0.12 ± 0.02 ML agrees well with the concentration of dangling bonds of D_B steps. The numerical fit shows that the adsorption can be described by Langmuir kinetics with a sticking coefficient of 7×10^{-5}.

Step and terrace adsorption on Si(001) were investigated for various surface temperatures. The sticking coefficients deduced are summarized in Fig. 4 in the form of an Arrhenius plot. The sticking coefficients associated with terrace adsorption are all aligned for the different surfaces investigated. In the range from 450 to 900 K their temperature dependence is well described by $s_0 = A \times \exp(-E_a/kT_s)$. The values obtained for the activation energy of $E_a = 0.76 \pm 0.1$ eV and prefactor $A = 0.2$ are in excellent agreement with the results reported previously for the flat surface [5]. Adsorption at the step/defect sites is characterized by absolute sticking probabilities that are orders of magnitude higher and negligible temperature dependence between 450 and 600 K.

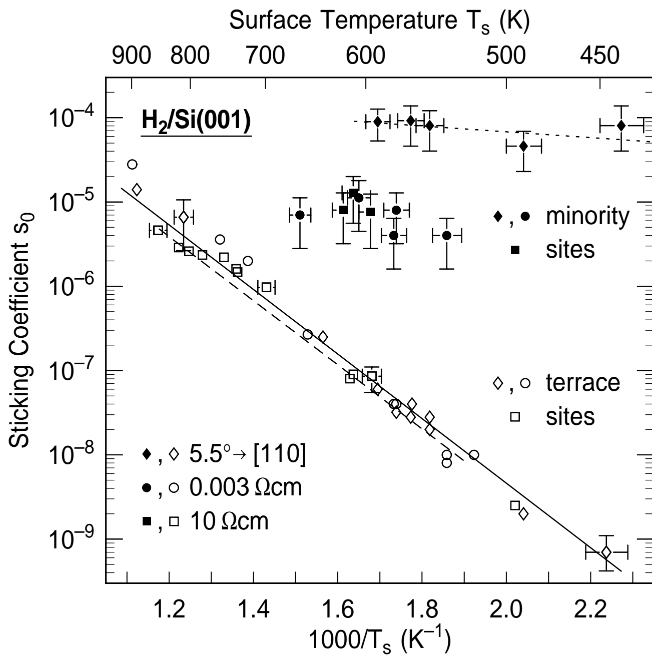

Fig. 4. Arrhenius plot of the initial sticking coefficients s_0 for dissociative adsorption of H_2 on flat and misoriented Si(001) surfaces as a function of surface temperature T_s. The *solid line* denotes a numerical fit to an exponential temperature dependence for the values derived from terrace adsorption with prefactor $A = 0.2$ and $E_a = 0.76 \pm 0.1$ eV. The *dashed parallel line* marks the results of our earlier experiments on flat Si(001) surfaces [5]. The *dotted line* indicates the weak temperature dependence found for sticking at the D_B steps of Si(001)5.5° → [110] over the full temperature range from 80 K to 600 K [37]

The highest sticking coefficients are observed for the surfaces with miscut towards [110] exhibiting the D_B steps. This is not an effect mainly of concentration but one of site-specific reactivity. The fast adsorption channel was observed to saturate at coverages of 0.12 ML in case of Si(001)5.5° → [110] and between 0.03 and 0.05 ML in the case of the misoriented 0.003 Ω cm and the etched 10 Ω cm-samples. In terms of the site-specific reactivity $\hat{s}$, obtained by normalizing the measured initial sticking coefficient by the aerial concentration, $\hat{s} = s_0\theta^{-1}$, one finds a $\hat{s}$ of the double-height steps that is 5 to 10 times higher than that of the other step and defect sites.

Based on ab-initio calculations, Kratzer et al. recently suggested [37] that molecular hydrogen is able to dissociate without barrier and to form directly a monohydride at two neighboring sites of the D_B-steps. This is possible because, in contrast to the buckled dimers on the terraces, the dangling bonds of the rebonded Si atoms at the D_B steps are almost degenerate. Upon the approach of parallel aligned H_2 molecules, these surface states rehybridize easily and thus interact efficiently with the H_2 molecular orbitals. On the basis of theoretical and experimental evidence, hydrogen dissociation at these sites proceeding via dihydride intermediates was excluded [37].

The efficient formation of dihydrides requires isolated defects with two dangling bonds per Si atom [16]. Since such single-atom defects would certainly have the highest probabilty for H_2 dissociation of all sites, the present results suggest that their concentration is extremely small on perfectly as well as on slightly misoriented Si(001) surfaces. This conclusion is in agreement with STM investigations that find dimerized defects but no isolated Si atoms on similarly prepared surfaces [38, 39] and with kinetic stability arguments [40]. Reconstruction even results in threefold coordinated Si atoms at the kinks of Si(001) steps [34]. We therefore believe that a direct dissociation mechanism, similar to the one found for the D_B steps, but probably slightly less efficient, is in operation at the single-height S_B steps of the Si(001) surfaces with small misoritentations and on the etched surface.

2.2 *Vicinal* Si(111) 7 × 7

Whereas the different vicinal Si(001) surfaces provide an appreciable number of highly reactive sites, the effect of misorientation on the sticking of H_2 was found to be much weaker in the case of the investigated Si(111) surface that was misoriented by 5° towards [1$\bar{1}$0]. The surface is characterized by wide terraces of 7×7 structure coexisting with facets oriented approximately 20° off [111] [41, 42]. Measurements of the extremely small sticking coefficients determined for this surface at low temperatures are shown in Fig. 5. For surface temperatures between 500 and 600 K, the sticking coefficient at the minority sites is 3 to 4 orders of magnitude lower than the corresponding values for the 5° miscut (001) surface and only 1 to 2 orders of magnitude higher than the values obtained for the terraces. With increasing surface temperature the total, non-site-specific sticking coefficient increases drastically and approaches the values obtained previously for flat surfaces [4, 8]. At 800 K, for example, the sticking coefficient

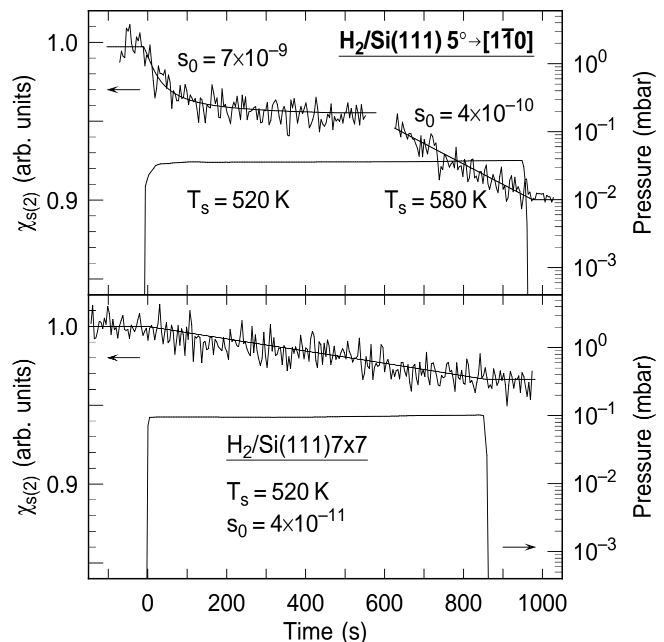

Fig. 5. Nonlinear response $\chi_s^{(2)}$ of Si(111)7 × 7 misoriented by 5° towards [1$\bar{1}$0]. *Top:* H_2 exposure of the clean surface at $T_s = 520$ K leads to adsorption at minority (step) sites (∼ 0.06 ML) with a sticking coefficient of 5×10^{-9}; adsorption continues on the terraces if the sample temperature is raised ($s_0 = 4 \times 10^{-10}$ for $T_s = 580$ K). *Bottom:* After the minority sites are saturated, the sticking coefficient at $T_s = 520$ K drops to a value as low as 4×10^{-11}. Gas fluxes of almost 10^6 ML/s are required for the adsorption of a 0.03 ML in 15 min. (1 ML = 0.30×10^{15} atoms/cm^2)

was found to be 1×10^{-6}, which is only a factor of two higher than the value reported in [4]. The finding that misorientation of Si(111) does not cause a similarly striking increase in reactivity as in the case of Si(001) surfaces further supports the direct dissociation mechanism discussed for vicinal Si(001). It requires a specific step structure that is not present on miscut Si(111) surfaces.

The adsorption of H_2 on Si(111) 5° → [1$\bar{1}$0] has been investigated before by Hansen et al. [25]. The reported values for the sticking coefficient in the temperature range between 540 and 660 K fall between 0.001 and 0.1 and are clearly at variance with the results of the present work. We were also not able to confirm the similarly high sticking coefficients they obtained for Si(001) misoriented by 3° towards the [010] direction but find a reactivity that is slightly reduced ($s_{0,\mathrm{stp}}(T_\mathrm{s} = 570\,\mathrm{K}) \simeq 3 \times 10^{-5}$, $s_{0,\mathrm{terr}}(T_\mathrm{s} = 570\,\mathrm{K}) = 8 \times 10^{-8}$) compared to that of the 5.5° surface with its regular array of D_B steps. Since Hansen et al. neither observed the two distinct reaction channels characteristic for all of our low temperature experiments on the vicinal surfaces nor compared them with results on flat surfaces, we currently cannot give a convincing explanation for the discrepancies.

2.3 *Kinetics of defect-mediated terrace adsorption*

The experiments presented above clearly indicate that for surface temperatures below 600 K, adsorption on the terraces occurs through a reaction channel that is independent of the steps. The direct experimental observation of the considerably less efficient adsorption reaction with the terrace sites is possible only because the barriers for hydrogen diffusion on silicon surfaces are quite large and prevent rapid migration between different adsorption sites. In the case of Si(001) miscut towards [110], we have investigated hydrogen diffusion systematically by selectively saturating the D_B steps with dissociatively adsorbed hydrogen and monitoring the depletion of steps in the temperature range 580–730 K [26]. The hopping rate was found to be thermally activated with a barrier of $E_\mathrm{d} \simeq 1.7\,\mathrm{eV}$ and a pre-factor of $10^{11}\,\mathrm{s}^{-1}$. This activation energy for H migration from the D_B steps to the terraces almost coincides with the barrier obtained for hydrogen diffusion along the dimer rows of the terraces of planar surfaces with scanning tunneling microcopy (STM) [43]. For H/Si(111)7×7, similarly high diffusion barriers ($E_\mathrm{d} = 1.5$–$2.2\,\mathrm{eV}$) were deduced from SHG diffraction experiments and STM studies [44, 45].

The diffusion experiments show that migration of atomic hydrogen becomes appreciable on the timescale of our adsorption experiments for $T_\mathrm{s} > 600\,\mathrm{K}$. This suggests that, even for moderately high step/defect densities, terrace adsorption via these minority sites can become competitive and even more efficient than the direct adsorption channel. For the quantitative description we extend (2) with a term that takes diffusion of atomic hydrogen from step sites into account:

$$\frac{\mathrm{d}\theta_\mathrm{H}}{\mathrm{d}t} = \Phi s_\mathrm{terr} + \theta_\mathrm{stp} n_\mathrm{H,stp} \nu_\mathrm{d} \,. \qquad (3)$$

Here θ_stp denotes the concentration of reactive step sites, $n_\mathrm{H,stp}$ their relative population with atomic hydrogen and ν_d is the hopping rate for hydrogen diffusion onto the terraces.

An overview of the resulting behavior can be obtained by making the simplifying assumption that the initial adsorption at the step sites is fast compared to the timescale over which filling of the whole terraces takes place. In this case, we can replace the time-dependent population $n_\mathrm{H,stp}(t)$ by its equilibrium value $\bar{n}_\mathrm{H,stp}$. In equilibrium, the depletion of step sites is compensated by re-adsorption from the gas. With the site-specific reactivity $\hat{s}_\mathrm{stp} = s_{0,\mathrm{stp}}\theta_\mathrm{stp}^{-1}$ and Langmuir-type site blocking the rate equilibrium is given by

$$\bar{n}_\mathrm{H,stp}\nu_\mathrm{d} = \Phi \hat{s}_\mathrm{stp}(1 - \bar{n}_\mathrm{H,stp}) \qquad (4)$$

and one obtains

$$\bar{n}_\mathrm{H,stp} = \frac{\Phi \hat{s}_\mathrm{stp}}{\Phi \hat{s}_\mathrm{stp} + \nu_\mathrm{d}} \,. \qquad (5)$$

Note that any back-migration from the terraces is neglected in (4), which is a good approximation only for small total coverage and a small number of step sites.

The effective sticking coefficient for step-mediated adsorption s^*, defined by dividing the second term of (3) by the incident gas flux Φ, then becomes

$$s^* = \frac{\hat{s}_\mathrm{stp}\nu_\mathrm{d}}{\Phi \hat{s}_\mathrm{stp} + \nu_\mathrm{d}} \theta_\mathrm{stp} \,. \qquad (6)$$

The two limiting cases

$$\Phi \hat{s}_\mathrm{stp} \ll \nu_\mathrm{d} : \quad s^* = \hat{s}_\mathrm{stp}\theta_\mathrm{stp} = s_{0,\mathrm{stp}} \qquad (7)$$

$$\Phi \hat{s}_\mathrm{stp} \gg \nu_\mathrm{d} : \quad s^* = \nu_\mathrm{d}\theta_\mathrm{stp}\Phi^{-1} \qquad (8)$$

show that the sticking coefficient s^* of H_2/Si will be determined by the reactivity of the minority sites $\hat{s}_\mathrm{stp}$ for high temperatures (7) and by the diffusion rate ν_d for low temperatures (8). Obviously, the high-temperature limit is experimentally indistinguishable from adsorption directly on the terraces because the hydrogen population $\bar{n}_\mathrm{H,stp}$ becomes small (5) and does not appear as a fast initial drop of the SH signal. In the low-temperature limit the defect-mediated channel can be suppressed against direct adsorption by using high enough H_2 fluxes Φ for exposure.

A measurement that illustrates the transition to step-mediated adsorption for the Si(001) surface with D_B steps is shown in Fig. 6. Both saturation of the step sites and diffusion of hydrogen to the terrace sites, leading to a higher effective sticking coefficient for terraces adsorption, are clearly visibly at the temperature of 640 K. With the present adsorption experiments and the study of diffusion [26], we have determined all the necessary quantities to simulate the behavior for that surface ($\Phi = 450\,\mathrm{ML/s}$, $\theta_\mathrm{stp} = 0.12\,\mathrm{ML}$, $\hat{s}_\mathrm{stp} = 4 \times 10^{-4}\,\mathrm{ML}^{-1}$, $\nu_\mathrm{d} = 4.2 \times 10^{-3}\,\mathrm{s}^{-1}$). Insertion in (6) predicts an apparent sticking coefficient of $s^* = 1.1 \times 10^{-6}$. This is in excellent agreement with the measured value of $s^* = 1.4 \times 10^{-6}$ and demonstrates the applicability of our simple model.

This example also confirms that the results for terrace adsorption shown in Fig. 4 and our previously published results for adsorption on flat surfaces are not likely to be affected by the defect-mediated channel discussed here. If we replace the density of minority sites of 0.12 ML by a realistic upper limit of 0.01 ML (that would still be visible as a fast

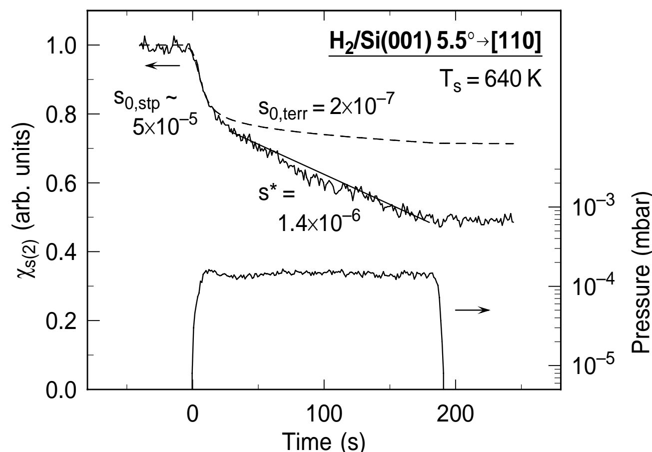

Fig. 6. Adsorption of hydrogen on the terraces of vicinal Si(001) mediated by H_2 dissociation at the D_B steps. The fast drop of $\chi_s^{(2)}$ is due to sticking at the steps with a sticking probability of 5×10^{-5}. The subsequent decrease corresponds to an adsorption rate of 7×10^{-4} ML/s. With an average exposure rate of 5×10^{2} ML/s, the step-mediated sticking coefficient becomes 1.4×10^{-6}. The *dashed line* indicates the behavior expected for the measured sticking coefficient for terrace adsorption of 2×10^{-7} in the absence of diffusion

drop of the SHG signal), and take into account the 5–10-fold lower reactivity of these sites as compared to the D_B steps, the effective sticking coefficient s^* already drops below the measured value of 2×10^{-7}. It is further reduced by the higher gas fluxes (typical pressure 10^{-3} mbar) applied in these experiments [5].

Similar considerations show that over the whole temperature range from 500 K to 1100 K for which we have determined sticking probabilities on flat surfaces [4, 5, 8], a defect-mediated mechanism can be dominant under our experimental conditions only if the number and/or the reactivity of the minority sites is considerably higher. Moreover, if terrace adsorption were mediated by the steps and defects of the misoriented surfaces, the sticking coefficient would scale with the step/defect density and they would fall off with a slope given by the barrier for hydrogen diffusion in the Arrhenius plot (Fig. 4). Obviously, the sticking coefficients for terrace adsorption are independent of the miscut of the surface and their temperature dependence agrees well with the previously deduced apparent activation energy for phonon-assisted sticking of 0.75 eV [5].

In the discussion so far, we have assumed that the number of minority sites is determined by misorientation and preparation of the surface but does not depend strongly on its temperature. Whereas the experiments indicated that this is indeed the case for the fast adsorption channel associated with steps and defects in the temperature range of 450–650 K, this does not exclude a more complicated defect-mediated adsorption channel with a temperature-dependent concentration of active sites from being responsible for terrace adsorption. It has been proposed that steps may serve as a source of isolated Si atoms [46] which, once formed, migrate away from the step edges [14, 16] and facilitate H_2 dissociation on the terraces [14–16].

It is difficult to distinguish such a mechanism from phonon-assisted sticking by varying the surface temperature alone. Although the observed temperature dependence of the sticking coefficient for H_2/Si(001) agrees perfectly with the predictions of the model of phonon-assisted sticking [8], the deduced activation energy of $E_a = 0.75$ could also be associated with the creation of these active sites. In fact, one may even view the adsorption via transient defects as an extreme case of phonon-assisted sticking [8]. One argument against this particular dynamic defect model is, of course, the observed independence of terrace adsorption on Si(001) from the step density of the surface. A more definitive discrimination is possible by investigating sticking as a function of the kinetic energy of the incident H_2 molecules. Whereas in the dynamical model of phonon-assisted sticking, H_2 dissociation is activated in both the lattice and the hydrogen degrees of freedom [7], an increased translational energy of the H_2 molecules is expected to have a much weaker effect in promoting sticking at single-atom defects.

3 Conclusions

In summary, the high sensitivity of SHG to the dangling bonds of Si surfaces and the possibility to monitor hydrogen adsorption in real time has allowed us to distinguish different reaction channels for the dissociative adsorption of H_2 on vicinal Si(001) and Si(111) surfaces in the temperature range between 450 and 650 K. Hydrogen adsorption at steps of Si(001) is characterized by initial sticking probabilities between 5×10^{-6} and 10^{-4}, depending on the miscut of the surface. Adsorption on the terraces is up to five orders of magnitude less efficient; the sticking coefficients exhibit the same strong increase as a function of surface temperature as for the nominally flat surfaces. Misorientation of Si(111), in contrast, leads only to a comparatively moderate increase of reactivity.

Within the range of investigated misorientations the sticking coefficients attributed to terrace adsorption and their temperature dependence agree perfectly with each other and with the corresponding values from the flat surfaces. Both the independence of the sticking coefficients from step density, and the observation that the adsorbed hydrogen atoms are rather immobile up to surface temperatures of ~ 600 K, rule out reaction mechanisms in which hydrogen adsorption on the terraces of Si(001) and Si(111) surfaces proceeds via steps or other static defect sites. Although the formation of dihydride intermediates at transiently created single-atom defects cannot definitely be excluded, a direct reaction mechanism involving the concerted excitation of the substrate degrees of freedom is more likely.

Acknowledgements. The authors would like to acknowledge valuable discussions with W. Brenig, E.A. Carter, M. Dürr, K. L. Kompa, P. Kratzer, and E. Pehlke, and thank M. Stutzmann for providing them with the highly doped silicon crystal. This project is part of the Sonderforschungsbereich 338 of the Deutsche Forschungsgemeinschaft.

References

1. K.W. Kolasinski: Int. J. Mod. Phys. B **21**, 2753 (1995)
2. D.J. Doren: Adv. Chem. Phys. **95**, 1 (1996)
3. U. Höfer: Appl. Phys. A **63**, 533 (1996)
4. P. Bratu, U. Höfer: Phys. Rev. Lett. **74**, 1625 (1995)
5. P. Bratu, K.L. Kompa, U. Höfer: Chem. Phys. Lett. **251**, 1 (1996)
6. K.W. Kolasinski, W. Nessler, A.D. Meijere, E. Hasselbrink: Phys. Rev. Lett. **72**, 1356 (1994)
7. W. Brenig, A. Gross, R. Russ: Z. Phys. B **96**, 231 (1994)

8. P. Bratu, W. Brenig, A. Groß, M. Hartmann, U. Höfer, P. Kratzer, R. Russ: Phys. Rev. B **54**, 5978 (1996)
9. P. Kratzer, B. Hammer, J.K. Nørskov: Chem. Phys. Lett. **229**, 645 (1994)
10. E. Pehlke, M. Scheffler: Phys. Rev. Lett. **74**, 952 (1995)
11. A. Vittadini, A. Selloni: Chem. Phys. Lett. **235**, 334 (1995)
12. A. Vittadini, A. Selloni: Surf. Sci. **383**, L779 (1997)
13. K. Cho, E. Kaxiras, J.D. Joannopoulos: Phys. Rev. Lett. **79**, 5078 (1997)
14. P. Nachtigall, K.D. Jordan, C. Sosa: J. Chem. Phys. **101**, 2648 (1994)
15. Z. Jing, J.L. Whitten: J. Chem. Phys. **102**, 3867 (1995)
16. M.R. Radeke, E.A. Carter: Phys. Rev. B **54**, 11 803 (1996); *ibid* **55**, 4649 (1997); A.J.R. da Silva, M.R. Radeke, E.A. Carter: Surf. Sci. **381**, L628 (1997)
17. P. Kratzer, R. Russ, W. Brenig: Surf. Sci. **345**, 125 (1996)
18. A. C. Luntz, P. Kratzer: J. Chem. Phys. **104**, 3075 (1996)
19. A. Gross, M. Bockstedte, M. Scheffler: Phys. Rev. Lett. **79**, 701 (1997)
20. U. Höfer, L. Li, T.F. Heinz: Phys. Rev. B **45**, 9485 (1992)
21. J.T. Law: J. Chem. Phys. **30**, 1568 (1959)
22. G. Schulze, M. Henzler: Surf. Sci. **124**, 336 (1983)
23. K.W. Kolasinski, W. Nessler, K.H. Bornscheuer, E. Hasselbrink: J. Chem. Phys. **101**, 7082 (1994)
24. H. Froitzheim, H. Lammering, H.-L. Günter: Phys. Rev. B **27**, 2278 (1983)
25. D.A. Hansen, M.R. Halbach, E.G. Seebauer: J. Chem. Phys. **104**, 7338 (1996)
26. M.B. Raschke, U. Höfer: Phys. Rev. B **59**, 2783 (1999)
27. A. Ishizaka, Y. Shiraki: J. Electrochem. Soc. **133**, 666 (1986)
28. Y.R. Shen: Ann. Rev. Phys. Chem **40**, 327 (1989)
29. T. Engel: Surf. Sci. Rep. **18**, 91 (1993)
30. E. Pehlke, P. Kratzer: Phys. Rev. B **59**, 2790 (1999)
31. O.L. Alerhand, A.N. Berker, J.D. Joannopoulos, D. Vanderbilt, R.J. Hamers, J.E. Demuth: Phys. Rev. Lett. **64**, 2406 (1990)
32. E. Pehlke, J. Tersoff: Phys. Rev. Lett. **67**, 1290 (1991)
33. E. Schröder-Bergen, W. Ranke: Surf. Sci. **259**, 323 (1991)
34. D.J. Chadi: Phys. Rev. Lett. **59**, 1691 (1987)
35. P.E. Wierenga, J.A. Kubby, J.E. Griffith: Phys. Rev. Lett. **59**, 2169 (1987)
36. H. Itoh, S. Narui, Z. Zang, T. Ichonokawa: Surf. Sci. **277**, L70 (1992)
37. P. Kratzer, E. Pehlke, M. Scheffler, M.B. Raschke, U. Höfer: Phys. Rev. Lett. **81**, 5596 (1998)
38. R.J. Hamers, U.K. Köhler: J. Vac. Sci. Technol. A **7**, 2854 (1989)
39. V.A. Ukraintsev, Z. Dohnálek, J.T. Yates, Jr., Surf. Sci. **388**, 132 (1997)
40. Z. Zhang, H. Metiu: Phys. Rev. B **48**, 8166 (1993)
41. R.J. Phaneuf, E.D. Williams: Phys. Rev. Lett. **58**, 2563 (1987)
42. B.S. Swartzentruber, Y.-W. Mo, M.B. Webb, M.G. Lagally: J. Vac. Sci. Technol. A **7**, 2901 (1989)
43. J.H.G. Owen, D.R. Bowler, C.M. Goringe, K. Miki, G.A.D. Briggs: Phys. Rev. B **54**, 14 153 (1996)
44. G.A. Reider, U. Höfer, T.F. Heinz: Phys. Rev. Lett. **66**, 1994 (1991)
45. R.-L. Lo, I.-S. Hwang, M.-S. Ho, T.T. Tsong: Phys. Rev. Lett. **80**, 5584 (1998)
46. Z. Jing, G. Lucovsky, J.L. Whitten: Surf. Sci. **296**, L33 (1993)