

Equilibrium and nonequilibrium hydrogen coverages on vicinal Si(001) surfaces: Diffusion barriers and binding energies

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The surface kinetics of hydrogen adsorbed on vicinal Si(001) surfaces, misoriented towards the [110] direction, is investigated by means of optical second-harmonic generation. Following the selective saturation of the double-height D_B steps by exposing the surface to a well-defined dose of molecular hydrogen, the transition from this nonequilibrium to an equilibrium hydrogen distribution is monitored in the temperature range between 580 and 730 K. A thermally activated diffusion process with a barrier of 1.7 ± 0.15 eV associated with the step depletion is observed. From measurements of the equilibrium hydrogen coverage the steps are found to be energetically favored with a H_2 -chemisorption energy difference of ~ 0.2 eV between step and terrace sites. [S0163-1829(99)13403-9]

I. INTRODUCTION

Steps and defects can influence chemistry at solid surfaces in many respects. They are generally more reactive than unperturbed terrace sites, tend to bind adsorbates more strongly and give rise to increased diffusion barriers that affect adsorbate kinetics. In the case of silicon surfaces, the chemical properties of steps are of considerable practical interest because they play a central role for homoepitaxial and heteroepitaxial growth,¹ chemical vapor deposition^{2,3} and the wet chemical preparation of surfaces with extremely low defect densities.⁴ Whereas on metal surfaces a qualitative understanding of the behavior of steps and defects is sometimes possible by simply regarding the coordination number of the atoms,⁵ the reconstruction of semiconductor surfaces renders such simple arguments impracticable. The Si atoms at the different types of single and double height steps and even at most kinks of Si(001) exhibit a threefold coordination like the dimerized terrace atoms.⁶ The chemical properties of these sites depend on details of the local geometric and electronic structure and are thus difficult to predict.

We have shown recently that dissociative adsorption of molecular hydrogen on vicinal Si(001) surfaces is highly site selective with a strong preference for double-height D_B steps.⁷ Here we exploit this finding to prepare nonequilibrium adsorbate layers for the investigation of lateral motion and binding energy differences of atomic hydrogen on these surfaces. Differences in sticking coefficients of many orders of magnitude allow for the preparation of selectively H-saturated steps with clean terraces in between. The transition from this metastable concentration profile to an equilibrium distribution is thermally activated. We obtain information about the underlying diffusion processes by monitoring the time evolution of step and terrace hydrogen population with optical second-harmonic generation (SHG). From the equilibrium distribution itself the effective energy difference between the adsorption sites is deduced.

The experimental approach to study diffusion is in some respect the reverse procedure applied by Reutt-Robey and

co-workers for CO adsorbed on vicinal Pt(111) and Ni(100) surfaces.⁸ These authors started from an initially random distribution of CO molecules and monitored diffusion towards the thermodynamically favored step sites by means of infrared spectroscopy. Our technique allows to determine hopping rates that are as small as 10^{-3} s^{-1} and is therefore particularly well suited for diffusion measurements on highly corrugated surfaces. From the temperature dependence of hydrogen diffusion from the steps to the terraces we obtain an energy barrier of 1.7 ± 0.15 eV. This value is of similar size as the diffusion barrier for hydrogen migration along the dimer rows of Si(001) determined recently by scanning tunneling microscopy.⁹

Hydrogen adsorption on silicon and germanium surfaces is not only accompanied by structural relaxation but also by charge redistribution between the dangling bonds.¹⁰⁻¹⁴ Both effects and their interplay do not allow for an *a priori* estimate of the binding energies at different sites. Our experiments show that the equilibrium hydrogen occupation of the D_B steps of Si(001) is considerably larger than expected for a random distribution of hydrogen between step and terrace sites. The measured equilibrium population varies systematically with miscut angle and temperature of the samples and yields a binding energy for hydrogen at the step sites that is higher than the average binding energy on the terraces. Our conclusions are corroborated by density functional calculations for hydrogen on vicinal Si(001) presented by Pehlke and Kratzer in the subsequent article of this issue.¹⁵

II. EXPERIMENT

A. Experimental setup and procedure

The experiments were performed in an ultrahigh vacuum system with a base pressure of $\leq 4 \times 10^{-11}$ mbar. A multi-stage pumping unit containing two turbomolecular, an ion pump and a cryopump separated from the chamber via gate valves ensured reaching the working pressure within a few seconds after gas dosing. For hydrogen exposure all filaments were turned off and the UHV chamber was backfilled

with H₂ purified from traces of residual H₂O from a liquid-nitrogen-cooled reservoir. Hydrogen pressures of 10⁻⁵ to 10⁻³ mbar were applied and recorded with a spinning rotor gauge (MKS instruments, absolute error ≤10%). The silicon samples were mounted on a liquid-nitrogen-cooled sample holder and could be heated resistively. A NiCr/NiAl thermocouple cemented on the backside of the samples and an infrared pyrometer were used to measure the temperature with an absolute accuracy of ±15 K. The relative uncertainty was estimated to ±5 K for one set of experiments with the same sample. In the temperature programmed desorption (TPD) experiments, the hydrogen flux from the sample was detected using a quadrupole mass spectrometer (QMS) with a “Feulner cap” around the ionizer.¹⁶ For optimal sensitivity, the whole assembly was mounted onto a translational stage and could be placed in front of the sample in a reproducible way.

As in our previous studies, we make use of the high sensitivity and *in situ* capability of SHG as a real-time monitor of adsorbate kinetics.¹⁷ For the SHG measurements, 1064-nm pump radiation 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 operating at a repetition rate of 30 Hz. With a laser fluence of 30 mJ/cm² we were well below influencing the reactivity of the sample by transient heating during the laser pulse. The continuous temperature rise due to the absorbed average laser power was below 3 K. For wavelengths near 1 μm SHG exhibits resonant enhancement by the silicon dangling-bond states that are quenched upon hydrogen adsorption.^{17–19} Therefore, 1064-nm laser light is very appropriate for sensitive, quantitative SHG measurements of hydrogen coverages on silicon surfaces.

The correlation of the changes of the nonlinear susceptibility $\chi_s^{(2)}$ (which is proportional to the square root of the measured SH signal) with hydrogen coverage θ has been established by means of TPD experiments.²⁰ The coverage dependence of $\chi_s^{(2)}$ can then be described by extending previously used expressions¹⁷ to take into account the resonant contributions from the steps $\chi_{s,\text{step}}^{(2)}$ and terraces $\chi_{s,\text{terr}}^{(2)}$ and a weakly coverage dependent nonresonant term $\chi_{s,\text{NR}}^{(2)}$,

$$\chi_s^{(2)} = \chi_{s,\text{step}}^{(2)}(1 - \alpha_{\text{step}}\theta_{\text{step}}) + \chi_{s,\text{terr}}^{(2)}(1 - \alpha_{\text{terr}}\theta_{\text{terr}}) + \chi_{s,\text{NR}}^{(2)}(\theta_{\text{step}}, \theta_{\text{terr}}). \quad (1)$$

The reduced symmetry of the vicinal surfaces allows for a variation of the SH contributions from the step compared to the terrace sites by adjusting the polarization and plane of incidence of the pump light.^{21,22} With the steps oriented perpendicular to the plane of incidence, the *s* and *p* components of the incident light were chosen in order to maximize the signal which was detected without a polarizer in the exit channel. Under these conditions $\chi_{s,\text{step}}^{(2)}$ was approximately four times larger than $\chi_{s,\text{terr}}^{(2)}$ with respect to the number of dangling bonds. This different sensitivity towards step and terrace sites is a prerequisite for the present experiments.

In general, the nonlinear susceptibility is a complex quantity ($\chi_s^{(2)} = |\chi_s^{(2)}|e^{i\Phi}$). The phase shift between the different contributing terms in Eq. (1) might thus lead to their partial cancellation.^{17,23} The observed monotonous behavior of the SH signal as a function of hydrogen coverage indicates that

the phase difference between step and terrace contribution is small and was neglected. Since the hydrogen coverages never exceeded 0.15 ML (1 ML is defined with respect to concentration of dangling bonds of the 2×1 reconstructed surface, $n = 0.68 \times 10^{15} \text{ cm}^{-2}$) the relative contribution from $\chi_{s,\text{NR}}^{(2)}$ to the total SH signal was small and neglected as well. With these approximations, the proportionality factors were calibrated to be $\alpha_{\text{terr}} \approx 3.1$ and $\alpha_{\text{step}} \approx 1$. The value of α_{terr} is identical to that determined previously for flat Si(001).²⁰ It is greater than unity, due to a significant nonlocal influence of the adsorbate on the surface electronic states. At the step edges the interaction between adsorption sites is expected to be much weaker and appears to be of negligible influence on $\chi_{s,\text{step}}^{(2)}$.

B. Crystal preparation and structure

Vicinal Si(001) samples with three different step densities were used for these experiments. They were cut from *n*-type 6–10 Ω cm wafers inclined towards the [110] direction by 2.5°, 5.5°, and 10° ± 0.5°. The surface orientations were determined *ex situ* with Laue x-ray diffraction and *in-situ* following the sample cleaning procedure via low-energy electron diffraction (LEED). The oxide layer was removed by repetitive heating to a maximal temperature of 1250 K. In order to prepare high-quality steps each adsorption measurement was preceded by flash annealing the sample to 1200 K followed by a slow cooling procedure. This preparation scheme resulted in sharp single-domain 2×1-LEED patterns characteristic of the misoriented surfaces with well-ordered terraces separated by double-layer steps. The double-height steps were apparent from the splitting distance of the diffraction spots. From LEED experiments the single-domain quality could be estimated to be better than 90% (80%) for the 5.5° (2.5°) samples. Surface impurity levels of oxygen and carbon were below the detection limit of the retarding field Auger spectrometer.

The properties of misoriented Si(001) surfaces have been addressed by number of groups, both experimentally^{24–26} and theoretically.^{6,27,28} These studies have led to a detailed understanding of the structural parameters of the surfaces and their dependence on miscut angle and temperature. For miscut angles >2°, it is energetically favorable for the two types of single layer high *S_A*- and *S_B*-type steps to coalesce and to form double-height rebonded *D_B* steps characterized by additional threefold coordinated silicon atoms attached to the step edge with one free dangling bond each. This results in terraces having all the same silicon dimer orientation with the dimer rows oriented perpendicular to the step edge. The average terrace widths are 14.7, 5.8, and 2.5 dimers for the 2.5°, the 5.5°, and the 10° miscut angles, respectively. For a detailed description of the relaxed geometries of clean and hydrogen covered vicinal surfaces see also Ref. 15. At finite temperature some kink formation and partial local splitting of the *D_B* steps in pairs of *S_A* and *S_B* steps occurs. However, it is known from STM studies that the configuration is stable and silicon atom motion is small for the temperatures of our experiments.²⁹

C. Nonequilibrium hydrogen coverage

In order to achieve the nonequilibrium hydrogen concentration profile we make use of the different adsorption energy

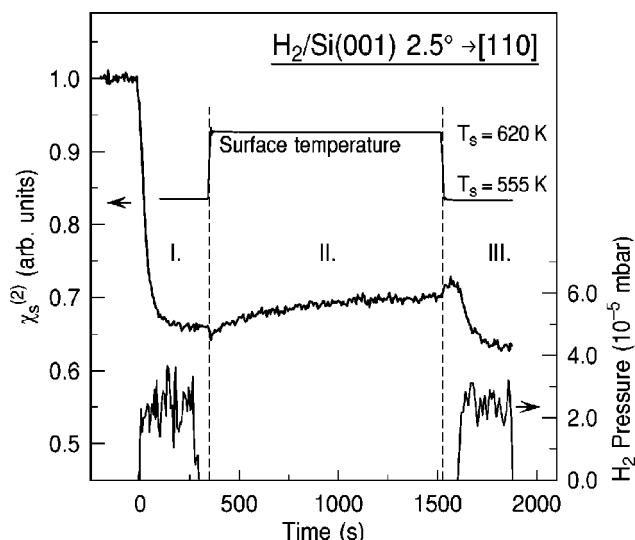


FIG. 1. Nonlinear susceptibility $\chi_s^{(2)}$, of vicinal Si(001), hydrogen pressure, and surface temperature during: I. Dissociative adsorption of molecular hydrogen at the steps until saturation for $T_s=555$ K. II. Diffusion of hydrogen onto the terraces at elevated temperature of $T_s=620$ K. III. After reaching equilibrium the temperature is quenched and hydrogen is readsorbed on the fraction of depleted step sites.

barriers of the step sites compared to the terrace dimers towards the dissociative adsorption of molecular hydrogen.⁷ The adsorption kinetics of vicinal Si(001) is addressed in detail elsewhere³⁰ and is only reviewed here to the extent required for the understanding of the present experiments: The reaction of molecular hydrogen with the stepped surface is characterized by an initial sticking coefficient as high as 10^{-4} , up to several orders of magnitude in excess of the corresponding terrace adsorption. A very weak surface temperature dependence with an apparent activation energy of only 0.09 eV was observed in contrast to 0.76 eV describing the adsorption both on the flat surface and on the terraces.

The hydrogen adsorption behavior at the steps can be seen in the first region of Fig. 1. The nonlinear susceptibility $\chi_s^{(2)}$ is monitored as a function of time during hydrogen exposure for the 2.5° misoriented Si(001) surface. The initially clean surface is kept at a temperature of 555 K and at $t=0$ the hydrogen pressure is increased to $\sim 2 \times 10^{-5}$ mbar, which leads to a signal decrease as a result of dissociatively adsorbed hydrogen. With the hydrogen coverage determined from the calibrated SH response the data can be fit satisfactorily assuming Langmuir adsorption kinetics and treating the sticking probability s_0 as the only free parameter. With a value of $\sim 10^{-4}$ the sticking coefficient of the stepped surface exceeds the corresponding value of 10^{-8} for terrace adsorption at that temperature by four orders of magnitude, therefore causing only negligible adsorption of hydrogen on the terraces.

The saturation coverage of the steps is determined with TPD to 0.07, 0.12, and 0.15 ML for the samples with miscut angles 2.5° , 5.5° , and 10° , respectively. For the monohydride configuration, the adsorbed quantity on the steps of the 2.5° and 5.5° samples are in good agreement with the theoretical saturation coverage of 1.0–0.85 times the total num-

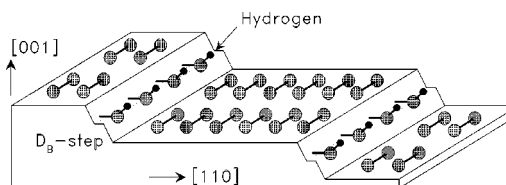


FIG. 2. Schematic representation of the vicinal Si(001) surface with atomic hydrogen saturated rebonded D_B steps. With six Si-dimer units per terrace this surface corresponds to a miscut angle of $\approx 5.5^\circ$. Note that the dimers of the real surface are buckled even at elevated temperatures (Ref. 33).

ber of step sites.³¹ Less hydrogen could be adsorbed on the 10° sample than expected from the miscut angle. This reduced number of reactive sites could be the result of faceting, which is known to occur for larger miscut angles.²⁵ However, as judged from the similar adsorption kinetics both for the steps and terrace sites of that surface compared to the 2.5° and 5.5° samples, the nature of the active sites still seems to be the same.

The surface structure resulting from our preparation is depicted schematically in Fig. 2. It consists of hydrogen in the monohydride state adsorbed at the rebonded silicon step atoms and unreacted terrace dimers.⁷

III. RESULTS AND DISCUSSION

A. Step-terrace diffusion

The surface with hydrogen-saturated steps and clean terraces in between is not in thermal equilibrium. Its free energy could be lowered by hydrogen diffusion onto the terraces due to the increase in configurational entropy. Although thermodynamically favored, the diffusion is hindered kinetically. To investigate this process the surface temperature is stepped to a value high enough to facilitate hydrogen diffusion as can be seen in region II of Fig. 1. The fast temperature rise from 555 to 620 K is followed by a continuous signal increase due to a net hydrogen transfer onto the terraces. The initial small signal decrease is a result of the temperature dependence of the nonlinear susceptibility³² and is fully reversible.

The time evolution of the nonlinear susceptibility $\chi_s^{(2)}$ for the 5.5° misoriented sample with initially hydrogen saturated steps is shown for a number of different surface temperatures in Fig. 3. The diffusion process eventually leads to an equilibrium distribution of hydrogen on the steps and terraces manifesting itself in a constant SH signal. For temperatures in excess of 650 K the onset of hydrogen desorption becomes visible leading to a continuing signal increase as seen for the data taken at 665 K. The diffusion rate, however, is sufficiently distinct from the desorption rate to allow for an independent determination.

The increase in SH intensity during the diffusion process can be related to the changes in step and terrace coverage by evaluating Eq. (1) for constant surface hydrogen coverage. In order to obtain quantitative results, the SH temperature dependence is taken into account. For the case of the 2.5° miscut sample converted data are plotted in Fig. 4 showing the step depletion until equilibrium for three different surface temperatures.

For an accurate analysis of the diffusion kinetics one would have to consider not only the rate for the initial step depletion process but also all the successive microscopic dif-

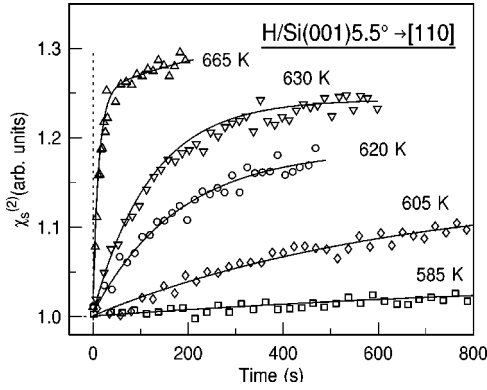


FIG. 3. Increase of the nonlinear susceptibility $\chi_s^{(2)}$ for the 5.5° sample during hydrogen diffusion from the initially saturated steps onto the terraces measured for different surface temperatures. The solid lines represent fits assuming an exponential time dependence. The continuing signal increase at $T_s = 665$ K is due to the onset of hydrogen desorption.

fusion events for a hydrogen atom after having moved onto the first terrace dimer. This would lead to an array of coupled linear differential equations and would require further assumptions about the diffusion dynamics. For the following analysis we assume that the diffusion on the terraces is fast compared to the migration from the steps. In that instance, the deviation of the step coverage from equilibrium $\Delta\theta(t) = \theta_{\text{step}}(t) - \theta_{\text{step}}(t \rightarrow \infty)$ decreases exponentially:

$$-\frac{d\Delta\theta(t)}{dt} = \Delta\theta(t)\nu_d(T) = \Delta\theta(t)\nu_0 \exp\left(-\frac{E_A}{kT_s}\right). \quad (2)$$

The first-order rate constant $\nu_d(T)$ represents the hopping rate for the thermally activated diffusion process. Its temperature dependence is expressed in terms of an activation energy E_A and a preexponential factor ν_0 . Since $\chi_s^{(2)}$ depends linearly on θ [Eq. (1)] the rate constants are determined directly from the time-dependent change of the nonlinear susceptibility.

Our method allows the determination of step depletion rates (diffusive hopping rates) from below 10^{-3} s^{-1} up to $\sim 1 \text{ s}^{-1}$. The values are summarized in Fig. 5 in the form of an Arrhenius plot. The upper temperature limit is determined by the finite heating rate. The adsorption of traces of residual

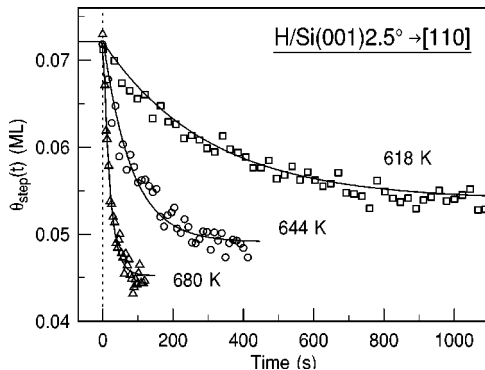


FIG. 4. Hydrogen population of the steps as a function of time obtained for the 2.5° misoriented surface. With higher temperatures one observes an increase in the rate for the step depletion and a decrease in equilibrium step coverage.

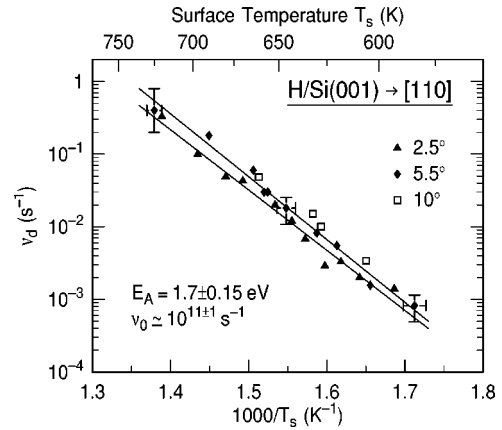


FIG. 5. Arrhenius plot of the rate constants for step depletion ν_d for the three different surface orientations investigated. The data for the 2.5° and 5.5° miscut angle correspond to an activation energy of 1.7 ± 0.15 eV.

gas on the surface can affect the diffusion process and therefore determines the lower limit. An activation energy of $E_A = 1.7 \pm 0.15$ eV and a prefactor of $\nu_0 = 10^{11 \pm 1} \text{ s}^{-1}$ is deduced for both the 2.5° and 5.5° misoriented surface. We obtained nearly identical results also for the 10° sample. The error of these values is dominated by the accuracy of the determination of the diffusion rate constants. Note that if the rapid equilibration on the terraces does not hold, the initial behavior can still be described by an equation similar to Eq. (2). Therefore, this would result only in a minor error of the activation energy since the rates change by three orders of magnitude in the temperature range investigated.

We interpret the activation energy of 1.7 ± 0.15 eV as the barrier for hydrogen atoms to migrate from the step sites onto the first dimer of the lower terrace next to the step edge. Experimentally, we cannot exclude diffusion onto the upper terrace. However, the theoretical value for the hydrogen chemisorption energy on the first dimer of the upper terrace is considerably lower than that of the lower terrace.¹⁵ Diffusion onto the upper terrace is thus likely to be associated with a larger barrier than diffusion onto the lower terrace.

Two cases have to be considered concerning the relationship of the observed barrier height with respect to the corresponding diffusion barrier on the terraces. First, a barrier for the terrace diffusion significantly in excess of 1.7 eV would result in a preferred population of the terrace sites in the vicinity of the step edge. This would lead to significantly different diffusion rates and step populations in successive diffusion cycles, which is in contrast to the experimental observations as described below. Thus a barrier for terrace diffusion equivalent to, or smaller than the 1.7 eV is likely. For an activation energy for step depletion slightly smaller as the one for terrace diffusion one would have a direct measure of the barrier for the terrace diffusion. The difference, however, must not exceed a few tenths of an eV, because otherwise a selective step saturation at $T_s = 550$ K, as observed experimentally, would not be possible. This conclusion agrees with the results of recent STM experiments that observed the hopping of single hydrogen atoms along the dimer rows of $\text{Si}(001)2 \times 1^9$ and deduced an activation barrier of 1.68 ± 0.15 eV.

The value for the diffusion barrier of 1.7 eV corresponds

to roughly half of the Si-H binding energy and 2/3 of the activation energy for desorption for Si(001).^{34–36} Such a large lateral corrugation is not special for diffusion at step sites. It is rather a consequence of the localized nature of the covalent Si-H bond and has not only been observed for hydrogen diffusion on flat Si(001)2×1 surfaces,^{9,37,38} but also in the case of the Si(111)7×7 surface.^{39,40} Theoretical investigations suggest that the diffusive motion of hydrogen on the terraces of silicon surfaces is accompanied by substantial distortion of the silicon atoms from their equilibrium positions.^{11,41,42} Since the distance from the adsorption site at the step to the nearest site on the lower terrace is smaller than to the nearest site on the upper terrace, diffusion to the latter is likely to involve more lattice distortion. This is a further argument supporting our belief that the diffusion barrier from the step to the lower terrace is associated with the smaller barrier and thus observed in our experiment.

B. Step-terrace equilibrium

The equilibrium hydrogen population of the steps and terraces can in principle be estimated from the coverage-converted SH data as shown in Fig. 4. However, due to the small temperature dependence of the SH signal and a possible phase shift between the different contributions to $\chi_s^{(2)}$, a more direct procedure, namely, titration of the emptied step sites, was applied for a precise determination. This is illustrated in region III of Fig. 1, where in a first step the sample temperature is quenched quickly to the initial value of 555 K after reaching the hydrogen adlayer equilibrium as indicated by a constant SH response. Since the surface temperature is decreased at a much higher rate than the diffusion rate, hydrogen motion is essentially frozen and the distribution corresponding to the higher temperature is preserved. It was verified with TPD that the total hydrogen coverage stayed constant during that procedure.

In the second step the surface is again exposed to molecular hydrogen. As indicated by the fast signal decrease, the partially depleted steps then readsorb hydrogen. The corresponding hydrogen uptake $\Delta\theta$ at the steps can be deduced from the calibrated SH response, and again has been verified by additional TPD experiments. TPD traces for the 5.5° misoriented surface are shown in Fig. 6 both from a solely step-saturated surface and from a surface on which hydrogen was readsorbed at the partially depleted step sites. The amount of hydrogen which has diffused onto the terraces is thus the areal difference between these two traces. Absolute values are obtained comparing the integrated peak areas with that of the fully monohydride terminated surface prepared by dosing atomic hydrogen created at a hot tungsten filament. These TPD results confirm the coverages determined from the calibrated SH response.

The reversibility of the diffusion process could be shown by slowly decreasing the surface temperature after the hydrogen coverage has reached equilibrium. This leads to a partial net back-migration of hydrogen towards the steps, which manifests itself in a reduced amount of hydrogen which could be readsorbed at the steps compared to the experiments when the sample temperature is quenched rapidly.

In Table I the equilibrium hydrogen distributions are summarized for various diffusion temperatures. θ_{step}^0 denotes the

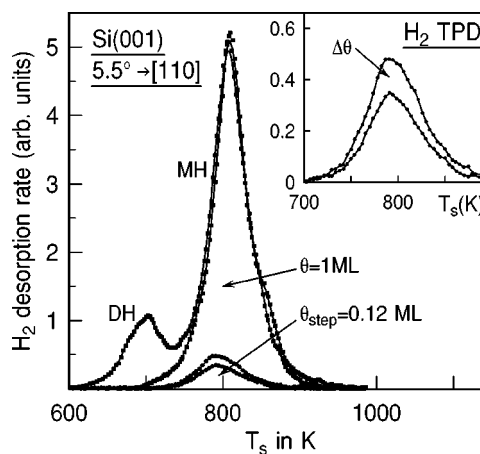


FIG. 6. Thermal desorption traces (heating rate ~ 3 K/s) of the step saturated 5.5°→[110] surface. Magnified in the inset are the data taken right after saturation of the steps of the initially clean sample (lower curve) and data taken after filling the depleted step sites after an equilibration experiment at $T_s=656$ K (upper curve). For comparison traces of the fully monohydride (MH) and partially dihydride (DH) covered surface are shown.

amount of hydrogen adsorbed at the steps prior to the diffusion experiment. The hydrogen uptake $\Delta\theta$ at the steps after the diffusion experiment can be identified with the amount of hydrogen that has diffused onto the terraces.

The equilibrium occupation of the step and terrace sites is determined by the minimum of the surface free energy. This is given by the energy difference between the different adsorption sites on the one hand, and the entropy gained by distributing the hydrogen atoms over the terraces on the other. With average terrace widths of 14.7, 5.8, and 2.5 silicon dimers for the 2.5°, 5.5°, and 10° misoriented surfaces, respectively, one observes a preferential occupation of the step sites with hydrogen compared to a random distribution. This together with the shift of the equilibrium distribution towards the terraces with increasing temperature indicates a higher binding energy for hydrogen at the steps.

In the following analysis we restrict ourselves to an estimate of this energy difference between the step- and terrace sites. A more detailed analysis and interpretation will be

TABLE I. Results for the equilibrium hydrogen distribution for various temperatures for the three surface misorientations investigated. ΔE_H^* is the effective energy difference with respect to single hydrogen atoms between the steps and terraces calculated using the simplified model described in the text. $\Delta E_{H_2}^{\text{chem}}$ is the difference in chemisorption energy for two hydrogen atoms as derived from the data employing Eq. (6).

α	θ_{step}^0	T_{dif} (K)	$\Delta\theta$	ΔE_H^* (eV)	$\Delta E_{H_2}^{\text{chem}}$ (eV)
2.5°	0.074	618	0.017	0.28	0.24
	0.068	636	0.021	0.25	0.22
	0.072	643	0.023	0.24	0.21
	0.070	644	0.021	0.26	0.22
	0.072	680	0.026	0.24	0.22
5.5°	0.115	656	0.038	0.22	0.15
10°	0.14	628	0.016	(0.32–0.35)	(0.18–0.23)

given by Pehlke and Kratzer who compare our experimental results with their calculated chemisorption energies for hydrogen adsorbed on different sites of vicinal Si(001) surfaces obtained from density-functional theory.¹⁵

In a simplified model, we assume for the moment that the silicon dangling bond sites both at the steps and on the terraces are independent from each other, i.e., the adsorption of a hydrogen atom on any one site does not affect the binding energy at neighboring Si atoms. This of course is a very crude assumption since it is known that the dangling bonds on the dimers of the terraces are characterized by a π -like bonding with an interaction energy of ~ 0.25 eV.³⁵ This leads to preferential pairing of two hydrogen atoms on the same dimer. Furthermore, we assume that the diffusive hydrogen motion across the surface is not restricted by the steps. The consequences of both intradimer interactions and a limited diffusion phase space on the derived value of the binding energy will be discussed below.

In thermal equilibrium the rates for the step to terrace and terrace to step diffusion are equal and one can write

$$\frac{n_{\text{terr}}(1-n_{\text{step}})}{n_{\text{step}}(1-n_{\text{terr}})} = \exp\left(\frac{-\Delta E_{\text{H}}^*}{kT_s}\right). \quad (3)$$

In this equation n_{terr} and n_{step} are the relative coverages for the specific adsorption sites expressed in terms of the observable coverages by the relationships

$$n_{\text{terr}} = \Delta\theta / (1 - \theta_{\text{step}}^0), \quad (4)$$

$$n_{\text{step}} = (\theta_{\text{step}}^0 - \Delta\theta) / \theta_{\text{step}}^0. \quad (5)$$

ΔE_{H}^* denotes the effective binding energy difference of a hydrogen atom between step and terrace sites. In the case of independent adsorption sites this is simply given by $\Delta E_{\text{H}}^* = E_{\text{terr}}^{\text{Si-H}} - E_{\text{step}}^{\text{Si-H}}$.

The resulting energies as derived from the equilibrium hydrogen distributions are summarized in Table I. Similar values are found for the different experiments for the 2.5° and 5.5° misorientations investigated with an average of $\Delta E_{\text{H}}^* \approx 0.25 \pm 0.05$ eV. The error is dominated by the accuracy of the absolute coverage determination and the uncertainty in miscut angle. The difference between the measured hydrogen saturation coverage and the nominal number of dangling bonds at the step edge renders the interpretation of the 10° misoriented sample difficult. We thus refer only to the results of the 2.5° and 5.5° miscut angles in the following discussion.

The estimate above is based on the assumption that the hydrogen atoms are distributed evenly across the terraces. Although we have no direct evidence, the following experiment can rule out that the hydrogen atoms having left the step sites preferentially populate the terrace dimers right next to the step edge. Here the cycle of diffusion and successively readsorbing hydrogen is repeated right after a first treatment has been performed. Within the accuracy of the experiment nearly the same diffusion rate is observed for the step depletion process. The higher initial terrace population prior to the second cycle reduces the entropy gain on the terrace and the equilibrium is shifted towards a higher relative step population. Therefore slightly less hydrogen can be readsorbed on the step edge.

The above model used to estimate the energy difference did not include the interaction energy between the silicon dangling bonds or restrictions in the free two-dimensional motion of the hydrogen atoms. The value of $\Delta E_{\text{H}}^* = 0.25$ eV should therefore be regarded as an upper limit of the binding energy difference between the step and terrace site and be viewed in terms of an effective energy difference.

The interaction energy between the dangling bonds within a single dimer leads to a preferred pairing of the hydrogen atoms on the dimers. This constraint results in a reduced entropy gain for the hydrogen atoms on the terrace. Therefore in order to explain the experimentally observed distribution between the step and terrace sites a reduced binding energy difference would be sufficient. Including the effect of the pairing energy of ~ 0.25 eV in our simple kinetic model, a value of $\Delta E_{\text{H}}^* = 0.16$ – 0.18 eV for the binding energy difference is obtained. The contributions of the pairing energy are therefore quite substantial, which can be made plausible with the following estimate. With the pairing energy of 0.25 eV, the fraction of hydrogen atoms that are paired on the terrace dimers can be calculated to 50–60 % for hydrogen coverages between 0.02 and 0.04 ML.³⁵ This leads to an average contribution of ~ 0.06 – 0.08 eV per hydrogen atom to the effective energy difference.

To account for both the influence of the pairing energy on the terraces and restrictions of the two-dimensional hydrogen motion, we employ a model Hamiltonian similar to the one described by Pehlke and Kratzer¹⁵:

$$H^{(D_B)} = -\frac{1}{2}(n_0^A + n_0^B)\Delta E_{\text{H}_2}^{\text{chem}} + \sum_{i=1}^N \left\{ \frac{1}{2} [n_i^A(1-n_i^B) + n_i^B(1-n_i^A)] \epsilon_{\text{pair}} \right\}. \quad (6)$$

Assuming that all terrace sites have the same hydrogen chemisorption energies, $\Delta E_{\text{H}_2}^{\text{chem}}$ describes the chemisorption energy difference between two hydrogen atoms adsorbed either at the step edge (index $i=0$) or the terrace dimers ($i=1 \dots N$). n_i^A and n_i^B denote the occupation numbers (0 or 1) of the silicon atoms A and B of the i th dimer. On the basis of recent experimental^{9,38} and theoretical results^{41–43} we assume that both interrow diffusion and hopping across the steps is negligible. With the hydrogen motion therefore restricted to single dimer rows of length N , the expectation values $\langle n_i^A \rangle = \langle n_i^B \rangle$ which relate to the measured relative coverages as $\langle n_0 \rangle = n_{\text{step}}$ and $\langle n_i^{i \geq 1} \rangle = n_{\text{terr}}$ are calculated within the canonical ensemble from the partition function.

With the pairing energy for the terrace dimers of $\epsilon_{\text{pair}} = 0.25$ eV, the resulting values for the chemisorption energy differences are shown in the last column of Table I. The error caused by experimental uncertainties in the determination of θ_{step}^0 and $\Delta\theta$ are ± 0.03 eV and ± 0.05 eV for the samples with 5.5° and 2.5° miscut, respectively. The average values for $\Delta E_{\text{H}_2}^{\text{chem}}$ of 0.15 eV and 0.22 eV thus agree within their experimental error bar. We also note that the theoretical chemisorption energy difference between a step site and a typical adsorption site in the middle of the Si(001) terraces of ~ 0.17 eV (Ref. 15) falls well within the range of experimental values of 0.15–0.22 eV. For a detailed comparison

between the experimental and theoretical results the reader is referred to the paper of Pehlke and Kratzer.¹⁵

IV. CONCLUSION

Intrinsic chemical properties of vicinal Si(001) surfaces allow for the formation of a periodic nonequilibrium hydrogen concentration profile. We take advantage of the different adsorption energy barriers of the step compared to the terrace sites towards the dissociative adsorption of molecular hydrogen to selectively saturate the steps. Monitoring the transition to thermal equilibrium of the surface hydrogen coverage an activation barrier for the step to terrace diffusion of 1.7 ± 0.15 eV was determined. From the equilibrium hydrogen occupation the steps are found to be energetically favored. The effective energy difference between step and terrace

sites amounts to ~ 0.25 eV. If both the hydrogen pairing energy of the silicon dimers on the terraces and restrictions in the free two-dimensional motion are taken into account, a chemisorption energy difference of ~ 0.2 eV per H₂ molecule between the step and terrace sites is derived. The preferred binding of the hydrogen atoms to the rebonded silicon step-edge atoms is in accordance with density functional calculations of Pehlke and Kratzer.¹⁵

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