

Real-space investigation of high-barrier hydrogen diffusion across the dimer rows of Si(001)C. H. Schwalb,¹ M. Dürr,^{1,2} and U. Höfer¹¹Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, D-35032 Marburg, Germany²Fakultät Angewandte Naturwissenschaften, Hochschule Esslingen, D-73728 Esslingen, Germany

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Hydrogen diffusion on Si(001) has been investigated on the atomic scale by means of a combination of laser-induced thermal heating and scanning tunneling microscopy. In addition to the well known diffusion path along the dimer rows, hydrogen diffusion across the rows was observed. At a surface temperature of 1385 K, the hopping rate of this high-barrier interrow diffusion pathway is $5.6 \times 10^7 \text{ s}^{-1}$ comparable to the intrarow hopping rate of $1.3 \times 10^8 \text{ s}^{-1}$. Thus, diffusion of hydrogen on Si(001), which is strongly anisotropic below 700 K, becomes almost isotropic at high temperatures.

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I. INTRODUCTION

Surface diffusion of atomic hydrogen is an essential step in the gas-source growth of silicon.¹ Moreover, hydrogen diffusion on silicon serves as a model system for the microscopic understanding of adsorbate diffusion on semiconductor surfaces in general.^{2–13} Under usual conditions, hydrogen diffuses by thermally activated hopping between silicon dangling bonds. In the case of the Si(001) surface, diffusion of hydrogen is expected to proceed along three different pathways (Fig. 1): (a) hopping between the two dangling bonds of one dimer (intradimer), (b) along one dimer row (intrarow), and (c) across the rows (interrow). *Ab initio* calculations predict that the diffusion barriers of these three pathways are correlated with the hopping distance of hydrogen and increase from (a) to (c).^{5–8} Experimentally, both intradimer (a) and intrarow diffusion (b) have been investigated in detail with scanning tunneling microscopy (STM) (Refs. 9–11); the deduced diffusion barriers are 1.0 eV and 1.75 eV, respectively.¹¹ In contrast, interrow diffusion (c) has not been observed and the theoretical values for the corresponding barrier are substantially higher than those calculated for intrarow diffusion.^{5–8} For that reason one might expect that the interrow pathway (c) does not play any significant role in hydrogen diffusion on Si(001). As a consequence, diffusion in a direction perpendicular to the dimer rows would be strongly suppressed on a perfect Si(001) sample and the establishment of full diffusion equilibrium would require the presence of steps and differently oriented terraces.¹³

In this work, we show that this expectation is not correct. Interrow diffusion, in fact, contributes substantially to hydrogen mobility on Si(001) at elevated surface temperatures, i.e., the technologically more relevant temperature regime.^{1,14} Whereas previous STM studies were restricted to temperatures below 700 K and hopping rates of less than 10^2 s^{-1} , the combination of laser-induced thermal heating and STM allows us to explore a completely different regime. By heating the surface to temperatures as high as 1400 K within a few nanoseconds, we are able to quantify diffusion rates as high as 10^8 s^{-1} with atomic precision. Surprisingly, the hopping rates for intrarow and interrow diffusion are found to be comparable under these conditions. These find-

ings are traced back to a pronounced influence of lattice distortions on adsorbate diffusion for this high-barrier pathway.

Furthermore, the results are compared to calculations for the energy barrier of the interrow pathway.^{5–8} They cover a large energy range from 1.8 to 3.1 eV leading to interrow diffusion rates that differ by several orders of magnitude even at high surface temperatures. Comparison with our experimental result at $T_S \approx 1400 \text{ K}$ clearly indicates that only a midrange energy barrier, e.g., as calculated by Hansen and Vogl,⁸ can provide satisfactory agreement between calculated and measured interrow diffusion rates.

II. EXPERIMENT AND RESULTS

The experiments were performed with a commercial STM (OMICRON VT-STM) in an ultrahigh vacuum chamber (base pressure $< 5 \times 10^{-11} \text{ mbar}$). The experimental procedure for the observation of hydrogen diffusion on Si by means of laser-induced thermal heating and STM was described in more detail recently.¹⁵ In short, we start with a monohydride covered Si(001) surface and hydrogen desorption from this surface was initiated by heating the surface with a single laser pulse from the frequency doubled output of a Nd:YAG (yttrium aluminum garnet) laser ($\lambda = 532 \text{ nm}$,

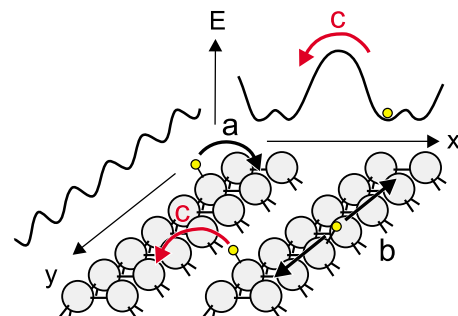


FIG. 1. (Color online) Ball-and-stick model of the expected situation on Si(001). Hydrogen (small balls) can diffuse from one to another Si atom (large balls) on one dimer (a), along the dimers of a dimer row (b), and between the dimer rows (c). The latter process is depicted with a red (gray) arrow and the highest diffusion barrier is attributed to this pathway as shown in the sketch of the potential energy surface.

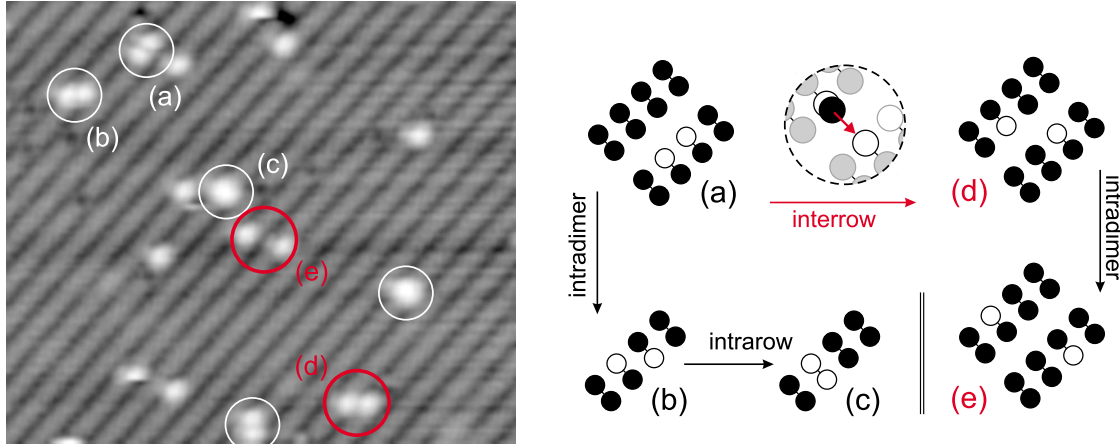


FIG. 2. (Color online) Left: STM image ($15 \times 13 \text{ nm}^2$, $U_{\text{gap}} = -2.1 \text{ V}$, $I_{\text{tun}} = 0.8 \text{ nA}$) of a Si(001) surface after saturation with one monolayer of H atoms and subsequent laser-induced thermal heating. Different dbs configurations are observed: labeled with white circles are configurations of two dbs restricted to one dimer row. Interrow diffusion leads to configurations labeled with red (gray) circles. The sketch on the right illustrates the different configurations with black disks (H-saturated Si atoms) and white disks (dbs) as well as how hydrogen diffusion changes these configurations. For details, see main text.

pulse duration 9 ns) that was focused on the silicon sample with a spot diameter of $\sim 500 \mu\text{m}$. Recombinative desorption takes place from two neighbored Si dimers^{16,17} and the created configuration consists of two dangling bond states (dbs) on two neighbored silicon dimers as sketched in Fig. 2 [labeled (a)]. Hydrogen diffusion may lead to a reorganization during the time left of the primary pulse or during a subsequent heating pulse. Effective cooling of the silicon surface due to thermal diffusion into the bulk^{15,18,19} in combination with the exponential dependence of both desorption and diffusion rate on surface temperature restricts the time window for these processes during one laser pulse to about 3–4 ns.^{15,16} The configurations of dbs are then investigated at room temperature by means of STM as shown in Fig. 2. Especially, the different configurations of pairs of dangling bonds were counted in a total area of 10^4 nm^2 . They are classified by the number and sort of diffusion processes which contributed to the generation of these configurations. From the total amount of desorbed hydrogen, we calculate the desorption temperature using the known temperature dependence for the desorption process.^{15,20}

The three main types of paired dbs configurations are shown and labeled in Fig. 2. The majority of dbs pairs are found to sit on two neighbored dimers, i.e., with a separation along the dimer row of the width of one dimer unit [labeled (a) in Fig. 2]. Diffusion of hydrogen on one dimer is assumed to be fast and does not change the projected separation of dbs along the dimer rows; the resulting configuration is labeled (b) in Fig. 2. Diffusion along the dimer row leads both to configurations with two dbs on one dimer [labeled (c) in Fig. 2, no separation along the dimer row] and to configurations with the dbs separated by one or two additional dimers, i.e., with a total distance of two or three dimer units (not shown). Additionally, pairs of dbs are observed on dimers of two neighbored dimer rows, the majority again with a separation of one dimer unit along the dimer rows [labeled (d) and (e) in Fig. 2]. They are attributed to diffusion of a hydrogen atom across the dimer rows. Furthermore, we

registered single dbs, i.e., with no second dbs in close vicinity. These configurations were attributed to single hydrogen atoms that diffuse from the surface into the silicon bulk, therefore creating single dbs at the surface.^{15,16,21} Although this process is expected to possess a high activation barrier,²² diffusion of single hydrogen atoms into the bulk might be realized due to the high temperature of our experiment. Regardless the physical origin of these single dbs, we have carefully checked that they are statistically distributed over the surface and thus are likely to contribute in a statistical manner to the configurations of paired dbs as well. To account for this contribution to the number of paired dbs, we simulated a statistical distribution of single dbs in an image size that was comparable to our experiment. The resulting statistical number of different pairs of dbs was counted in these simulated images and the respective experimental number of distributions has been corrected accordingly. As a result, we obtain distributions of pairs of dbs as shown in Fig. 3 for the situation after one laser pulse. The efficiency of the interrow diffusion pathway is readily observed by the relative weight of the configurations created by interrow and intrarow diffusion. E.g., the number of configurations after interrow diffusion almost equals the number of configurations with dbs separated by an additional dimer, i.e., after one intrarow diffusion hop away from the initial configuration, thus pointing toward similar diffusion rates for both processes.

To quantitatively evaluate the diffusion rates, Monte Carlo simulations were conducted. The procedure was similar to the one described in Ref. 15: over the effective time span of one laser shot, hydrogen is continuously desorbed from the monohydride surface via the two-dimer desorption channel up to the experimentally observed density of dangling bond pairs. The subsequent diffusion processes are modeled by introducing hopping probabilities for the intradimer, intrarow, and interrow diffusion pathway. To account for the influence of the exact local configurations, i.e., the pairing energies ϵ for two H atoms on one dimer and ω

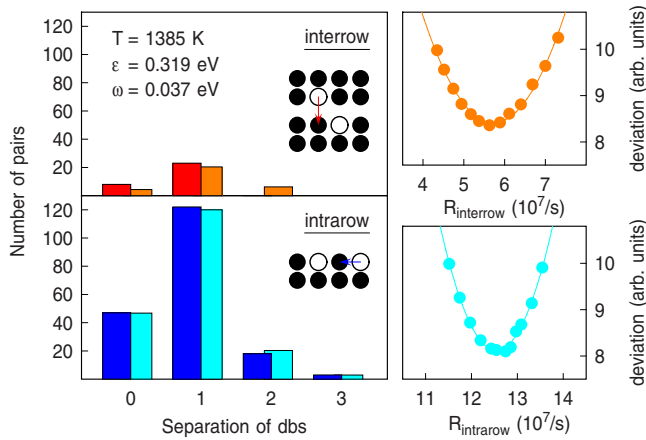


FIG. 3. (Color online) Left: distribution of pairs of dbs as obtained after one laser pulse. Experimental results are shown in dark blue and red (dark gray); results of optimized Monte Carlo simulations are shown in light blue and red (light gray). Right: calculated standard deviation between experimental and simulated distribution for different values of the diffusion rates. The solid lines are best quadratic fits to the data points; the minimum determines the respective diffusion rate.

for four H atoms on two neighbored dimers, the rates are adjusted according to the respective change in the diffusion barrier. E.g., diffusion from a two-dimer (two H atoms on two neighbored dimers) to a one-dimer (two H atoms on the same dimer) configuration results in an energy gain of about 0.3 eV (Refs. 23–26) and the lowering of the according diffusion barriers is approximated by half of this value.

In a first run we kept the values for diffusion on one dimer row fixed to the values used in Ref. 15 and varied only the newly introduced interrow diffusion rate. Already with such restricted boundary conditions, we achieved very good agreement between the experiment and the results of the simulation. The agreement was further improved when we allowed for a slight change in the intrarow diffusion rate which might be attributed to, e.g., a slightly different temporal laser profile of the lasers used in the two experiments. In Fig. 3, the optimization procedure is shown for R_{interrow} and R_{intrarow} (right panels) and the optimized result for the distribution after one shot is compared to the experimental distribution (left panel). From the number of performed hopping events in the simulations we calculate diffusion rates of $5.6 \times 10^7 \text{ s}^{-1}$ and $1.3 \times 10^8 \text{ s}^{-1}$ for interrow and intrarow diffusion, respectively. The same ratio between the two hopping rates was obtained when we applied the simulations to a set of data obtained after two subsequent laser shots with similar temperature distribution during the single heating cycles.

All the experiments were performed in the high coverage regime. This leads to an increased intrarow diffusion rate when compared to the low-coverage regime since the increased hopping probability from a two-dimer into a one-dimer configuration overcompensates a reduction in the hopping rate caused by blocking of potential diffusion sites. On the other hand, for our starting configuration with two dbs on two neighbored dimers, interrow diffusion is almost unaffected by these high coverage effects. As a consequence, the diffusion rates along the dimer rows and across the dimer

rows are even closer in the low-coverage regime, with $R_{\text{intrarow}} = 1.1 \times 10^8 \text{ s}^{-1}$ being only twice the value of $R_{\text{interrow}} = 5.6 \times 10^7 \text{ s}^{-1}$.

III. DISCUSSION

To discuss our surprising experimental result we first compare it with theoretical studies of hydrogen diffusion on Si(001) before considering its possible origin and implication for silicon processing at high temperatures. This comparison is difficult because on the one hand—with the notable exception of the work by Wu *et al.*⁶—theoretical values are only available for diffusion barriers but not for prefactors.^{5,7,8} Therefore, it is not possible to compare the calculations directly with the measured diffusion rates. On the other hand, the temperature range in which the combination of laser heating and STM can observe diffusion is presently limited to about 100 K,¹⁵ which is not enough to deduce activation energies with sufficient accuracy. However, experimental investigations of intrarow diffusion of H/Si(001) and diffusion of H/Si(111) at lower temperature have reported prefactors between 10^{12} s^{-1} and 10^{16} s^{-1} .^{2,4,11} Especially for intrarow diffusion on Si(001), Hill *et al.* report a prefactor of $A = 10^{14.5} \text{ s}^{-1}$.¹¹ Taking into account that interrow diffusion directly relates to the stretching mode of the H-Si vibration, while diffusion along the row is related to the bending modes, which are lower in frequency, a somewhat higher prefactor between $A = 10^{15} \text{ s}^{-1}$ and $A = 10^{16} \text{ s}^{-1}$ for the high-barrier interrow diffusion pathway seems to be a reasonable choice.⁶ For the comparison of the theoretical data depicted in Fig. 4 we have therefore set the prefactor to $A = 3 \times 10^{15} \text{ s}^{-1}$.

Figure 4 clearly indicates that the results of Wu *et al.*⁶ and Nachtigall *et al.*⁷ with relatively high barriers cannot reproduce our experimental data, even if one allows for even higher prefactors. On the other hand, the results by Vittadini *et al.*⁵ could match our high-temperature data with a reduced prefactor; however, the predicted low diffusion barrier is incompatible with the low-temperature data of Hill *et al.*¹¹ if we assume that the interrow diffusion pathway would have been observed in these experiments in case the rate was higher than a twentieth of the intrarow diffusion rate, i.e., 0.2 s^{-1} . Taking into account this upper limit for interrow diffusion at low temperatures, our experimental results for the diffusion rate at high temperatures actually set the lower limit for both the prefactor and diffusion barrier to 10^{15} s^{-1} and 2.0 eV, respectively. As a consequence, only the calculations of Hansen and Vogl with a medium diffusion barrier of $E_{\text{interrow}} = 2.4 \text{ eV}$ (Ref. 8) match both criteria, i.e., reasonable agreement with our result and a low enough diffusion rate at $T_s = 630 \text{ K}$. Both a somewhat higher prefactor and a lower diffusion barrier would still be in agreement with the experimentally determined diffusion rates; e.g., $E_{\text{interrow}} = 2.2 \text{ eV}$ and $A = 10^{16} \text{ s}^{-1}$ perfectly match our result and are well compatible with the low-temperature data.

According to the present experiment, the rate for interrow diffusion approaches that for intrarow diffusion at high temperatures although the distance between the involved hydrogen adsorption sites is considerably larger in case of the in-

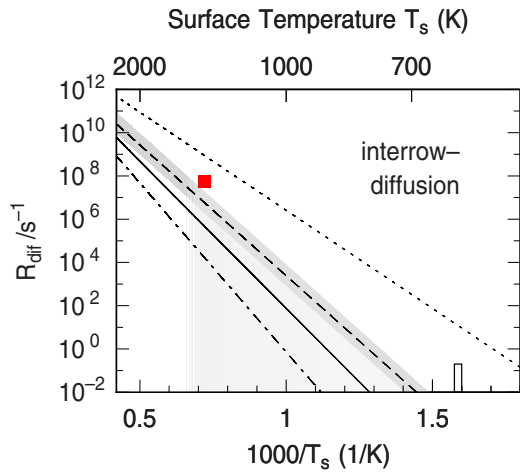


FIG. 4. (Color online) Arrhenius plot of interrow diffusion rates as obtained by various theoretical studies. Dot-dashed line: Ref. 7, $E_{\text{interrow}}=3.1$ eV; straight line: Ref. 6, $E_{\text{interrow}}=2.7$ eV; dashed line: Ref. 8, $E_{\text{interrow}}=2.4$ eV; dotted line: Ref. 5, $E_{\text{interrow}}=1.8$ eV. Prefactor $A=3 \times 10^{15} \text{ s}^{-1}$ for all data shown, the gray band around the data of Ref. 8 represents diffusion rates which fulfill $E_{\text{interrow}}=2.4$ eV and $10^{15} \text{ s}^{-1} \leq A \leq 10^{16} \text{ s}^{-1}$. The experimental value at high temperature is shown as a square; the white bar depicts the range of values which are in accordance with low-temperature results if one assumes that the interrow pathway would have been observed in these experiments in case the rate was higher than a twentieth of the intrarow diffusion (Ref. 11).

terrow pathway (the underlying Si atoms are separated by 5.3 Å compared to 3.8 Å for intrarow diffusion). An important effect for a qualitative understanding of this result is therefore the movement of the silicon lattice during the diffusion process. As was first pointed out by Vittadini *et al.*,⁵ surface relaxation in the transition state can lead to drastically reduced diffusion barriers. Both, their work and that of Hansen and Vogl,⁸ clearly show that this reduction is strongest in case of the interdimer pathway (0.8–1.1 eV compared to 0.5–0.7 eV for intradimer diffusion). This pronounced reduction becomes plausible if one considers that the large distance for interrow hopping is a consequence of the dimer reconstruction of the Si(001) surface. The dimerization is partly reversed in the transition state of interrow diffusion as the Si dimer bond is weakened and the two H adsorption

sites move toward each other.⁵ Consequently, this process is expected to cost comparably little energy and efficiently promotes interrow diffusion. A similar effect is important for hydrogen diffusion on Si(111)7×7. On this surface, hydrogen has to overcome a distance of 5.2 Å when hopping from an adatom to a rest atom site. Nevertheless, measured diffusion barriers are lower than 2.0 eV.^{2,4} According to theory, one of the adatom backbonds is strongly weakened in the transition state for this diffusive motion and bending the Si adatom brings it closer to the rest atom.³

Our observation of the interrow diffusion being as fast as half times the intrarow diffusion means that even for a strongly anisotropic surface reconstruction, like that of Si(001), diffusion gets almost isotropic at elevated temperatures. This is of special technological relevance since crystal growth on Si(001) via chemical vapor deposition typically proceeds at temperatures comparable to that of our experiment.¹⁴ As a consequence, during the growth process thermodynamic equilibrium can be rapidly established on each single domain without the need for the adsorbates to cross the domain boundaries.¹³ Within the classical picture of anisotropic diffusion along the dimer rows, such rapid equilibration on the domains would have been strongly suppressed.

IV. CONCLUSION

In summary, by combining nanosecond laser heating with scanning tunneling microscopy, we have investigated hopping of atomic hydrogen across the dimer rows of Si(001). At surface temperatures around 1400 K, this diffusion pathway, which has not been observed for temperatures below 700 K in previous STM studies, becomes comparable in rate with diffusion along the rows. This unexpected result is interpreted in terms of an efficient substrate reorganization in the transition state. Similar mechanisms of lattice distortion should be operative on other semiconductor surfaces as well, leading to a comparable softening of surface anisotropy with respect to diffusion barriers.

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