

Diffusion of hydrogen on the Si(001) surface investigated by STM atom tracking

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The scanning tunneling microscopy atom-tracking technique is used to follow the individual diffusive hops of single H and D atoms on the Si(001) surface in ultrahigh vacuum. Attempt frequencies and activation energies for diffusion along the dimer row (intrarow) and between the atoms of a single Si dimer (intradimer) are extracted. For intrarow H diffusion, an activation energy of 1.75 ± 0.10 eV and an attempt frequency of $10^{14.5 \pm 0.8}$ Hz are found. For intradimer H diffusion, an activation energy of 1.01 ± 0.05 eV and a low attempt frequency of $10^{10.3 \pm 0.5}$ Hz are found. The ratios of H to D attempt frequencies for intradimer and intrarow diffusion are also determined. [S0163-1829(99)10247-9]

I. INTRODUCTION

The Si(001) surface is of great significance in the semiconductor industry and has been the subject of extensive theoretical and experimental investigations. From a fundamental perspective, H atoms on the Si(001) surface provide a complex model surface dynamics system, with three distinct diffusive channels and three different high-coverage surface reconstructions.^{1,2} The dynamics of H on Si(001) are also of interest as they pertain to chemical vapor deposition (CVD) and nanolithographic processes. Hydrogen passivation of the Si(001) surface is a detriment to CVD processes in which H clogs growth sites. For nanolithography, this passivation and the ability to locally remove H makes it a good atomic resist.³ For these reasons, H on the Si(001) surface has been the subject of numerous investigations.¹⁻¹⁵

The theoretical work has generally focused on the simplest case, that of a single H atom diffusing on a bare surface. For this, three diffusive channels and their activation energies and attempt frequencies have been studied. The two lower energy channels, intradimer and intrarow, are indicated in Fig. 1.¹⁶ While there is general agreement on the ordering of the energetic barriers, predicted values differ by as much as 1 eV.

In spite of the theoretical effort and disagreement, there has been only one quantitative experimental study of H diffusion along one of the channels.¹⁰ Bowler *et al.* used conventional scanning tunneling microscopy (STM) techniques to determine the intrarow diffusion rate as a function of temperature. However, the range of rates was limited by the time resolution of conventional STM.

In this work, the STM atom-tracking technique is used in its first single atom application.^{17,18} Atom tracking extends the range of diffusion rates that can be measured by STM and thereby allows a more accurate determination of attempt frequencies and activation energies. Hydrogen and deuterium diffusion are investigated along the two channels indicated in Fig. 1, intrarow and intradimer. Results are compared to theoretical predictions, the previous experimental work, and vibrational spectroscopy results.

II. EXPERIMENT

The experiment was performed with custom built variable temperature STM's in ultrahigh vacuum with base pressure

below 1×10^{-10} torr. Samples are prepared by degassing and then briefly flashing to 1250 °C.¹⁹ This yields a clean surface displaying the (2×1) dimer row reconstruction with a minimum of defects. The samples are then transferred to the STM stage. Hydrogen or deuterium adatoms are produced by dosing the surface with high purity water (H_2O) or heavy water (D_2O) vapor. The surface is then heated above 500 K in order to decompose the water.²⁰ Alternatively, samples are exposed to H which is produced by cracking H_2 with a hot tungsten filament.²¹ For elevated temperature investigations, the sample is resistively heated and allowed to equilibrate between 2 and 12 h. Sample temperatures are measured with a heated thermocouple and an optical pyrometer as has been described elsewhere.¹⁷ The thermocouple calibration was found to be correct within 2 K before and after the experiment.

For D investigations, an initial population of H is tracked before the sample is dosed with D. After dosing, D and H are alternately tracked. Since D and H produce identical STM features, the two species are distinguished by their diffusion rates. The rate measurements agreeing with the predose value are identified with H and the others are identified with D. For the D studies, the H rate measurements are used to determine the sample temperature.

Constant current images are acquired with the bias voltage between -1.2 and $+1.2$ V and with a tunneling current

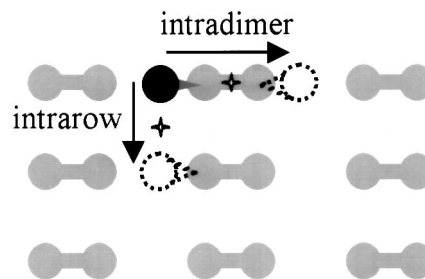


FIG. 1. Two diffusive modes for H on bare Si(001): intradimer and intrarow diffusion. The dumbbells represent silicon surface atoms paired as dimers, the black ball represents a hydrogen atom at a potential minimum/bonding site, the dotted balls represent sites to which the hydrogen can diffuse, and the stars represent the potential saddle points crossed in diffusion.

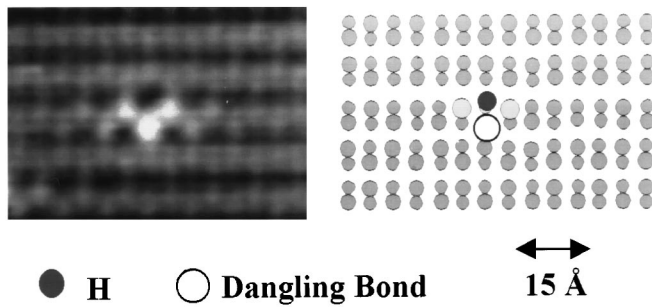


FIG. 2. STM image and schematic of H on the Si(001)- 2×1 surface at room temperature. The dimer rows run horizontally. The bright spot is a Si dangling bond produced by H adsorption. It is flanked by frozen-in buckled dimers along the dimer row. Bias = -1.5 V.

setpoint between 0.02 and 0.1 nA. Since H adsorption breaks the Si dimer's π bond in order to bond to a single Si atom, a dangling bond is produced at the other Si atom of the dimer. For the H atoms in the STM image of Fig. 2, it is this dangling bond that images bright, and the tip locks onto this for atom tracking. We have previously described our atom-tracker setup in detail.¹⁷ In brief, the STM tip is locked above a feature using lateral feedback electronics, and its diffusive motion is followed for rates up to 20 Hz. Typical atom-tracking data is displayed in Fig. 3. We note that at room temperature no diffusion is observed; this sets an upper bound of 10^{-3} Hz for tip-induced events. For the range of rates measured in this experiment, such an effect would not play a significant role.

III. RESULTS

Atom tracking is used to determine the average H intrarow hop rate as a function of temperature over the range

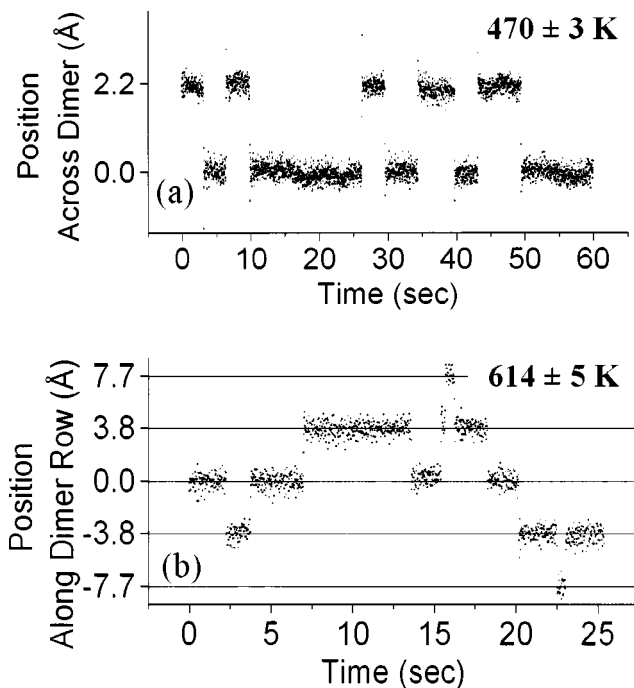


FIG. 3. (a) Intradimer and (b) intrarow atom-tracking data. The position of the H atom was sampled at 50 Hz.

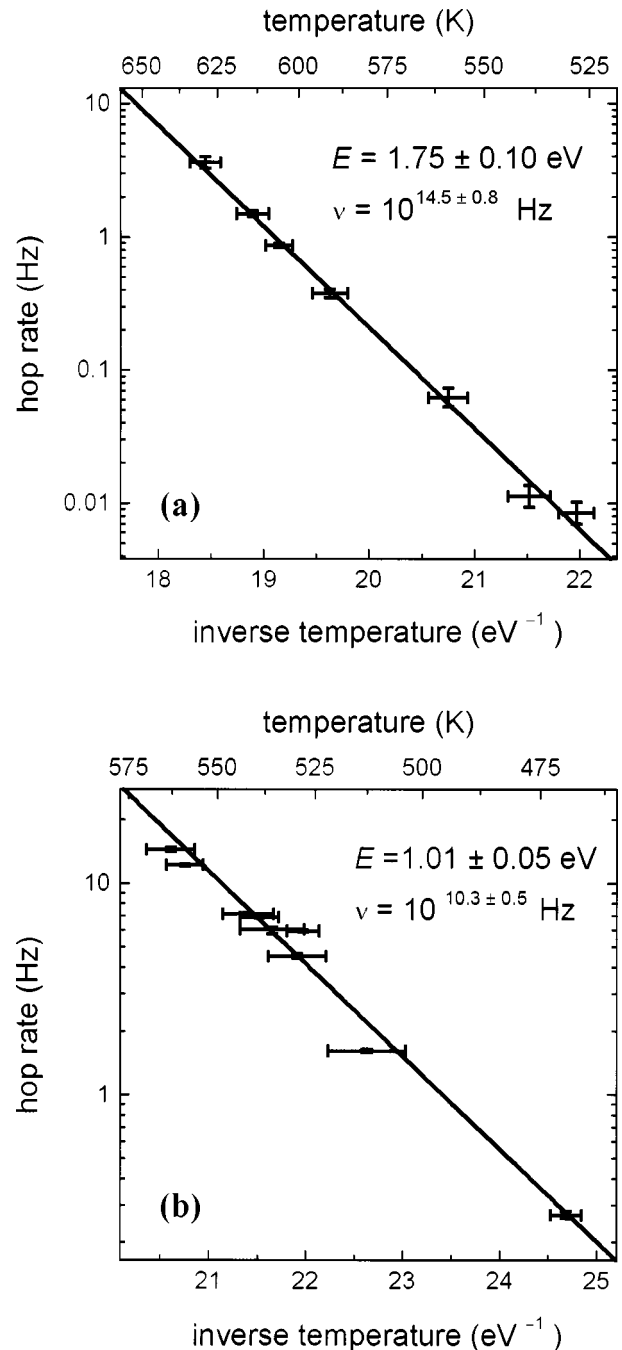


FIG. 4. Arrhenius plots for (a) intrarow and (b) intradimer H diffusion. The solid lines are weighted fits. From the slopes of these lines, we find the activation energies, E , and from the intercepts we find the attempt frequencies, ν .

525 to 625 K. For each temperature, a number of H atoms are tracked as they diffuse along the dimer rows. Since the H atom is likely to interact with other surface features such as step edges and dimer vacancies, no data acquired while the H atom is near another feature is used in determining the hop rates. The average hop rate is expected to follow the Arrhenius relation for a thermally activated process: $r = \nu e^{-E/kT}$, where r is the rate, E is the activation energy, ν is the attempt frequency, T is the temperature, and k is Boltzmann's constant. Figure 4(a) shows an Arrhenius plot constructed from intrarow data. From the slope and intercept of the fitted line,²² an activation energy of 1.75 ± 0.10 eV and an attempt

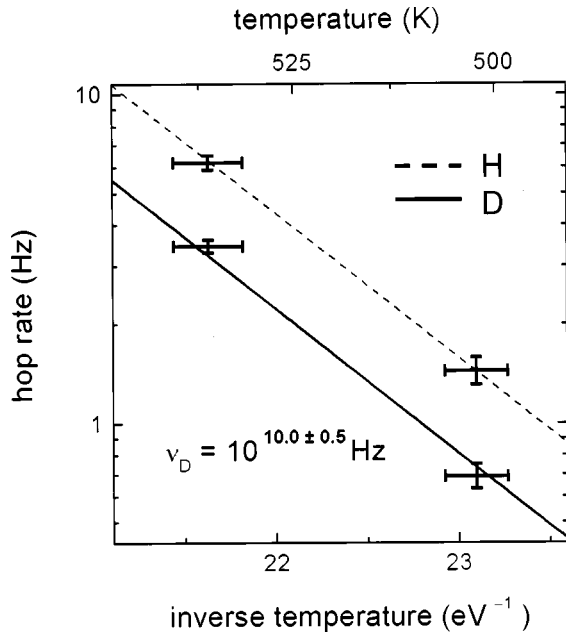


FIG. 5. Arrhenius plot for D intradimer diffusion. Deuterium data are along the solid line and hydrogen data are along the dashed line. The H and D data were acquired simultaneously and the H rates were used to determine the temperature. (See Ref. 23).

frequency of $10^{14.5 \pm 0.8}$ Hz are found.

Over the temperature range 470 to 560 K, intradimer diffusion is studied in the same manner. Above this range, the intradimer diffusion rate is high enough that STM atom tracking cannot resolve individual intradimer hops. Figure 4(b) shows an Arrhenius plot constructed from the intradimer data. From the slope and intercept of the fitted line, an activation energy of 1.01 ± 0.05 eV and an attempt frequency of $10^{10.3 \pm 0.5}$ Hz are found.

Tracking H and D at a few temperatures allows a preliminary determination of relative attempt frequencies. For this purpose, the H rate measurements are used to determine the temperatures. The activation energies (slopes in Fig. 5) are

assumed to be the same for the two isotopes since a difference in mass is expected to affect only the attempt frequency (intercept). The ratio of H to D intrarow diffusion attempt frequencies is $\nu_H/\nu_D = 1.3 \pm 0.6$ and the ratio for intradimer diffusion is $\nu_H/\nu_D = 2.0 \pm 0.4$.²⁴

IV. DISCUSSION AND CONCLUSIONS

A. Activation barriers

Recent experimental and theoretical values for H diffusion are presented in chronological order in Table I and are briefly discussed here. The reason for the broad range of predicted values lies in the range of approximations, the different types of models, the lack of early experimental values, and the increase in computational power over recent years. Fundamentally, models employing empirical potentials are limited by their input dataset; while more computationally intensive *ab initio* methods are limited by computing resources.

For their Monte Carlo simulation, Wu *et al.* produced the first empirical potential for H motion on the Si(001) surface.⁶ The H-Si interaction was approximated by an empirical Stillinger-Weber potential derived from their previous *ab initio* work. However, there are inherent uncertainties in describing a system with a simple empirical potential and Stillinger-Weber has been unreliable for surfaces. There is also a particular difficulty in extrapolating to weakly bound transition states. Given these difficulties, the intrarow predictions of their work agree fairly well with the measurements presented here; however, there is marked disagreement of the intradimer results.⁶ Vittadini *et al.* employed a local density approximation and the Car-Parrinello approach with pseudo-potentials to describe the H and Si atoms.⁸ This model produces good intradimer but poor intrarow agreement. Nachtigall *et al.* performed an intensive calculation which explicitly treated all electrons,⁹ yet, the predicted intrarow and intradimer activation energies are much higher than those measured.

TABLE I. Recent theoretical and experimental values for the activation energies for atomic H diffusion on the bare Si(001) surface. MBT=many body theory, DFT=density functional theory, LDA=local density approximation, MC-TST=Monte Carlo transition state theory.

Method	Intrarow		Intradimer	
	Attempt frequency (Hz)	Activation energy (eV)	Attempt frequency (Hz)	Activation energy (eV)
MC-TST ^a	$10^{15.4 \pm 0.5}$	1.65 ± 0.07	$10^{13.8 \pm 0.6}$	1.58 ± 0.10
Slab-model DFT ^b		1.3		1.1
DFT-cluster ^c		2.3		1.7
STM ^d	10^{13} (assumed)	1.68 ± 0.15		
Tight binding ^e		1.66 ± 0.15		
Classical MBT ^f		1.8		1.1
STM atom tracking ^g	$10^{14.5 \pm 0.8}$	1.75 ± 0.10	$10^{10.3 \pm 0.5}$	1.01 ± 0.05

^aReference 6.

^bReference 8.

^cReference 9.

^dReference 11.

^eReferences 11 and 14.

^fReference 15.

^gThis work.

Considering the previous experimental work, there is a fairly good agreement between the intrarow diffusion barrier value of Bowler's work and that of the current experimental work. However, because of the limited time resolution, it had been necessary for the previous work to assume an attempt frequency in order to extract an activation energy.^{11,25}

The two most recent theoretical works converge on the experimental values. The theoretical work of Bowler *et al.* employed a tight binding model,^{11,14} and that of Hansen *et al.* used an empirical, many-body potential.¹⁵ Hansen's model is the only one that predicts both intradimer and intrarow diffusion barriers in agreement with the present work. It was built upon a variety of *ab initio* data and used a new Si-H interaction potential that had been optimized for the Si surface and to reproduce properties of silicon hydride molecules.²⁶ The work's central predictions pertain to H and D sticking and abstraction probabilities; diffusion and desorption values are offered as test points for the model. While the model does remarkably well for H intradimer and intrarow diffusion, the 2.4-eV prediction for cross-row diffusion and the 2.9-eV prediction for recombinative H₂ desorption seem high compared to the desorption values produced by experiment: 2.48±0.10 eV from the optical second-harmonic work of Höfer *et al.*²⁷ or 2.22±0.20 eV from the recent STM work of Lin *et al.*²⁸

The implication of the intrarow diffusion results for the H-resist lithographic process is briefly discussed here. The STM H-resist process demonstrates high selectivity, particularly when CVD is the means of material delivery, and very fine pattern definition. Since intrarow diffusion can degrade pattern definition, it sets an upper temperature limit for lithographic processes. Depending on process times and tolerances, this limit can be 50 to 100 K lower than that set by H desorption.²⁹

B. Attempt frequencies

It is informative to compare the results of the present work with related infrared and electron energy loss measurements of H-Si bond vibrational frequencies. The H-Si bond stretch frequency has been measured at $\nu_s = 10^{13.78}$ Hz, and the bend frequency at $\nu_b = 10^{13.26}$ Hz.³⁰ Applying simplifying approximations to simple transition state theory (STST) allows an order of magnitude comparison between these val-

ues and diffusion attempt frequencies. According to STST, a transition attempt frequency is $\nu = N(\Pi\nu_{\min\perp} / \Pi\nu_{\text{saddle}\perp})\nu_{\min\parallel}$, where N is the number of equivalent transitions and ν is the system's frequency of oscillation perpendicular (\perp) or parallel (\parallel) to the transition path, at the minimum of the potential well or the saddle point of the barrier. Assuming that the perpendicular components are of the same order at the saddle point and in the well, the term in brackets should be of order unity. Under this approximation the attempt frequency is $\sim N\nu_{\min\parallel}$. Applying this to intrarow diffusion, there are two equivalent transitions, up and down the dimer row (see Fig. 1), and a reasonable value for $\nu_{\min\parallel}$ is ν_b .⁶ This simple model then suggests $\nu \approx 2\nu_b = 10^{13.6}$ Hz.

According to this simple model, the ratio of H to D attempt frequencies should be the ratio of the bond vibrational frequencies. The ratio of H to D bend frequencies is $(\nu_H/\nu_D)_{\text{bend}} = 1.39 \pm 0.11$,³⁰ that of H to D intrarow attempt frequencies is $\nu_H/\nu_D = 1.3 \pm 0.6$ and that of intradimer attempt frequencies is $\nu_H/\nu_D = 2.0 \pm 0.4$. These values agree with the expectation that the two species behave as simple harmonic oscillators differing only by mass: $\nu_H/\nu_D = \sqrt{m_D}/\sqrt{m_H} = \sqrt{2} \approx 1.4$.

Considering intradimer diffusion, there is only one transition path and the H-Si bond is bent along the dimer. The simple model predicts $\nu \approx \nu_b = 10^{13.3}$ Hz which is three orders of magnitude higher than the observed attempt frequency of $10^{10.3 \pm 0.5}$ Hz. The prediction is not significantly changed by the calculation of $\Pi\nu_{\min\perp} / \Pi\nu_{\text{saddle}\perp}$ from the vibrational frequencies generated by the model of Hansen *et al.*³¹ An upper bound of 0.001 Hz for room temperature intradimer diffusion discounts the possibility of tunneling or tip induced diffusion significantly enhancing rates at the low end of the temperature range in Fig. 3(b). An explanation of the low attempt frequency requires further investigation.

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