Piecewise diffusion of the silicon dimer

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We present a detailed view of the diffusion of silicon dimers on the silicon (001) surface. Through a combination of atom tracking and *ab initio* modeling, the dimer is shown to move one atom at a time rather than as a two-atom unit. The details of the pathway depend on the diffusion channel: On top of dimer rows, the two atoms of a dimer separate but remain bound during diffusion. In the troughs between dimer rows, the two atoms separate completely and move independently before rejoining in a new location.
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Since the 1960s, techniques for imaging with atomic resolution have provided us with a remarkable look at the variety of ways in which atoms and small molecules move on surfaces. Often the diffusion process observed is quite simple, involving a series of random hops between adjacent binding sites. However, beginning in the late 1970s, experiments using field-ion microscopy revealed unusual diffusion mechanisms. Diffusion by atomic exchange was observed, a process in which an atom on top of a surface replaces an atom in the first layer of the surface, while the replaced atom moves to the top.[1–4] More recently, long jumps spanning several nearest-neighbor sites were observed.[5,6] When the diffusing species is a cluster of two or more atoms, the opportunity for variety is further enhanced. For instance, platinum dimers on platinum (001) were found to move one atom at a time by atomic exchange, whereas trimers were found to move by a combination of site-to-site hopping and exchange.[7] Surprisingly, small clusters were often observed to move at rates comparable to or faster than individual atoms.[8–10] Studies of two-dimensional metal-island diffusion on metal surfaces reveal evaporation condensation and periphery diffusion mechanisms.[11] The advent of the scanning tunneling microscope (STM) in the 1980s has allowed the extension of atomic-scale diffusion studies to a much broader range of systems involving both metal and semiconductor surfaces. Furthermore, a technique for directly measuring surface diffusion, called ''atom tracking,'' was applied in a study of silicon dimers on silicon (001) by Swartzentruber in 1996.[12] Nevertheless, a detailed understanding of the atomic pathway for dimer diffusion has not been achieved for Si on Si(001), an important model system in studies of growth on covalently-bonded semiconductor surfaces.[13] Modeling of this class of systems has proven difficult, and much of the theoretical insight into atomistic processes has resulted from computationally intensive *ab initio* techniques. In this paper we discuss atom-tracking studies and *ab initio* calculations that produce a significant advance in our understanding of dimer diffusion on Si(001), revealing piecewise diffusion pathways.

The Si(001) surface consists of parallel rows of dimer bonds that are the result of pairs of surface atoms binding together in order to reduce the overall surface energy. These dimer rows are separated by 7.7 Å, and the spaces in between them are called troughs. Rows and troughs are distinct one-dimensional diffusion channels for Si ad-dimers. Theoretical work has shown that a dimer is very likely to form whenever two monomers meet, since dimer formation requires no energy barrier beyond that of monomer diffusion.[14,15] Once formed, a dimer is very strongly bound. The energy required to separate a dimer has been calculated to be 1.33 eV for dimers on top of dimer rows.[14,15] Energetically, the row sites are more favorable than trough sites.[14–17] However, the distribution of dimers occupying the two types of sites upon formation is kinetically determined: one-third form on rows and two-thirds form in troughs.[18]

Our experiments on Si dimers are performed using a custom-built STM that is capable of imaging at elevated temperatures. It is housed in an ultrahigh vacuum chamber with a base pressure of 5×10^{-11} torr. The samples are prepared by degassing then briefly flashing to 1250 °C using resistive heating. They are then transferred to the STM stage and allowed to equilibrate overnight at the desired temperature between 300–500 K. A small amount of material (<0.01 ML) is subsequently deposited onto the surface from a resistively-heated Si wafer. The sample temperatures were measured with a heated thermocouple probe whose accuracy in the temperature range of interest was carefully checked in a calibration procedure using the known melting point of indium 430 K.[19] In some cases, the temperature was found by measuring the hop rate of dimers along dimer rows and using the calibration curve shown in Fig. 1. We have previously described our atom-tracker setup in detail.[19] In brief, the STM tip is locked above an adsorbate using lateral feedback electronics, and diffusive motion is followed with a time resolution up to 70 Hz.

We first discuss results for diffusion along dimer rows. Diffusion in this channel is activated just slightly above room temperature. Using atom tracking, we determine the corresponding energy barrier by measuring the average hop rate as a function of temperature over the range 360–460 K.[20] For each temperature, one or more dimers are tracked as they diffuse along a dimer row. In most cases, the dimer's motion is bounded by two features that serve as end points to a clean segment of dimer row. These features are either step edges, small Si islands, or defects such as dimer vacancies. Since the dimer interacts slightly with these features, data from the center portion of the segment are used to calculate the average hop rate while data near the end points are ig-

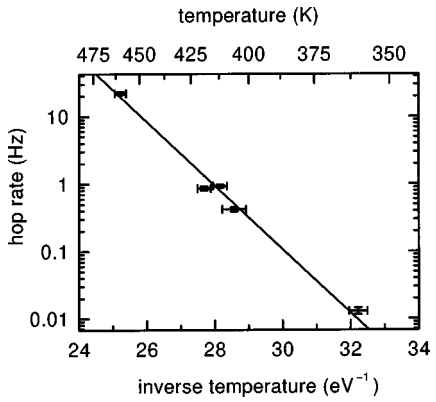

FIG. 1. An Arrhenius plot for dimer diffusion along the top of a substrate dimer row. The solid line is a weighted fit. From the slope and intercept of this line, we find an activation energy of 1.09 ± 0.05 eV and an attempt frequency of $10^{13.2\pm0.6}$ Hz.

nored. 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 and ν are the activation energy and attempt frequency, T is the temperature, and k is Boltzmann's constant. Figure 1 shows an Arrhenius plot constructed from our data. From the slope and intercept of the fitted line, we find an activation energy of 1.09 ± 0.05 eV and an attempt frequency of $10^{13.2\pm0.6}$ Hz.

The experimental result described above provides a strong basis from which to evaluate theoretical models of row diffusion. Yamasaki, Uda, and Terakura have performed unpublished *ab initio* modeling of row diffusion that we summarize here, in addition to their earlier studies,[14,15,21] *Ab initio* methods are generally known to be more reliable than less computationally intensive semiempirical methods, especially for calculations of surface structure. However, the configuration space containing all possible diffusion pathways is prohibitively large to fully explore within the limits of current technology, so it is always possible that a given calculation will not find the lowest-energy pathway. The result of the first calculation by Yamasaki, Uda, and Terakura was an intuitively reasonable pathway in which the dimer moves forward as a unit, with its dimer bond length remaining roughly constant.[14,15] However, the corresponding energy barrier, 1.44 eV, proved to be very high compared to the experimental value. This prompted the investigation of alternative pathways. This investigation has led to a pathway for row diffusion that is in very good agreement with the atom-tracking result. The proposed pathway is shown schematically in Fig. 2(a), with the total energy at key points shown on the right. This pathway is unexpected in that the dimer moves one atom at a time rather than as a unit. First, a 1.08-eV barrier is crossed as the first atom moves ahead, leaving the dimer in a weakly bound intermediate state with the atoms separated. Then it is equally likely that the second atom follows, resulting in diffusion to an adjacent site, or that the first atom moves back. The possibilities that the dimer either dissociates or undergoes an exchange with the substrate after entering the intermediate state have also been investigated. The energy barriers for these processes are significantly larger, 1.6 and 1.28 eV, respectively, and should be extremely rare at these temperatures. Eliminating these possibilities, Yamasaki, Uda, and Terakura conclude that

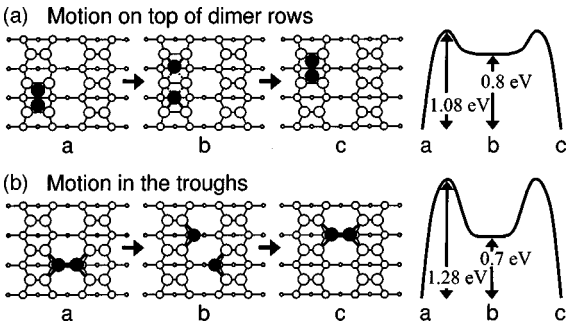

FIG. 2. Schematic diagrams of the calculated diffusion pathways for row and trough diffusion. These were constructed from the results of *ab initio* modeling by Yamasaki, Terakura, and Uda (Ref. 21) for row diffusion, and by Goringe and Bowler (Ref. 22) for trough diffusion. Solid circles represent the two atoms of an ad dimer and open circles represent substrate atoms. Smaller circles represent atoms deeper in the substrate. Segments of two neighboring dimer rows are shown in each diagram, running vertically. The total energy at key points along each pathway is depicted on the right. Both pathways involve the dimer moving one atom at a time rather than as a unit. In (a), the dimer enters a weakly bound state as one atom moves ahead (*b*), but remains together during diffusion. In (b), the dimer dissociates as one atom moves ahead (*b*), and the two atoms move up and down the trough independently until they meet again and reform the dimer in a new location.

row diffusion occurs with the dimer moving one atom at a time but remaining bound as it hops from site to site. The calculated energy barrier of 1.08 eV for this pathway is in close agreement with our experimental result of 1.09 ± 0.05 eV. Atom-tracking data confirms that all hops during row diffusion are between adjacent sites along the row, as expected for the proposed pathway.

We now report atom-tracking results for trough diffusion, motivated by a recent *ab initio* study by Goringe and Bowler.[22] Goringe and Bowler propose that, as for row diffusion, trough diffusion requires the dimer to move one atom at a time, as shown schematically in Fig. 2(b). Although rather than remaining bound as the first atom moves ahead, the dimer completely breaks apart and its two atoms move nearly independently along the trough until they meet again and reform the dimer. This breaking apart is the most costly step energetically, with a calculated energy barrier of 1.28 eV.[23] The two atoms may come back together immediately after dissociating, as in Fig. 2(b). However, it is equally likely that they will move away from each other and continue to execute simultaneous one-dimensional random walks until they meet each other and reform the dimer.[24] It is important to note that these single-atom random walks occur on a much shorter time scale than the average time between breakup events, since the calculated energy barrier is much smaller, 0.6 eV compared with 1.28 eV.[25] Therefore, atom-tracking data should appear as instantaneous hops on the time scale that we observe. A simple statistical analysis results in the probability distribution for the dimer to reform a given number of sites away from its original site. Assuming no long-range interaction, Goringe and Bowler conclude that nearly 40% of the time the dimer reforms at its original site. The remaining dissociations result in observable hops, and the majority of the hops (71%) are expected to be between adjacent sites one spacing away. However, a significant frac-

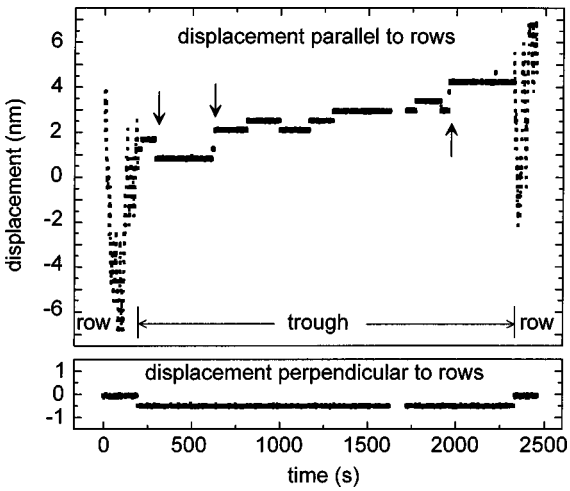

FIG. 3. Atom-tracking data at 433 ± 8 K. The position of the dimer was sampled at 100 Hz. The data are shown as displacement versus time both along the dimer row (top) and perpendicular to the dimer row (bottom). (The pause in the data near 1650 sec was for imaging the area and verifying our identification of the dimer configuration.) For the first 200 sec, the dimer diffused rapidly on top of a dimer row, with an average hop rate of 3.4 Hz. Then, the dimer hopped sideways one spacing into the trough. For the next 2150 sec, the dimer hopped along the trough at a much slower rate of 6.5×10^{-3} Hz. Finally, the dimer hopped back onto the original dimer row and resumed rapid diffusion. The arrows point to three long hops of two spacings that occurred while in the trough.

tion of hops are predicted to be longer than one spacing: 16% two, 6% three, and the rest more than three spacings. The presence or absence of these unusual long jumps in atom-tracking data provides a rather direct test of the proposed diffusion mode.

Atom-tracking studies of trough diffusion confirm the presence of long jumps in this diffusion channel. Examples of this are shown in Fig. 3, a set of atom-tracking data at 433 K that demonstrates the possibilities for diffusion at higher temperatures.[26] In summary, this figure shows a dimer continuously tracked as it first diffuses on top of a dimer row, then hops sideways into a neighboring trough, diffuses along the trough, and finally hops back on top of the original dimer row. The arrows point to three long jumps of two spacings among a total of 14 hops in the trough. It is striking how much slower diffusion in the trough is than diffusion on top of a dimer row. Using the statistical analysis described above, we find a value of 1.27 ± 0.08 eV for the energy barrier of trough diffusion.[27] The calculated barrier of 1.28 eV is in close agreement with this value. We have summarized our results for row and trough diffusion in Table I.[28] In each case, the observed hop length distribution is in good agreement with that expected according to whether theoretical modeling favors the dimer remaining bound or breaking apart during diffusion. The elevated percentage of single hops observed for trough diffusion may be attributed to a weak interaction between the atoms when they are only one site apart that results in a slightly enhanced probability for reforming the dimer.

TABLE I. A tabulation of the measured hop length distributions for row and trough diffusion (Ref. 28). These are compared to the distributions expected for two possibilities: when the dimer remains bound during diffusion and when the dimer dissociates during diffusion. We conclude that the dimer remains bound during row diffusion but dissociates during trough diffusion. These findings are in agreement with the results of theoretical modeling.

Hop length	% observed	% if bound	% if dissociated
	Row diffusion (87 hops)		
1	100	100	71
2	0	0	16
3	0	0	6
	Trough diffusion (73 hops)		
1	85	100	71
2	12	0	16
3	3	0	6

We have presented atom-tracking and *ab initio* studies that combine to reveal piecewise diffusion pathways for the Si dimer on Si(001). The dimer diffuses one atom at a time and not as a unit, becoming weakly bound (on the rows) or completely dissociating (in the troughs) during motion from site to site. The calculated channel-specific energy barriers are in excellent agreement with atom-tracking results. For diffusion in the trough, we observe long jumps spanning two and three lattice sites, a direct signature of the dimer's dissociation and reformation during diffusion. In the future we expect atom tracking to be applied to still more complex diffusion systems. For instance, it may be possible to follow changes in a large molecule's position, orientation, and bonding as it moves along a surface.[29]

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[20] We have measured the hop rate at room temperature and determined that it is dominated by tip-induced hops. We have also determined that this very low rate of tip-induced hops does not affect the rates measured in the temperature range from 360 to 460 K. See Ref. 19.
[21] Detailed information on the pathway of Yamasaki, Uda, and Terakura was obtained in communication with the authors. For a brief description, see Ref. 15.
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[23] The highest energy reached along the calculated pathway is 1.28 eV (see Fig. 1 of Ref. 22). Therefore, this is the value of the energy barrier for diffusion in the trough. A value of 1.15 eV was misquoted as the energy barrier in the text of Ref. 22.
[24] C. M. Goringe and D. R. Bowler note that the possibility of the adatoms diffusing across the rows instead of along them may be discounted since this involves a higher energy barrier, 0.71 eV compared with 0.6 eV (Ref. 17), and will be so unlikely as to affect only the tails of the probability distributions presented.
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[26] It was necessary to use a positive sample bias voltage so that the STM image of the trough dimer contrasts sufficiently with the substrate to allow for atom tracking. For hops larger than three lattice spacings, the tracker presumably loses lock and drifts off ending the data set. For information on the identification and bias dependence of the trough dimer, see Ref. 16 and B. Borovsky, M. Krueger, and E. Ganz, Phys. Rev. Lett. **78**, 4229 (1997).
[27] This value is obtained from a series of data at 483 ± 8 K. Forty hops occurred in 122 sec, giving an average hop rate of 0.33 Hz. According to the model of Goringe and Bowler, only 62% of breakup events result in observable hops, so the rate of breakup events is 0.53 Hz. Assuming a typical prefactor of 10^{13} Hz, we find an energy barrier of 1.27 ± 0.08 eV. The error bar reflects an uncertainty of 8 K in the temperature and a factor of 4 in the assumed prefactor, as suggested by our measurement of row diffusion.
[28] The row diffusion data are taken from atom-tracking runs at 360 ± 8 K. The trough diffusion data are taken from all available atom-tracking runs at temperatures above 430 K. In all cases, the tracker speed ($\sim$50 Hz) is at least two orders of magnitude greater than the average hop rate. In this extremely rare event regime, the probability that two single hops will occur in an interval short enough to appear as one double hop is negligible. This allows us to rule out the possibility that the long hops observed were the result of a rapid succession of single hops.
[29] Additional information, including STM movies of diffusion in both channels, is available at our web site: http://www.spa.umn.edu/groups/stmlab/