# One-Dimensional Defect-Mediated Diffusion of Si Adatoms on the Si(111)-(5 × 2)-Au Surface

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Using scanning tunneling microscopy, we determine that the one-dimensional diffusion of Si adatoms along the Si(111)-(5 × 2)-Au surface reconstruction occurs by a defect-mediated mechanism. Distinctive diffusion statistics, especially correlations between sequential adatom displacements, imply that the displacements are triggered by an interaction with a defect that is localized to the adatom. The defect is intrinsic and thermally activated. The measured diffusion statistics are modeled accurately by a Monte Carlo simulation. The measured adatom diffusion activation barrier is 1.24 ± 0.08 eV.

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The Si(111)-(5 × 2)-Au surface is a member of a family of metal-induced chain reconstructions of Si [1–8]. Studies of these chain reconstructions have yielded new understanding of the physics of one-dimensional (1D) electronic states [1–8]. The (5 × 2)-Au surface is speckled with Si adatoms, which sit on-top of the chains at a coverage of 0.25/5 × 2 cell. Owing to a repulsion between adatoms, the adatoms occupy a (half-filled) 5 × 4 lattice [8]. The 5 × 4 adatom superlattice is intimately linked with the electronic properties of the surface [4–6]. In segments covered by Si adatoms, the otherwise metallic chains are semiconducting [6]. An earlier qualitative STM study found that the adatoms diffuse along the chains by hops of $2a$ (7.68 Å) between neighboring 5 × 2 cells for $T >$ 473 K [9]. Adatom hopping causes nanometer-scale fluctuations in the surface electronic properties. The individual Si adatoms have also been utilized as bits in an atomic-scale memory [10]. In this application, adatom hopping causes errors in the stored information. A direct determination of the adatom diffusion mechanism and activation barrier is essential in predicting the time-evolution of both the nanometer-scale surface structure and electronic properties. By a statistical characterization of the diffusion, we demonstrate that the Si adatoms hop along the chains by a defect-mediated mechanism similar to the vacancy-mediated diffusion observed on some metal surfaces.

Diffusion of adatoms and surface-embedded atoms often occurs by mechanisms more complex than thermally activated random hopping from one site to the next. Random walks with several hop lengths [11,12], exchange [13,14], and vacancy-mediated diffusion [15–19] have all been observed in experiments. Vacancy-mediated surface diffusion was first identified on Cu surfaces, where it plays an essential role in alloying and the stability of surface structure [18,19]. Vacancy-mediated diffusion is an instance of so-called hopover processes [20]. In a hopover process, an atom's diffusive displacements are triggered by the random arrival of some hop-instigating defect, e.g., a vacancy. The defining element of hopover diffusion is that once the diffusion event occurs, the defect is on the opposite side of the atom from its initial approach. This simple feature leads to time and direction correlations in atom displacements and diffusion statistics different from those for any uncorrelated process, e.g., random-walk diffusion [16]. Intuitively, hopover diffusion is impossible in a strictly 1D system, because sequential diffusion events arising from the defect migration are always in opposite directions leading to zero net displacement.

We prepare (5 × 2)-Au surfaces by depositing 0.4 ML Au onto clean Si(111) substrates at $T \sim 650\,^{\circ}\mathrm{C}$ [1,2]. The sample preparation and measurements are performed in a variable-temperature STM at pressures $<10^{-10}$ Torr. The (111) samples are miscut by ∼1.0° toward the [100] azimuth. On the resulting stepped surface, each terrace (10–20 nm wide) supports only one of the three possible 5 × 2 domain orientations—that in which the chains run parallel to the steps. Figure 1(a) shows a STM image of a typical surface. The Si adatoms appear as bright protru-

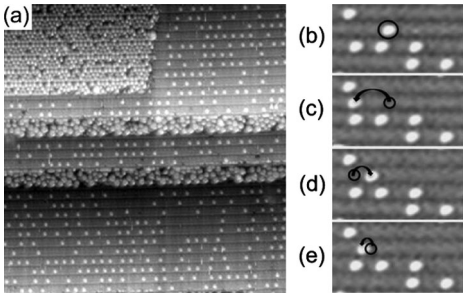


FIG. 1. (a) A STM image showing a typical (5 × 2)-Au surface (50 × 50 nm$^2$, −1.5 V, 0.1 nA). A clean 7 × 7 domain (upper left) coexists with the (5 × 2)-Au reconstruction. (b)–(e) Excerpts from a STM movie at 457 K illustrating a burst of displacements (11 × 7 nm$^2$, −2.0 V, 0.1 nA, 7.1 s/frame). (b) The adatom in the circle rests for 19 frames (135 s), then moves in three consecutive frames (c)–(e) by $-8a$, $+4a$, and $-2a$, as indicated by arrows. It then remains at rest for 14 frames (99 s). The circle indicates the adatom position in the preceding frame.

 

sions sitting on top of the $5 \times 2$ chain structures. Surfaces prepared at 650 °C have adatom coverages of $0.21 \pm 0.03/5 \times 2$ cell. A coverage near 0.25 adatoms/$5 \times 2$ cell is obtained by annealing at 900 °C for 1 min. The coverage established during the preparation remains constant in the temperature range (145–215 °C) of the diffusion measurements.

To measure adatom diffusion, we take sequences of STM images at a fixed rate to create a movie. Movies consist of constant-current (0.1 nA) filled-state images acquired with −1.5 V to −2.1 V dc bias (sample) [21]. The adatoms are labeled in every frame and linked between sequential frames. The displacements are measured by following each adatom from frame-to-frame. In a typical movie, less than 15% of the 30–50 adatoms in the field of view move from frame-to-frame, so the assignment of displacements is unambiguous. The finite time for STM image acquisition restricts us to observe only net displacements from one frame to the next, not the exact sequence of hops that caused the displacement.

The most straightforward way to measure the adatom diffusion barrier is to measure the ensemble mean-square displacement rate as a function of temperature. The inset in Fig. 2 shows the measured mean-square adatom displacements between sequential frames at a few temperatures. The mean-square displacement initially increases linearly with time before turning over due to adatom crowding. Figure 2 shows the measured adatom mean-square displacement rates versus temperature from 418 to 488 K. The Arrhenius relation yields an activation energy barrier of $1.24 \pm 0.08$ eV and a prefactor $10^{11.6 \pm 0.9}$ $s^{-1}$. This

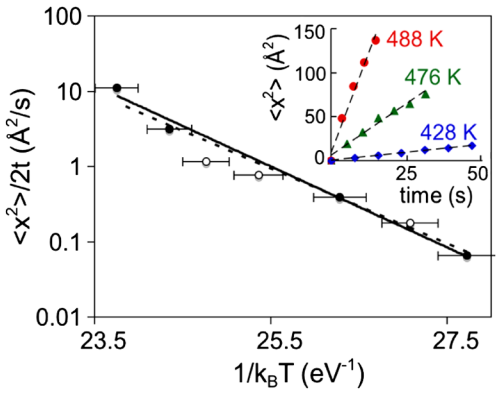


FIG. 2 (color online). Arrhenius plot of the mean-square adatom displacement versus temperature. The effective activation barrier, $1.24 \pm 0.08$ eV, is extracted from the fit (solid line) to the displacements (solid circles) measured with $0.25 \pm 0.03$ adatoms/$5 \times 2$ cell. Open circles are for lower coverages (0.14–0.2). The broken line, activation barrier 1.15 eV and prefactor $10^{11}$ $s^{-1}$, shows the temperature-dependence predicted by using our model to fit the displacement distributions. Statistical error bars in displacements are smaller than plot symbols, temperature error bars are ±5 K. (Inset) Mean-square displacements vs time.

energy represents an effective activation barrier for the temperature-dependent time evolution of the entire system.

To identify the true nature of the adatom diffusion process, we must examine the diffusion statistics explicitly: the direction and time correlations, neighbor correlations, and the displacement distribution. Our observations point directly to defect-mediated hopover diffusion.

The clearest indication of hopover diffusion is seen in a correlation of displacement direction. A direction correlation occurs because, as mentioned, an adatom hop over the defect places the defect on the opposite side of the adatom, leading to increased probability of the adatom hopping back and forth. In our experiments, we measure a directional correlation: sequential displacements in opposite directions are 1.5 times more likely than in the same direction.

We also observe that the displacements of a given adatom do not occur randomly with a constant probability per unit time. Rather, they are correlated in bursts separated by longer periods of inactivity. This is a distinctive feature of hopover diffusion. That is, displacements occur in rapid succession when the defect is in the immediate vicinity, separated by periods of inactivity when the defect wanders away or is annihilated. The sequence of images shown in Fig. 1(b)–1(e), from a movie at 457 K, reveals this character of the diffusion process.

Burst behavior is quantified by measuring the time correlation between displacements. The time correlation is $c(k) = p(k)/P$, where $p(k)$ is the measured rate for two displacements to occur separated in time by $k$ frames, regardless of intervening displacements, and $P$ is the average frequency of displacements for the whole ensemble over the duration of the STM movie. For a random process with a constant probability per unit time, the correlation is $c(k) = 1$. We measure both the self-correlation, relating the displacement of a given adatom to its own future displacements, and a neighbor-correlation function, $c_n(k, r)$, relating the displacements of an adatom to those of all other adatoms within a radius $r$. Figure 3(a) shows the self- and neighbor-correlation functions ($r = 50$ Å) measured from a movie (6.8 s/image) at 468 K. The displacements of a given adatom are correlated over several frames ($c > 1$), but become uncorrelated over longer periods. By contrast, displacements within a neighborhood are uncorrelated at all times, $c_n(k, 50\ \text{Å}) = 1$. That the displacements of neighboring adatoms are uncorrelated implies that the hop-instigating defect remains localized near a given adatom, instead of wandering over the surface. Since neighboring adatoms may be separated by as few as two $5 \times 2$ cells, the defect must be restricted to only a few atomic sites to either side of the adatom.

The wait-time distribution, which is related to the time correlation function, also reveals the burstlike character of the diffusion. The wait-time distribution measures the probability for two sequential displacements to occur sepa-

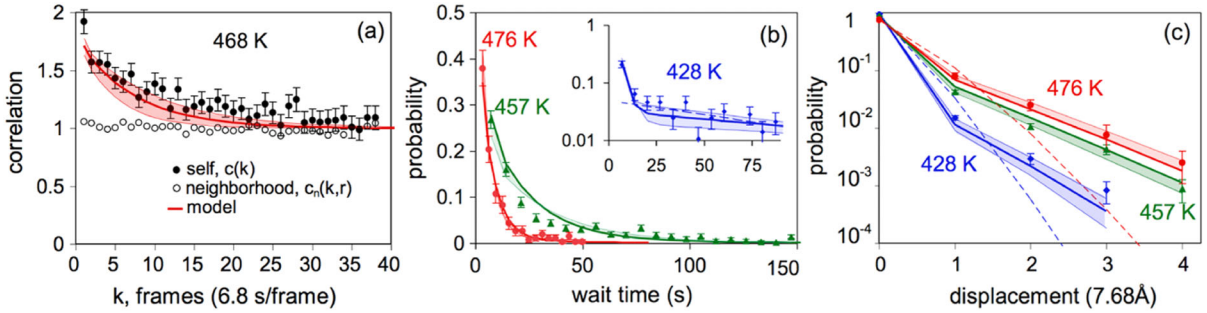


FIG. 3 (color online). Diffusion statistics for Si adatoms on the (5 × 2)-Au surface. Experimental measurements are represented by symbols. Solid lines, with shaded error bars, are the results of our defect-mediated model. (a) Time correlations between adatom displacements. (b) Wait-time distributions. The inset shows a comparison with a random-walk model (broken line), which fails for short wait times. (c) Displacement distributions. Broken lines are for a random walk.

rated by a specific time interval. In a random process with a constant probability per unit time, wait times are exponentially distributed. However, the measured wait-time distributions, Fig. 3(b) and inset, are not exponential. They show upward curvature on a log plot [inset of Fig. 3(b)], indicating a high probability for rapid sequential displacements, and a long tail attributed to the extended time between subsequent revisitations of the defect to the adatom.

Incidentally, this burst behavior is not observed for vacancy-mediated diffusion of embedded atoms on Cu surfaces because the duration of the interaction between the atom and the fast-moving vacancy is much shorter than the image acquisition time [16,17]. The burst character of diffusion on Cu shows up only in the displacement distribution. The displacement distribution for hopover diffusion does not follow the binomial form characteristic of a random walk. Rather, there is a higher probability for long displacements owing to the increased number of hops during a burst. The deviation from random-walk behavior in our data is clearly seen in Fig. 3(c), in which we plot the measured frame-to-frame displacement distributions at a few temperatures along with binomial distributions of the same width.

We quantify the connection between the measured statistics and defect-mediated diffusion using a Monte Carlo simulation. A schematic for our model is shown in Fig. 4. An adatom and a hop-instigating defect sit on a row of sites. The defect wanders within a space of length $L$, including at most only a few sites near the adatom. The essence of the 1D hopover process is described with three rates: $r$, the rate at which the defect hops on lattice sites away from the adatom; $r_1$, the rate at which the defect passes to the other side of the adatom without affecting the adatom position; and $r_2$, the rate at which the adatom hops over the defect causing a diffusion event. We use the respective activation barriers, $E$, $E_1$, and $E_2$, with a common prefactor to determine the rates in the simulation. In order to model the diffusion statistics accurately at all temperatures, it is also necessary to include a defect lifetime. The defect lifetime is determined through detailed balance by including an activation barrier for defect creation, $E_c$, and a defect formation energy, $\Delta E$ [22].

By an extensive exploration of possible parameter values, we have found a set of *best-fit* values that allows our model to accurately reproduce both the displacement and time statistics, as well as the correct temperature dependence of these statistics across the experimental temperature range. The measured distributions and results of the model are shown in Fig. 3. The signature nonexponential and nonbinomial shapes of the wait-time and displacement distributions, respectively, are well represented. The model also reproduces the expected directional correlation of displacements. In experiment we measure sequential displacements to be in opposite directions at a rate of 60 ± 6%, at 457 K, while the model yields 55%. The diffusion statistics are simulated with the parameters: $E = 1.21$ eV, $E_1 = 1.07$ eV, and $E_2 = 1.07$ eV, and a prefactor $= 2 \times 10^{12}$ s$^{-1}$. The choice of $L = 5$ sites, two sites on each side of the adatom, is arbitrary and mainly determines the prefactor. The defect lifetime is determined by a formation energy, $\Delta E = 0.11$ eV, and a creation barrier, $E_c = 1.21$ eV. Uncertainties in the energies are <50 meV. Owing to uncertainty in our temperature measurements, the results of the simulations (heavy solid lines) at the measured temperatures (428, 457, and 476 K) are displayed with shaded temperature error bars (±5, −5, and 5 K, respectively) in Figs. 3(b) and 3(c). The scatter of

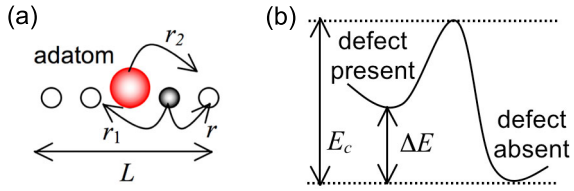


FIG. 4 (color online). (a) Schematic for our model of 1D defect-mediated hopover diffusion. The diffusive hops of the adatom (large ball) are mediated by a localized defect (black ball). (b) The potential energy surface which determines the lifetime of the defect.

displacements in Fig. 3(c) and mean-square displacements in Fig. 2 is consistent with uncertainties of a few Kelvin.

In our model, $E_1$ or $E_2$ may be rate limiting and thereby set the adatom diffusion barrier. Since $E_1$ and $E_2$ are identical (1.07 eV), the barrier is sensitive to both. In this situation, we have been unable to find a closed-form expression for the activation barrier. We have numerically determined the model activation barrier to be 1.15 eV, which is near the sum $E_2 + \Delta E = 1.07\ \text{eV} + 0.11\ \text{eV} = 1.18\ \text{eV} (= E_1 + \Delta E)$. The activation barrier measured in experiments is $1.24 \pm 0.08$ eV (see Fig. 2).

Establishing that diffusion is defect mediated does not reveal the nature of the defect. STM images do not offer a clear candidate, which suggests that the defect may reside subsurface or involve subtle atomic arrangements that cannot be resolved with STM. The detailed structure and arrangement of Au and Si atoms on the $(5 \times 2)$-Au surface, as well as the binding site of the Si adatom, is unsettled [23,24]. Because of the relatively large unit cell, first-principles calculations are difficult and yield several structures with similar configuration energies [25]. The measurements presented here offer some clues and provide a test for the calculated adatom binding energies. The defect is localized in the neighborhood of an adatom, and its formation energy is small ($\sim$0.10 eV), suggesting that it may well be an integral part of the reconstruction that becomes activated to migrate around the adatom before relaxing again to its most stable configuration.

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[1] J. N. Crain, J. L. McChesney, F. Zheng, M. C. Gallagher, P. C. Snijders, M. Bissen, C. Gundelach, S. C. Erwin, and F. J. Himpsel, Phys. Rev. B **69**, 125401 (2004).
[2] I. Barke, T. K. Rügheimer, F. Zheng, and F. J. Himpsel, Appl. Surf. Sci. **254**, 4 (2007).
[3] I. Barke, R. Bennewitz, J. N. Crain, S. C. Erwin, A. Kirakosian, J. L. McChesney, and F. J. Himpsel, Solid State Commun. **142**, 617 (2007).
[4] S. C. Erwin, Phys. Rev. Lett. **91**, 206101 (2003).
[5] J. L. McChesney, J. N. Crain, V. Perez-Dieste, F. Zheng, M. C. Gallagher, M. Bissen, C. Gundelach, and F. J. Himpsel, Phys. Rev. B **70**, 195430 (2004).
[6] H. S. Yoon, S. J. Park, J. E. Lee, C. N. Whang, and I.-W. Lyo, Phys. Rev. Lett. **92**, 096801 (2004).
[7] Y. Yagi, K. Kakitani, and A. Yoshimori, Surf. Sci. **356**, 47 (1996).
[8] A. Kirakosian, R. Bennewitz, F. J. Himpsel, and L. W. Bruch, Phys. Rev. B **67**, 205412 (2003).
[9] T. Hasegawa and S. Hosoki, Phys. Rev. B **54**, 10 300 (1996).
[10] R. Bennewitz, J. N. Crain, A. Kirakosian, J.-L. Lin, J. L. McChesney, D. Y. Petrovykh, and F. J. Himpsel, Nanotechnology **13**, 499 (2002).
[11] S. C. Wang, J. D. Wrigley, and G. Ehrlich, J. Chem. Phys. **91**, 5087 (1989).
[12] D. C. Senft and G. Ehrlich, Phys. Rev. Lett. **74**, 294 (1995).
[13] G. L. Kellogg and P. J. Feibelman, Phys. Rev. Lett. **64**, 3143 (1990).
[14] G. L. Kellogg, Surf. Sci. Rep. **21**, 1 (1994).
[15] T. Flores, S. Junghans, and M. Wuttig, Surf. Sci. **371**, 1 (1997).
[16] R. van Gastel, E. Somfai, S. B. van Albada, W. van Saarloos, and J. W. M. Frenken, Phys. Rev. Lett. **86**, 1562 (2001).
[17] M. L. Grant, B. S. Swartzentruber, N. C. Bartelt, and J. B. Hannon, Phys. Rev. Lett. **86**, 4588 (2001).
[18] M. L. Anderson, M. J. D'Amato, P. J. Feibelman, and B. S. Swartzentruber, Phys. Rev. Lett. **90**, 126102 (2003).
[19] J. B. Hannon, C. Klünker, M. Giesen, H. Ibach, N. C. Bartelt, and J. C. Hamilton, Phys. Rev. Lett. **79**, 2506 (1997).
[20] R. K. P. Zia and Z. Toroczkai, J. Phys. A **31**, 9667 (1998).
[21] We have explored the influence of the STM tip on diffusion. The mean-square displacement rate and displacement distribution are not significantly affected by the scan rate or angle relative to the rows of the reconstruction. We have also looked for correlations between adatom displacements and the passage of the tip. We find that 1%–8% of displacements may occur by tip-influence. This small correlation implies that the tip may lower the adatom diffusion barrier by less than 10 meV.
[22] Our model treats a single adatom-defect pair. Adatom interactions must be considered. A repulsive interaction between adatoms nearly excludes adatom occupation of adjacent $5 \times 2$ sites along-chain [7,8]. The effects of adatom crowding and repulsion are estimated by extracting the diffusion statistics of *isolated* adatoms with no neighbors at or within three sites in both directions along-chain. The defect-mediated characteristic shape of their displacement distribution is nearly identical to that for the ensemble, but the average frequency of displacements is $\sim$20% greater. Rate differences of 20% correspond to small (10 meV) modifications to the diffusion activation barriers, or $\sim$20% adjustments of the hop prefactor.
[23] S. Riikonen and D. Sanchez-Portal, Phys. Rev. B **71**, 235423 (2005).
[24] H. S. Yoon, J. E. Lee, S. J. Park, I.-W. Lyo, and M.-H. Kang, Phys. Rev. B **72**, 155443 (2005).
[25] S. C. Erwin (private communication).