Real-Time Observations of Vacancy Diffusion on Si(001)-(2×1) by Scanning Tunneling Microscopy

N. Kitamura, M. G. Lagally, and M. B. Webb
University of Wisconsin-Madison, Madison, Wisconsin 53706
(Received 1 June 1993)

The motion of naturally occurring vacancies on Si(001)-(2×1) has been investigated in real time with scanning tunneling microscopy, using a novel method in which repeated line scans are displayed in the form of a time-versus-position pseudoimage. Individual jumps of the vacancies are resolved. Vacancy diffusion is one dimensional along the dimer row. An activation energy of 1.7 ± 0.4 eV has been measured for the diffusion of the single dimer vacancy.

PACS numbers: 68.35.Fx, 61.16.Ch, 68.35.Dv, 68.35.Ja

Surface defects, such as vacancies, steps, and antiphase domain boundaries, often play a key role in thin-film growth processes. Because of its technological importance, as well as its relatively simple structure, the Si(001)-(2×1) surface has been investigated as a model system for both equilibrium structures and surface kinetic processes. The abundance of surface dimer vacancies and vacancy clusters on Si(001)-(2×1) has been recognized since this surface was first observed with a scanning tunneling microscope (STM) [1]. Theoretical studies have concluded that vacancy formation is mediated by surface strain relaxation and the reduction of dangling bonds [2–4]. Experimentally, there have been several studies of structures [5–7] and kinetics [7–10] of vacancies on this surface. Indirect evidence of the anisotropic diffusion of vacancies was shown in a reflection high-energy electron microscope (RHEEM) study [8], in which the nucleation of large elongated "vacancy islands" was observed during oxygen exposure of Si(001) at temperatures above 773 K. In this study, the preferential nucleation of the vacancy islands on the 2×1 domains was attributed to the anisotropic diffusion of vacancies created by the sublimation of SiO. Recently, from the observation of reflection high-energy electron diffraction (RHEED) intensity oscillations during sputter removal, it was demonstrated that vacancies created by Xe sputtering on Si(001) are mobile at ~723 K [9,10]. If one assumes that sputter etching produces a random distribution of vacancies, oscillations can occur only if the vacancies migrate and coalesce to form vacancy islands. However, some of the conclusions applicable to these artificially created vacancies and vacancy clusters may not be transferable directly to vacancies which are found on clean Si(001).

Scanning tunneling microscopy is ideal for investigating atomic-size defects. Morphological features and structures that are observed at room temperature, however, are usually interpreted as representing a quasiequilibrium structure at some higher freezeout temperature. With the capability to image the surface at elevated sample temperatures, one can obtain direct information on both the structure and the dynamics of defects at the atomic level. In this Letter, we report, using a high-temperature scanning tunneling microscope (HT-STM), the first direct real-time observations of the diffusion of vacancies. In order to improve the time resolution of the dynamic observations, we employ a novel technique in which single-line scans are repeatedly taken along the same path and the time evolution of the scans is displayed in the form of a time-versus-position pseudoimage. Using this technique, we observe individual jumps of dimer vacancies on Si(001), as well as their creation and annihilation. We extract an activation energy for dimer vacancy diffusion from the dependence of the jump rate on temperature.

The STM used in this study was equipped with a Burleigh Inchworm motor for the coarse approach and a tube scanner for the fine approach and scanning. In addition to the tip rastering signals, linear voltage ramps were superimposed on the x and y quadrants of the tube scanner, in order to reduce the relative thermal drift between the tip and the sample to ~0.01 Å/sec. The low drift allows us to rescan repeatedly the identical area for several minutes. A sample bias of -2 V with respect to the tip and a tunneling current of 0.1 nA were used. The Si(001) sample (p doped, 10 Ω cm) was miscut 0.5° toward [110], and was prepared by a conventional procedure that has been described elsewhere [11]. The sample heating in the STM was achieved by passing a dc current through the sample. The sample temperature was determined by bringing a thermocouple (W-5%Re-W-26%Re) in contact with the back side of the sample. In order to avoid sample contamination, this was done only after all the experiments were finished.

We have taken long sequences of topographic images at ~12 sec intervals for over 1 h at sample temperatures between 490–525 K. We observe (i) motion of dimer vacancies and clusters of them, (ii) vacancy motion is virtually restricted along the dimer rows, (iii) clusters spanning more than one dimer row and/or involving more than a few missing dimers tend to have irregular shapes, and often change in both their shape and area between successive image frames, (iv) creation and annihilation with no apparent interactions with steps, are seen. We will discuss the above features in future publications [12]. In the present Letter, we report our quantitative observations of the motion of isolated single dimer vacancies (SDV's), using a repeated-line scan approach.

STM images of "clean" Si(001) have exhibited a large

0031-9007/93/71(13)/2082(4)$06.00

range of vacancy concentrations as well as cluster size distribution. In our case, after the first cleaning, vacancies occupy approximately 1% of the surface sites in the form of dimer vacancies or clusters of them. Both the average size and concentration of vacancies, however, do increase as the sample undergoes repeated thermal cleaning, likely indicating a presence of impurities that build up in time. Therefore, the vacancies we find do not represent an equilibrium concentration intrinsic to the clean Si(001) surface. However, examination of STM "movie" images shows no evidence that individual dimer vacancies are either pinned or directly influenced by impurities. Therefore, it is reasonable to assume that the kinetic behavior of isolated dimer vacancy approximate that of intrinsic dimer vacancies.

We now focus our attention on a quantitative characterization of the motion of the isolated SDV's. In the usual HT-STM operation, a sequence of 2D images is taken as fast as possible and the images are analyzed later on. These 2D images are usually composed of several hundred line scans. If, instead of forming a 2D image, a single line along the same path on the surface is repeatedly scanned, any given site along the scanning path is probed ~ 100 times more frequently than in sequential 2D imaging. We apply this technique to analyze the motion of isolated SDV's.

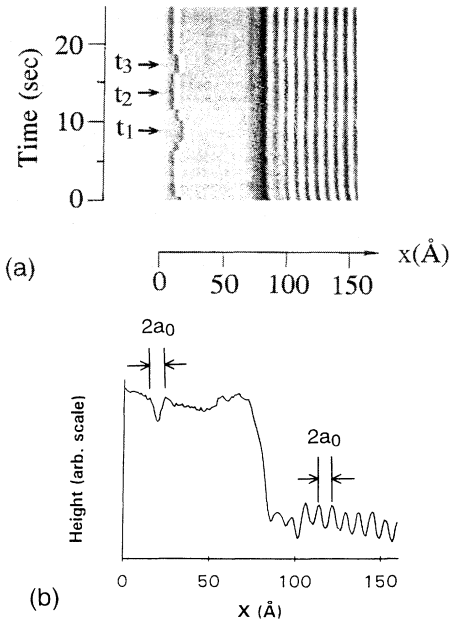

FIG. 1. Time-versus-position measurement of Si(001) vacancy motion. (a) Time-versus-position pseudoimage. In order to show the height contrast on both the upper and lower terraces, the pseudoimage is presented in derivative mode. One can consider the image being illuminated from the left. The image consists of 180 line scans taken at a fixed sample location at a rate of 70 msec/line (140 msec/round trip). The scanning direction was along (across) the dimer rows on the upper (lower) terrace. The corrugation due to crossing the dimer rows is visible on the lower terrace. The jumps of a single dimer vacancy by a distance a_0 is visible as abrupt changes in its position in the dimer row on the upper terrace. (b) A single line scan corresponding to $t=t_1$ in (a).

In Fig. 1(a), we show an example of a time series of such repeated-line scans in the form of a time-versus-position pseudoimage. (This is a 30 sec segment of a pseudoimage lasting several minutes.) The image consists of 180 line scans taken at a rate of 70 msec/line (140 msec per round trip). The image shows a type S_B step [13] at $x \sim 85$ Å. The scan direction was chosen so that it was parallel to the dimer row on the upper terrace which is seen on the left side of the image. The corrugation due to the dimer rows with periodicity $2a_0$ ($a_0=3.8$ Å, the surface lattice constant) is visible for the lower terrace in the right half of the image, whereas in the left half, the image appears smooth because the corrugation along the dimer row is below the vertical resolution of the instrument under the bias condition used. A dimer vacancy imaged at $x \sim 20$ Å is also seen in the plot of a single line scan corresponding to $t=8$ sec [Fig. 1(b)]. The width of the "opening" of the vacancy imaged in Figs. 1(a) and 1(b) is equal to $2a_0$ or the distance between the two adjacent dimers, confirming that it is a single dimer vacancy.

Occasional jumps of the vacancy in the direction parallel to the dimer row are clearly resolved in Fig. 1(a). Each jump is completed within a time period much shorter than that required to obtain a single line scan. Thus, the vacancy displacement is seen as a discontinuity in its "world line." The fact that we see many kinks in the world lines demonstrates the very strong anisotropy in the diffusion.

The images like the one in Fig. 1 show that the unit jump length of the SDV is equal to a_0. Occasionally, SDV's appear to have moved by a distance greater than a_0 during a scan period. However, within statistical error, the frequency of such long jumps can be explained as

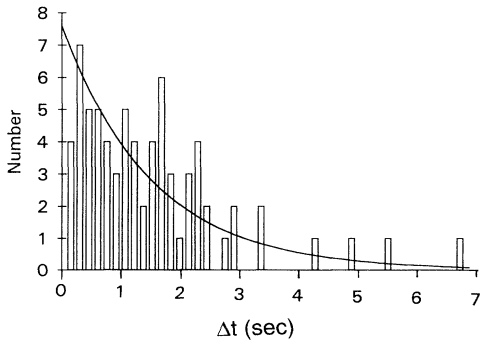

FIG. 2. Measured histogram for the time separation between successive jumps, Δt, for the motion of the single dimer vacancy (SDV) at 507 K. The curve is proportional to $\exp(-\Delta t/\tau)$, where τ is the mean time between jumps.

a result of successive random jumps of a unit distance occurring within the scan period. Analysis of the data shows that the jumps of SDV's are equally probable in both directions. Furthermore, the jump directions for two successive jumps are uncorrelated. In Fig. 2, we show the measured distribution for the time interval between successive jumps Δt. The solid curve is the function $\exp(-\Delta t/\tau)$, where τ is the mean time between successive jumps, which would be expected if the SDV jumps occur randomly in time. These results allow us to treat the SDV motion as a one-dimensional random walk. Figure 3 shows an Arrhenius plot for the jump rate $1/\tau$. The Arrhenius plot gives us an activation energy of $E_a = 1.7 \pm 0.4$ eV and a prefactor of $\tau_0 = 10^{-16\pm4}$ sec. The large ranges of error for the activation energy and the prefactor are mainly due to the rather narrow temperature window available for this type of measurement. The upper temperature limit is such that the mean time between jumps approaches the scan period, whereas the lower temperature limit is determined by the magnitude of the tip-sample drift, i.e., how long the scan can be repeated over a single vacancy. These limitations allow us a temperature window with this particular instrument of $\sim 40\,^{\circ}$C.

A sudden appearance or termination of a vacancy world line can occur either due to a creation and/or annihilation event or to a vacancy jump perpendicular to the dimer row. Judging from videos of 2D images, the former is the dominant effect governing the duration of the world line. Nevertheless, by assuming that the finite duration of world lines is entirely due to motion perpendicular to the dimer row, we can find a generous upper limit on the side hop frequency. Our preliminary measurements show that the duration of world lines is longer than several hundred seconds at 500 K and on the order of 10 sec at 525 K. Thus, we obtain a lower bound for the ratio between the jump frequencies parallel to and perpendicular to the dimer row of 100 at 500 K and 10 at 525 K.

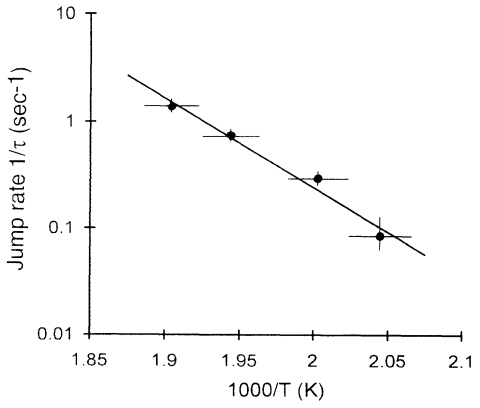

FIG. 3. Arrhenius plot for the SDV jump rate.

We now discuss briefly possible mechanisms for the vacancy motion. Theoretical estimates of the activation energy for the dimer vacancy jump assuming a sequence of simple bond breakings are considerably higher than 2 eV [4,14]. A possible mechanism [15] that circumvents this difficulty involves a coherent exchange of pairs of atoms between the top and the second layer, rather than a simple lateral displacement involving only the top-layer atoms. The place exchange would then proceed as a result of a concerted atomic motion that follows a trajectory that is energetically more favorable than a simple bond breaking. This process guarantees the conservation of the vacancy size during the jump process. The place exchange mechanism is analogous to the adatom jump processes found in some metal systems, in which adatom jumps take place by an exchange of atomic positions between the adatom and the substrate [16–18]. The activation barriers in those cases are found to be significantly lower than what one would expect from simple adatom jumps.

Finally, one may ask if the vacancy motion is in any way assisted by the presence of the STM tip. We rule out this possibility for the following reason. We have measured the mean square displacements of the vacancies from the two-dimensional images taken at 15 sec intervals covering the same region. In this case, a given site is visited by the tip only once in 15 sec. Nevertheless, the mean square displacement is consistent with the measurement that we described in the above repeated-line-scan method, in which each site is revisited every 140 msec. Therefore, the influence of the tip must be so small that a factor of 100 in visits does not change the jump distribution. This is unlike the situation for polar semiconductor surfaces, in which vacancy jumps can be readily induced by the STM tip [19]. It has been demonstrated that a surface vacancy can also be created on Si(001) by applying a voltage pulse between the tip and sample via field evaporation [20–22]. However, such a process requires a significantly higher electric field between the tip and sample than in our present case.

In summary, we have investigated the thermal diffusion of naturally occurring vacancies on Si(001)-(2×1) using a novel application of STM. The vacancy motion is predominantly along the dimer rows. In particular, the diffusion of the single dimer vacancy has been analyzed in detail. The SDV motion can be treated as a one-dimensional random walk along the dimer row with a unit jump length of a_0. We measure an activation energy of 1.7 ± 0.4 eV for its diffusion. We propose that the SDV jump proceeds by a place exchange between the top-layer and the second-layer atom pairs.

We would like to thank Zhenyu Zhang for useful discussions and the suggestion of the model for vacancy motion, and Dr. P. Wagner of Wacker Chemitronics for providing the silicon samples used in this study. This work has been supported by ONR Physics Program and

NSF Grant No. DMR-9104437.

[1] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985).
[2] K. C. Pandey, in *Proceedings of the 7th International Conference on the Physics of Semiconductors,* edited by D. J. Chadi and W. A. Harrison (Springer, New York, 1985), p. 55.
[3] N. Roberts and R. J. Needs, Surf. Sci. **236**, 112 (1990).
[4] J. Wang, T. A. Arias, and J. D. Joannopoulos, Phys. Rev. B **47**, 10497 (1993).
[5] H. Niehus, U. K. Köhler, M. Copel, and J. E. Demuth, J. Microscopy **152**, 735 (1988).
[6] R. J. Hamers and U. K. Köhler, J. Vac. Sci. Technol. A **7**, 2854 (1989).
[7] H. J. W. Zandvliet, H. B. Elswijk, E. J. van Loenen, and I. S. T. Tsong, Phys. Rev. B **46**, 7581 (1992).
[8] H. Kahata and K. Yagi, Surf. Sci. **220**, 131 (1989); Jpn. J. Appl. Phys. **28**, L1042 (1989).
[9] P. Bedrossian, J. E. Houston, E. Chason, J. Y. Tsao, and S. T. Picraux, Phys. Rev. Lett. **67**, 124 (1991).
[10] P. Bedrossian and T. Klitsner, Phys. Rev. Lett. **68**, 646 (1992).
[11] B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **7**, 2901 (1989).
[12] N. Kitamura, M. G. Lagally, and M. B. Webb (to be published).
[13] D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).
[14] Z. Y. Zhang and H. Metiu, Phys. Rev. B (to be published).
[15] Z. Y. Zhang (to be published).
[16] J. D. Wrigley and G. Ehrlich, Phys. Rev. Lett. **44**, 661 (1980).
[17] G. L. Kellogg and P. J. Feibelman, Phys. Rev. Lett. **64**, 3143 (1990).
[18] C. Chen and T. T. Tsong, Phys. Rev. Lett. **26**, 3147 (1990).
[19] Ph. Ebert, M. G. Lagally, and K. Urban, Phys. Rev. Lett. **70**, 1437 (1993).
[20] I.-W. Lyo and Ph. Avouris, Science **253**, 173 (1991).
[21] M. Aono, A. Kobayashi, F. Grey, H. Uchida, and D.-H. Huang, Jpn. J. Appl. Phys. **32**, 1470 (1993).
[22] C. Salling and M. G. Lagally (to be published).

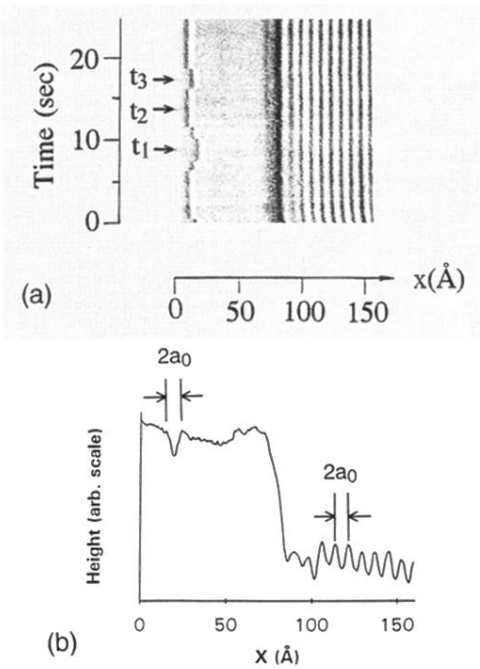

FIG. 1. Time-versus-position measurement of Si(001) vacancy motion. (a) Time-versus-position pseudoimage. In order to show the height contrast on both the upper and lower terraces, the pseudoimage is presented in derivative mode. One can consider the image being illuminated from the left. The image consists of 180 line scans taken at a fixed sample location at a rate of 70 msec/line (140 msec/round trip). The scanning direction was along (across) the dimer rows on the upper (lower) terrace. The corrugation due to crossing the dimer rows is visible on the lower terrace. The jumps of a single dimer vacancy by a distance a_0 is visible as abrupt changes in its position in the dimer row on the upper terrace. · (b) A single line scan corresponding to $t = t_1$ in (a).