RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 8 15 AUGUST 1993-II

Variable-temperature STM measurements of step kinetics on Si(001)

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

Using a variable-temperature scanning tunneling microscope we have measured the time evolution of the atomic-scale morphology of steps on Si(001) at temperatures up to 350 °C. Step-rearrangement events, i.e., local changes in the atomic arrangements, are observed between successive images at temperatures above 225 °C. The observed events always involve single or multiple units of four atoms and occur most frequently at kink sites and at the ends of dimer rows. By measuring the event rate we determine an effective activation-energy barrier of 1.4–1.7 eV. The events cannot be completely characterized as successive random arrangements involving only single units. Rather, correlations are observed between neighboring dimer columns, and the event rate depends on the local atomic-step configuration.

I. INTRODUCTION

A number of surface properties are affected by defects. It is generally believed that defects, such as steps, are active sites on the surface. Defects can control the nucleation and subsequent growth of epitaxial and three-dimensional (3D) overlayers. The chemical reactivity of the surface, as well as the sticking and surface diffusion of adsorbed species can be altered by the presence of defects. To elucidate the role that defects play in these processes it is important to understand some of the fundamental kinetic parameters that control the behavior of surface defects. These include, among others, defect-formation energies, activation energy barriers for defect migration, and defect-defect interaction energies.

Because of its atomic resolution, the scanning tunneling microscope (STM) is inherently well suited for studying surface defects. By making detailed measurements of the morphology of steps and the distribution of defects, previous STM studies have been able to determine quantitatively, for example, step and kink formation energies,[1,2] step-step interactions,[3,4] surface diffusion coefficients of adsorbed species,[5] and sticking coefficients of adatoms[6] and vacancies.[7] These measurements were, however, performed "after the fact," on quenched surfaces, assuming either (1) that the configuration of surface defects (steps, kinks) reflects an equilibrium distribution at some "freeze-out" temperature, or (2) that the model-dependent kinetic parameter (e.g., surface diffusion or edge sticking coefficient) can be extracted from an overlayer adatom- or vacancy-island size distribution or density.

Recently a number of workers have developed the capability to image surfaces with STM at elevated temperatures[8–15] in order to investigate dynamic processes on surfaces. Dynamic processes that have to surmount activation barriers greater than ~0.75 eV require temperatures above room temperature in order to proceed at an appreciable rate. In the current study we investigate the dynamic properties of steps on the Si(001) surface at temperatures up to 350 °C using variable-temperature STM.

The Si(001) surface reconstructs to form rows of dimerized atoms with a 2×1 symmetry. Because of the structure of the diamond lattice, dimer rows on terraces separated by an odd number of monatomic steps are orthogonal. Consequently, there are two inequivalent types of steps. Step segments that run parallel to the upper terrace dimer rows are denoted as SA and step segments that are perpendicular to the upper terrace dimer rows are denoted as SB.[16] On surfaces that are miscut at a small angle toward a [110] direction, alternating steps have a distinctly different character. One step, with the SA segments parallel to the nominal step direction, contains few kinks and appears smooth; whereas the other step, with the SB segments parallel to the nominal step direction, contains many kinks and appears rough. On these surfaces the terraces are denoted as either 1×2 or 2×1. The 1×2 terraces consist of dimer rows that run parallel to the steps and the dimer rows in the 2×1 terraces run perpendicular to the steps. We commonly refer to the dimer rows on the 2×1 terraces as "columns" of dimers. The terrace width at a particular dimer row is indicated by the "height" of the column.

II. EXPERIMENT

The UHV STM is described elsewhere.[11,17] Here we point out some of the salient features of the variable-temperature version. The sample is heated resistively on the microscope stage by applying a voltage from a floating current-limited dc power supply. A potentiometer, the wiper of which is floating at the tip-sample bias, is in parallel with the sample across the terminals of the power supply. The potentiometer is adjusted to compensate for the voltage drop of the heating power supply across the sample. Since the tip is positioned near the center of the sample, the potentiometer is usually set near the middle of its range and adjusted so that zero bias lies somewhere in the middle of the band gap. The applied bias is then within ±0.5 V of the actual tunneling voltage drop.

As the sample temperature is changed, thermal gradients develop that generate thermal drifts. Although the sample holding arrangement is designed to minimize drift, slow long-term drift occurs with a $1/e$ time constant of about 250 min. Because the time constant is long, we can compensate for the drift by adding linear

analog voltage ramps to the scanning piezo. This enables us to scan repeatedly over the same region of the sample within 10 min after the sample temperature is changed by 250 °C. The drift compensation is adjusted periodically to match the decrease in the drift rate with time. With this method we have operated the microscope at sample temperatures up to about 600 °C.

The samples used in this study are 0.5-mm-thick, low-resistivity Si(001) wafers, 3 mm wide, and 12.5 or 25 mm long. The surface is prepared using a standard cleaning procedure,[17] heating the sample *in situ* to 1250 °C. Upon cooling, the sample is transferred to the microscope stage where its temperature can be continuously adjusted as described above. The uncertainty in the temperature is about ±10 °C.

III. RESULTS AND DISCUSSION

Data are acquired as sequences of image frames at a particular temperature. The frame acquisition time is typically 15 sec for a 200×200 Å^2 image. These image frames are chained together to form a "movie image." Surface dynamic events are observed as differences in the atomic configuration between sequential frames. In Fig. 1 we show a sequence of four consecutive images of the surface at 245 °C.

By looking at the differences between consecutive frames, particularly at the rough step, we see that atomic rearrangement events occur at 245 °C on the time scale of the frame rate. For example, inside the circle in Fig. 1, step rearrangement events, i.e., the addition or subtraction of atoms from the ends of the dimer rows, are observed between each frame. All of the events that we measure are comprised of units of four atoms (two dimers). This observation is consistent with the energetically favorable way in which the ends of the dimer rows terminate on the lower terrace,[1,2,13,16,18] which has a periodicity of two perpendicular to the step. Another feature of the data is that we cannot tell where the atoms go or from where they come. The units that detach from one dimer column do not simply reattach at one of the two neighboring columns. In fact, there is no identifiable correlation, within the area of the images, between detaching and attaching units; except, of course, that detailed balance is obeyed. This implies that either the events occur though exchange with the 2D monomer "gas" on the terraces, or there is rapid long-range edge diffusion along the steps. Finally, we note that the formation, diffusion, and annihilation of surface vacancies is also observed in these images. The details of the kinetic behavior of surface vacancies will be discussed elsewhere.[19]

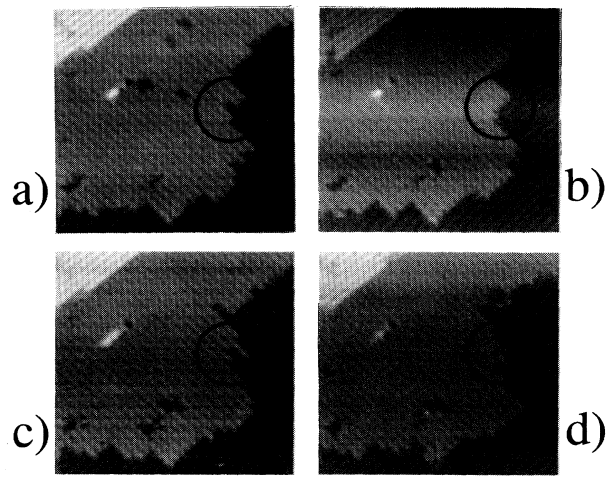

FIG. 1. Four sequential 300×300 Å^2 STM images of the Si(001) surface taken at 245 °C showing step rearrangement events occurring between images. Each image was acquired in about 15 sec.

Although the temperature of the sample is adjusted so that the event rate is sufficiently slow to enable individual events to be distinguished between frames, it is a misnomer to say that these images are taken in "real time." It is more appropriate to say that the STM images are taken in "human time," for the actual atomic-event time scale is many orders of magnitude faster than can be captured by STM. Increasing the data acquisition rate of the microscope by several orders of magnitude will increase the resolution with which events can be distinguished (e.g., allow an increase of the sample temperature and hence the event rate); however, it will *not* allow us to probe the microscopic-atomic details of the single events themselves.

In order to extract quantitative data from the images, the atomic configuration of steps in each frame is digitized.[1] The differences between sequential images are analyzed to extract the event statistics. We illustrate this schematically in Fig. 2. In Fig. 2(a), the column height as a function of position, i.e., configuration of the rough step, in two sequential images is indicated as the solid and dashed lines. We plot the column height difference Δh between the two frames in Fig. 2(b). We analyze these data on several levels. First, we treat the column height changes within an "independent-event" model where we simply measure the probability of any column changing by Δh units. On a deeper level, we measure correlations in the events: correlations in the probability of neighboring columns changing, and the dependence on the initial local step configuration of the probability that a column will change. We will see that the rearrangement events *are* significantly correlated. It is nevertheless instructive to examine the data within the independent-event model.

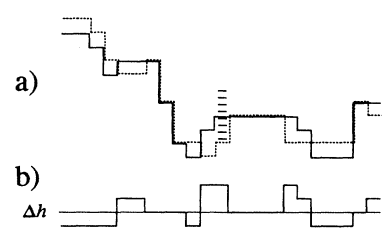

FIG. 2. A schematic representation of the digitized steps. (a) We show the column height along the rough step for two sequential images as the solid and dashed lines. (b) A plot of the column height difference Δh between the two sequential images as a function of position.

The measured probability $P(\Delta h)$ of observing a net column change of Δh units at 230 °C after 13 sec (the image acquisition time), is plotted in Fig. 3. In the independent-event model each column is performing a random walk within the time interval Δt of the acquisition of a single image. If individual events are made up of only single-unit changes, then the probability of observing a net column height change of Δh units after Δt seconds is

$$P(\Delta h)=\exp(-R\Delta t)(R\Delta t/2)^{|\Delta h|}\sum_{n=0}^{\infty}\frac{(R\Delta t/2)^{2n}}{(N+n)!n!}$$
$$=\exp(-R\Delta t)I_{|\Delta h|}(R\Delta t)\ , \qquad (1)$$

where R is the single-event probability per unit time, and $I_{|\Delta h|}$ is the $|\Delta h|$th modified Bessel function. We have plotted this function in Fig. 3 as the solid line for $\Delta t=13$ sec and the best fit, $R=0.025\ \text{sec}^{-1}$.

In order to quantify the event dynamics within the context of this simple model, it is possible to extract an "effective" activation energy. We use this effective energy barrier to describe the kinetics of the step rearrangements in the context of individual four-atom-unit events. The microscopic details of a single-unit event are inaccessible to STM investigation. We can only speculate as to its exact nature; that is, whether all four atoms leave at once, or atom pairs dissociate, or there exists a rate limiting step for the first atom to leave followed immediately by the dissociation of the other three, etc., cannot be determined. Therefore, the use of the term "effective" is an important qualification in discussing a derived activation energy for this system.

If we assume that we have a simple activated process with a prefactor of 10^{13}–$10^{15}\ \text{sec}^{-1}$, then using the event rate measured at 230±10 °C from the independent-event model yields an effective activation energy of 1.4–1.7 eV. We also have an idea of how the event rate changes with temperature. At about 250 °C the events occur on the time scale of the image frames, that is, ~1 every 10 sec. On the other hand, at around 325–350 °C the events occur on the time scale of the individual scan *lines* within a frame, or ~1 every 0.1 sec. A factor of 100 change in the rate over 75–100 °C corresponds to an effective activation energy of 1.1–1.4 eV. The total activation energy (2.2 eV) for a process on the Si(001) surface that involves the mass transport of atoms from one step to a neighboring step has been measured.[20] This activation energy was evaluated as the sum of two parts: the energy to form a diffusing species (presumably the atom-step detachment energy), and the migration energy. The Si adatom migration energy barrier (0.7 eV) has been separately measured.[5] It follows that the difference between these two measurements (1.5 eV) is the activation energy for atom detachment from steps. This is in reasonable agreement with the value extracted from our simple independent-event model.

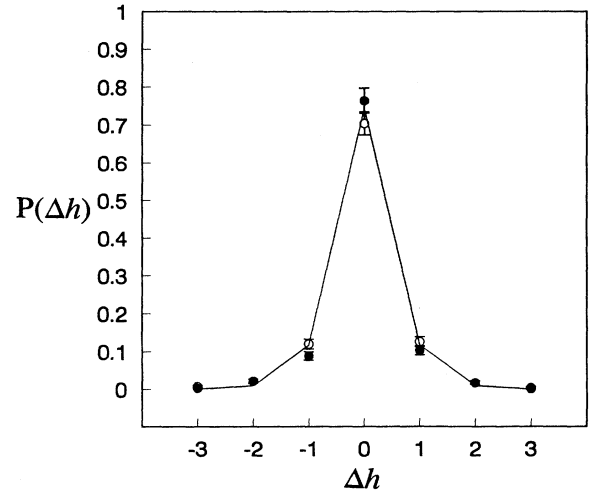

FIG. 3. The measured probability of a column changing by Δh units as a function of Δh. The two data sets were taken from a sample at 230 °C with an image frame acquisition time Δt of 13 sec and are comprised of several hundred nonzero events out of ~750 potential event sites. The solid line is a fit to the independent-column model.

If we consider only the column height changes, then the measured data are described reasonably well by an independent-event model from which an effective activation energy can be extracted. However, as mentioned above, the events are not strictly independent—they exhibit significant correlations in both the nearest-neighbor-column event rate and in the configuration-dependent event rate. Once the step configurations in the image frames are digitized, it is trivial to extract a myriad of correlations, limited only by the statistics.

We consider first the joint probability of changes in two neighboring columns. We define the probability that *both* neighboring columns change either in the positive or negative directions as $P(++)$ and $(P--)$, respectively. The probability that neighboring columns change in opposite directions is defined as $P(+-)$ and $P(-+)$. Any independent-event model would predict that all four of these possibilities is equally likely. From the data taken at 230 °C, $\Delta t=13$ sec, we measure $P(++)=0.042$, $P(--)=0.040$, $P(+-)=0.012$, and $P(-+)=0.018$. The probability that two neighboring columns move together, either into or out of the terrace, is almost a factor of 3 times the probability that neighboring columns move in opposite directions. Earlier we mentioned that the step rearrangement events are not observed as being comprised of units that simply move from one column to the next, for if this were the case we would measure a strong anticorrelation in the joint probability of neighboring column changes. The step rearrangement events are, however, comprised of some type of correlated motion involving neighboring columns.

We consider now how the event rate depends on the local step configuration. Every column is grouped into one of two classes. As illustrated in Fig. 4, a "kinkless" column is defined as a dimer row that terminates at the step with no neighboring kink, whereas, a "kinked" column terminates with at least one neighboring kink of arbitrary length. Dividing the columns into these classes enables us to measure and compare the relative probabilities that an event will occur as a function of the local step configuration. At 230 °C the relative probability that an event occurs at a kinked column is 2.5–3 times higher

FIG. 4. A schematic representation of "kinkless" vs "kinked" columns. (a) A kinkless column is defined as a dimer row that terminates at the step with no neighboring kink, whereas (b) a kinked column terminates with at least one neighboring kink of arbitrary length.

than the relative probability that an event occurs at a kinkless column. This implies an effective activation energy difference of 0.030–0.054 eV for events occurring at the two classes of sites. (As an aside, we note that this measured difference in effective activation energy is of the same order as the difference in configurational energy between kinked and kinkless columns.[1,2])

IV. CONCLUSIONS

In summary, we have measured the time evolution of the atomic-scale arrangement of steps on Si(001) at temperatures up to 350 °C using a variable-temperature STM. Step rearrangement events are observed between successive images at temperatures above 225 °C. The observed events always involve single or multiple units of four atoms and occur most frequently at kink sites and at the ends of dimer rows. By measuring the event rate, within the context of an independent-event model, we determine an effective activation energy barrier of 1.4–1.7 eV. Correlations are observed between neighboring dimer columns, and the event rate depends on the local atomic-step configuration. By examining the correlations we see that the microscopic details of the step rearrangement kinetics are quite complicated and, in fact, cannot be completely described by a simple model. This information could not have been obtained from after-the-fact experiments that rely predominantly on kinetic models. We have begun to elucidate some of the processes that are involved in atom detachment and attachment at steps.

ACKNOWLEDGMENTS

We would like to acknowledge useful discussions with Mike Schacht regarding the independent-event model. We thank Dr. P. Wagner of Wacker Chemitronics, Burghausen, Germany for supplying many of the samples used in this study. This research has been supported by NSF Grant No. DMR-9104437 and in part by the ONR Physics Program.

*Permanent address: Division 1114, Sandia National Laboratories, Albuquerque, NM 87185.

[1]B. S. Swartzentruber, Y. W. Mo, R. Kariotis, M. G. Lagally, and M. B. Webb, Phys. Rev. Lett. **65**, 1913 (1990).

[2]H. J. W. Zandvliet, H. B. Elswijk, E. J. van Loenen, and D. Dijkkamp, Phys. Rev. B **45**, 5965 (1992).

[3]B. S. Swartzentruber, N. Kitamura, R. Kariotis, M. G. Lagally, and M. B. Webb, Phys. Rev. B **47**, 13 432 (1993).

[4]X. S. Wang, J. L. Goldberg, N. C. Bartelt, T. L. Einstein, and E. D. Williams, Phys. Rev. Lett. **65**, 2430 (1990); J. L. Goldberg, X. S. Wang, J. Wei, N. C. Bartelt, and E. D. Williams, J. Vac. Sci. Technol. A **9**, 1868 (1991); J. L. Goldberg, X. S. Wang, N. C. Bartelt, and E. D. Williams, Surf. Sci. Lett. **249**, L285 (1991).

[5]Y. W. Mo, B. S. Swartzentruber, R. Kariotis, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **63**, 2393 (1989); Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, *ibid.* **66**, 1998 (1991).

[6]Y. W. Mo and M. G. Lagally, Surf. Sci. **248**, 313 (1991); Y. N. Yang, Y. S. Luo, and J. H. Weaver, Phys. Rev. B **45**, 13 803 (1992).

[7]P. Bedrossian and T. Klitsner, Phys. Rev. Lett. **68**, 646 (1992).

[8]J. W. M. Frenken, R. J. Hamers, and J. E. Demuth, J. Vac. Sci. Technol. A **8**, 293 (1990).

[9]S. Kitamura, T. Sato, and M. Iwatsuki, Nature **351**, 215 (1991).

[10]R. M. Feenstra, A. J. Slavin, G. A. Held, and M. A. Lutz, Phys. Rev. Lett. **66**, 3257 (1991).

[11]B. S. Swartzentruber, Ph. D. thesis, University of Wisconsin—Madison, 1992.

[12]E. Ganz, S. K. Theiss, I. S. Hwang, and J. A. Golovchenko, Phys. Rev. Lett. **68**, 1567 (1992).

[13]H. J. W. Zandvliet, H. B. Elswijk, and E. J. van Loenen, Surf. Sci. **272**, 264 (1992).

[14]A. Feltz, U. Memmert, and R. J. Behm, Chem. Phys. Lett. **192**, 271 (1992).

[15]For a recent review see, H. Tokumoto and M. Iwatsuki, Jpn. J. Appl. Phys. **32**, 86 (1993).

[16]J. D. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).

[17]B. S. Swartzentruber, Y. W. Mo, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **8**, 210 (1990).

[18]T. W. Poon, S. Yip, P. S. Ho, and F. F. Abraham, Phys. Rev. Lett. **65**, 2161 (1990); Phys. Rev. B **45**, 3521 (1992).

[19]N. Kitamura, M. G. Lagally, and M. B. Webb (unpublished).

[20]M. B. Webb, F. K. Men, B. S. Swartzentruber, R. Kariotis, and M. G. Lagally, in *Kinetics of Ordering and Growth at Surfaces,* edited by M. G. Lagally (Plenum, New York, 1990); Surf. Sci. **242**, 23 (1991).

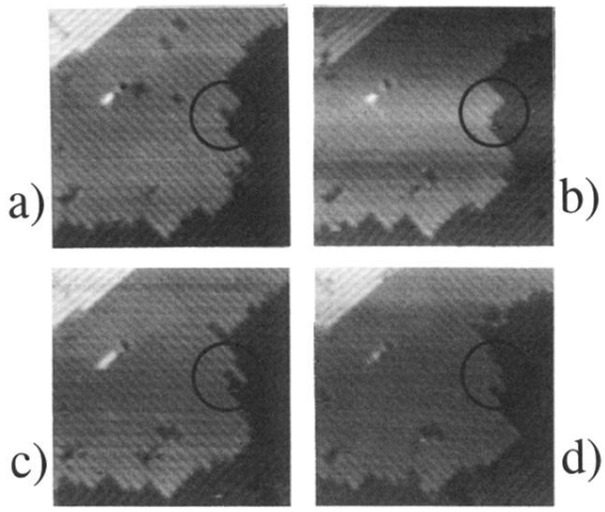

FIG. 1. Four sequential 300×300 Å^2 STM images of the Si(001) surface taken at 245 °C showing step rearrangement events occurring between images. Each image was acquired in about 15 sec.