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The dynamics of the flip-flop motion of single buckled dimers of Si(100) was elucidated by locating the tip of a scanning tunneling microscope over a single flip-flopping dimer and measuring the tunneling current (time trace). Based on a statistical analysis of the time trace, we succeeded in estimating the activation energy and the energy splitting between the two stable configurations of buckling. Strong dependence of the dynamics of the flip-flop motion on the local environment was found: Activation energy differs significantly (directly measured 32 meV, estimated ~110 meV) for dimers in different domains.

Progress in nanotechnology and the general trend to fabricate devices on an ever-smaller dimension spur the demand to understand the local characteristics (electronic, optical, and dynamical) of the surface at the atomic scale. This is because the atomic scale local characteristics of the surface influence fundamental processes (e.g., crystal growth, chemical reaction, and etching) that are involved in fabricating nanostructures. Influence of the fluctuation of the atomic scale local characteristics would be smeared out on a macroscopic scale, though it would become increasingly important at smaller scales.

On the Si(100) surface, which is the standard template of modern silicon technology, the buckled dimers are the basic building blocks of the surface reconstruction. According to the symmetry of the structure, there exist two identical stable configurations for the buckling [look at schematic Fig. 1(a)]. Buckling and dimerization generate a strong stress field on the surface that is possible to partially relax by an antiferromagnetic ordering of the buckled dimers. This effect leads to a strong- and long-ranged correlation between the configuration of the dimers. Defects, steps, and impurities disturb this ordering, and, as a result, the local characteristics (configuration, phase transition temperature, and electronic structure) of the surface show a strong atomic scale local fluctuation [1–12]. For example, the S_A steps are reported to suppress the symmetric-buckled phase temperature observed around 200 K [6].

One particular feature of the dynamics of the buckled dimers is the flip-flop motion; i.e., at room temperature, the dimers are vibrating between the two possible configurations. Any local fluctuation of the dynamics of the flip-flop motion would seriously influence the local properties of many important processes such as epitaxial growth, etching, and chemical reaction. In this sense, it is very important to measure the dynamics of the flip-flop motion and spatially map out its local fluctuation.

Recently, Sato *et al.* have shown that the flip-flop motion of the buckled dimers of Ge(100) can be observed by scanning tunneling microscopy (STM) at reduced temperatures [12]. They noticed flickering features at particular regions in the STM images of the dimers that they interpreted to be caused by a sudden change of the height of the dimer as a result of a flip-flop motion. When the tip was located above the flickering features, the tunneling current switched between two particular values. In this way, several (up to ten) consecutive flip-flop events of a single dimer were observed.

In this article, we used this method to observe the atomic scale local fluctuation of the dynamics of the flip-flop motion of Si(100). A large accumulation number (up to 200 000) of sequential dynamical flip-flop events of a single dimer enables one to carry out quantitative statistical analyses, from which we succeed in estimating the activation energy and the energy splitting between the two configurations of buckling. Spatially mapping of the dynamics of single dimers shows that the dynamics differs significantly from dimer to dimer and domain to domain. Our results show that the atomic scale local environment of the surface, e.g., surrounding defects, steps, and domains, seriously influences the dynamics of the surface.

Standard methodology was employed to fabricate a clean Si(100) surface [11]. Figure 1(b) shows an STM image of the clean Si(100) surface obtained at 70 K. In both sides of the image, static buckled dimers aligned in the $c(4 \times 2)$ phase that belong to different domains are observed [13]. In the middle, dimers appear somewhat more symmetric and numerous flickers are observed here and there. An enlarged image [Fig. 1(c)] shows that the flickering features are observed only in particular regions, excluding the possibility of flickering features caused by a noisy tip. A careful registry reveals that the flickering regions are located on top of the atoms of the dimers. One scanning line was extracted and displayed with the envelope curves of the flickering features [Fig. 1(d)].

Based on this finding, we placed the tunneling tip over a preselected flickering feature and measured the tunneling
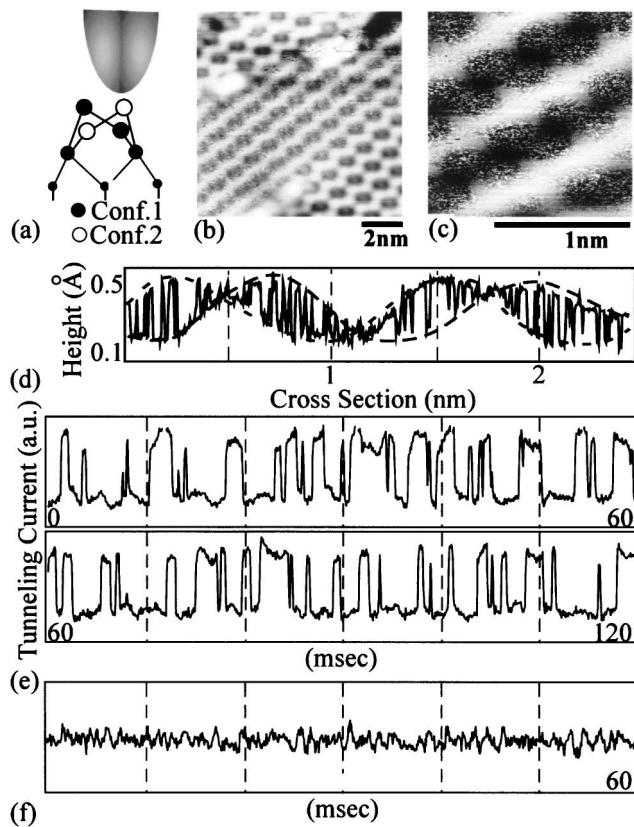
FIG. 1. (a) Schematic of the two stable configurations of a buckled dimer. Assignment of configuration 1 or 2 is an arbitrary choice provided the same rules are adopted for all of the dimers. (b) An STM image showing coexistence of flip-flopping and static dimers. (c) Enlarged STM image of the middle region of (b). (d) One scanning line of (c). Sample preparation procedure: Si(100) samples were prebaked at ~600 °C for 12 h followed by a flashing at 1200 °C for 30 s, and an additional flashing (~5 s). Phosphorus-doped (0.1 Ω cm) Si samples were used. Base pressure: 3×10^{-9} Pa. All of the measurements were carried out at 70 K. (e) Time trace of an atom of flip-flopping dimer. Sampling rate 16.7 kHz. (f) Time trace of an atom of a static buckled dimer. Imaging conditions: $V_s = +0.6$ V, $It = 1.0$ nA, $T = 70$ K.

current, a typical example shown in Fig. 1(e). Immediately, it is apparent that the tunneling current switches to and fro between two particular values that reflect the two possible configurations of buckling. We conclude that we are observing the flip-flop motion. Switching was not observed in the time traces obtained on static buckled dimers [Fig. 1(f)]. The sampling rate was 16.7 kHz, and, for this particular case, frequency of the flip-flop motion ν was 0.81 kHz. Typical time traces of the flip-flop motion of a single dimer consisted of ~500 000–1 500 000 sampling points, and contains ~20 000–200 000 flip-flop events.

From the time traces, we calculate the histogram, $H(t)$, of the interval between flip-flop events [Fig. 2(a)]. If we assume a stochastic process, an assumption whose validity would be addressed below, $H(t)$ should be described by a simple equation as

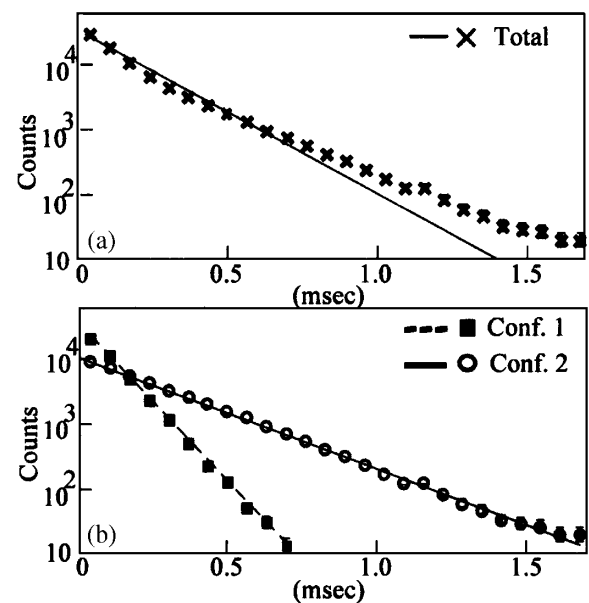$$H(t) = Np(1 - p)^t, \qquad (1)$$

FIG. 2. (a) Total interval histogram of a single flip-flopping dimer at 70 K with the theoretical curve based on a random event. (b) Interval histograms of the two configurations and their corresponding theoretical curves. Note: a different dimer from that shown in Fig. 1.

where p is the probability to flip-flop, N is the number of flip-flop events, and t is time. Since N and p can be determined from the time trace, no fitting parameter exists, and $H(t)$ can be obtained solely, displayed in Fig. 2(a) as the real line. The fit of Eq. (1) to $H(t)$ is substantial at short intervals, though deviates significantly at long intervals. We can definitely state the existence of this deviation because the error bar is small even at long intervals, a situation that is made possible due to large N. The failure of Eq. (1) is because the dimer feels a preference for one configuration. $H(t)$s of the two configurations (configurations 1 and 2) are deduced individually from a time trace with their corresponding theoretical curves [Fig. 2(b)]. Immediately, it is apparent that the average intervals of the two stable configurations are different and that matching between the experimental data and theoretical curves is excellent. Hence, the total interval histogram of a buckled dimer can be described as

$$H(t) = \frac{N}{2} p_1(1 - p_1)^t + \frac{N}{2} p_2(1 - p_2)^t, \qquad (2)$$

where p_1 and p_2 are the probability to flip-flop at configurations 1 and 2, respectively. $N/2$ comes from the switching characteristic of the flip-flop motion. The characteristics of the total histogram at long (short) intervals are determined by the histogram of configuration 1 (2) [configuration with longer (shorter) mean interval]. This is the reason of the deviation in Eq. (1) [$p_1 = p_2$ gives Eq. (1)].

The influence of the local environment on the dynamics of the flop-flop motion can be mapped out by executing the measurements on neighboring dimers. We found that the details of the dynamics of the flip-flop motion

differ from dimer to dimer. Time traces of 11 dimers in the same dimer domain were measured, of which four examples are shown in Figs. 3(a)–3(d) with their locations indicated in Fig. 3(d). In some cases, a preferred configuration exists which has a strong tendency to switch alternatively both in the dimer and dimer row directions [Figs. 3(a)–3(c)]. In other cases, no preferred configuration was found [Fig. 3(d)]. All of the dimers measured in this domain had a similar ν on the range of 1–2 kHz. This was not a peculiar case, and, for all of the measured domains (more than ten), most of the dimers, except those at the boundaries, had a similar ν that we nominate as the average flip-flop frequency of a domain, ν_{dom}.

From domain to domain, ν_{dom} varies many orders, an aspect demonstrated by three time traces [Fig. 4(a)] taken from dimers that belong to different domains. In fact, the time traces presented in this article represent cases of which ν_{dom} occasionally fell into the bandwidth of the preamplifier, and most of the apparent symmetric dimers are flip-flopping much faster, thus they must have a smaller activation energy, E [14]. On the other end, the static buckled dimers that constitute most of the surface can be considered as dimers that have larger E. At this stage, no apparent relationship was found between ν_{dom} and the size and shape of the domains.

A further statistical analysis based on the autocorrelation function provides deeper insight of the nature of the flip-flop motion. We assume stochastic dynamics, and adopt a doubled well potential energy curve [Fig. 4(b)] of a function of the tilting angle, θ, to describe the flip-flop dynamics. The two global minimums at $\pm\theta_0$ represent the two stable buckling configurations, and the transition rate constants between them are taken as k_1 and k_2. Furthermore, we assume thermal equilibrium at temperature $T = 70$ K. The autocorrelation function of the configuration of a dimer, separated by delay τ, is defined as

$$g(\tau) = \langle S(t + \tau)S(t)\rangle/\langle S(t)\rangle^2, \qquad (3)$$

where $S(\tau) = \pm 1$ corresponds to the two stable configurations at $\pm\theta_0$. A simple probability calculation based on the stochastic scheme leads to the following theoretical expression for the correlation function:

$$g(\tau) = 4\frac{k_1 k_2}{(k_1 + k_2)^2} e^{-(k_1+k_2)\tau} + \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2. \qquad (4)$$
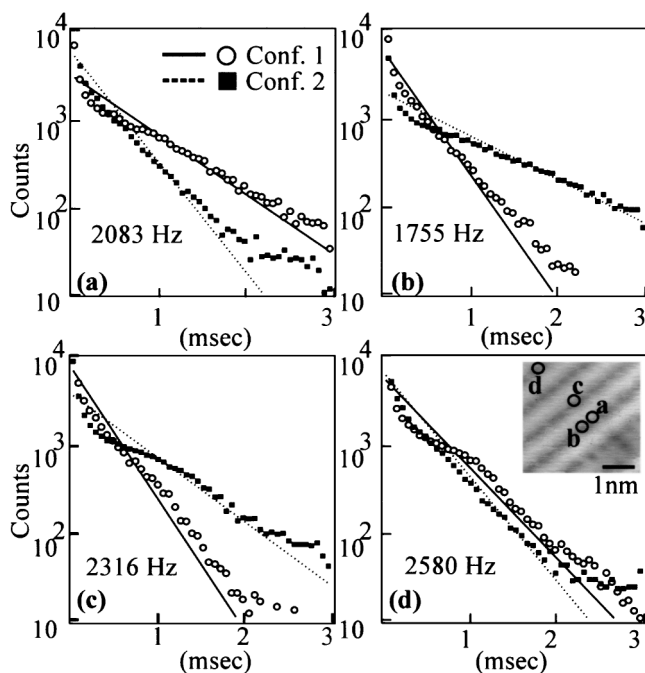
FIG. 3. Interval histograms (configurations 1 and 2) of four dimers that belong to a same domain with lines of theoretical predictions. Locations of the dimers are shown in the inset of (d). Imaging conditions: $V_s = +0.6$ V, $I_t = 1.0$ nA, $T = 70$ K. The average flip-flopping frequencies are displayed in the figures. Note: This experiment is extremely sensitive to noise, and the small deviations from the theoretical lines are caused by bubbling of liquid nitrogen.
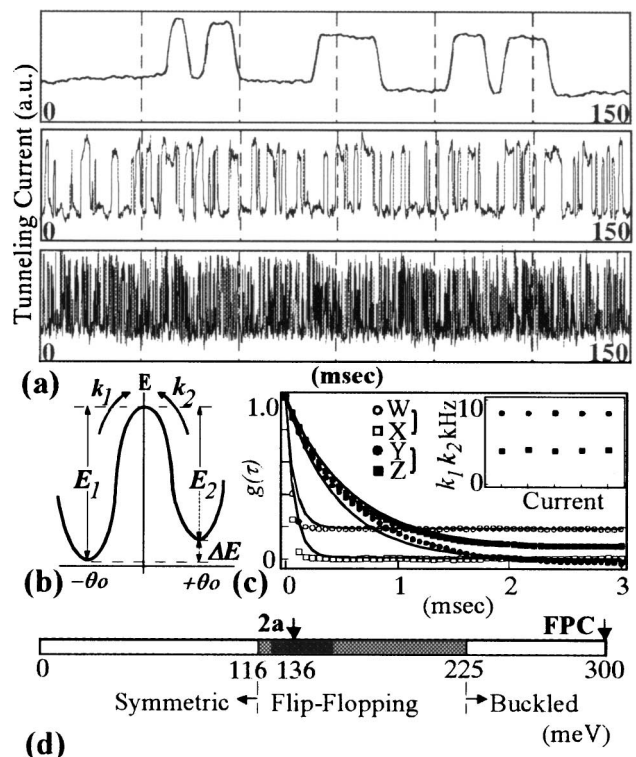
FIG. 4. (a) Three time traces of single dimers that belong to different domains. All of the other measured dimers in the domains showed a similar flip-flop frequency. Imaging conditions: $V_s = +0.6$ V, $I_t = 1.0$ nA, $T = 70$ K. (b) A schematic of a doubled well potential energy curve. (c) Autocorrelation functions of four flip-flopping dimers of where (W, X) and (Y, Z) belong to the same domain at 70 K. The inset shows the dependence of the rate transitions, k_1, (circles) and k_2, (squares) on the tunneling current (200 pA, 500 pA, 1 nA, 2 nA, 4 nA, from the left). $V_t = +0.6$ V, $T = 70$ K. All of the measurements were carried out on the same dimer, and for each condition more than 50 000 flip-flop events were counted. (d) The black and gray bars show the measured and estimated relative difference in E, respectively. The absolute values in the bottom were obtained with an assumption of $\nu_0 = 4.8 \times 10^{12}$ Hz. 2a: E of the dimer in Fig. 2(a). FPC: E obtained by first principle calculation (Ref. [17]).

No fitting parameter exists in Eq. (4) because k_1 and k_2 can be determined from the time traces. Figure 4(c) shows the autocorrelation functions of four dimers $W \sim Z$, with the corresponding theoretical curves. Dimers (X, Y) that have no preferred configurations obey $\lim_{\tau \to \infty} g(\tau) = 0$, while those (W, Z) that have a preferred configuration do not. Correlation functions of dimers (W, X) that belong to the same domain show a decay characteristic on the same time scale that is different from the other dimers (Y, Z) located in a different domain. Matching between the theoretical and experimental autocorrelation functions is substantial; thus, we conclude that the flip-flop motion is indeed a stochastic process described by a two level system and that thermal equilibrium holds for dimers having ν above 1 kHz at 70 K.

As a result of coupling to the local environment, individual dimers feel a preference for one configuration that gives an energy splitting, ΔE. Under thermal equilibrium, ΔE can be obtained by a detailed balance: $k_1/k_2 = \exp(-\Delta E/k_b T)$. The energy splitting, ΔE, was measured for 47 dimers, and lay in the range from 0 to 10 meV (for most cases only a few meV). If we assume that the attempt frequency, ν_0, is independent of site, the relative difference of E among dimers can be obtained by comparing the average flip-flop transition rates. For the slowest and fastest flip-flopping dimers shown in Fig. 4, the difference in E is 32 meV. However, as mentioned above, there are dimers both at the faster and slower ends. If we estimate 20 kHz (sampling rate) as the slowest limit for the symmetric dimers, and 2.7×10^{-4} Hz (one flip-flop per hour, a typical observation time) as the fastest limit for the static buckled dimers, the relative difference in E would be 110 meV. Obviously, faster and slower dimers exist; hence, the maximum difference should be larger.

Knowledge of ν_0 is required to obtain the absolute value of E. However, conventional Arrhenius plot analysis cannot be applied, since the dynamics seriously differs from dimer to dimer; thus, the measurement must be carried out on the same dimer at different temperatures, a task that is intractable for our STM. Kawai [15] has estimated $\nu_0 = 4.8 \times 10^{12}$ Hz from the energy of the dimer rocking mode associated to buckling (20 meV) measured by electron energy loss spectroscopy [16]. If we use this value, E of the dimer in Fig. 2(a) is 136 meV. All of the estimated Es are presented in the energy bars in Fig. 4(d), where FPC indicates E calculated by first principle methods [17]. On an ideal and complete Si(100) surface without defects and steps, all of the dimers are identical and they should flip-flop with the same E (FPC). This means that the wide range of the activation energy must be induced by defects and steps on the surface. We believe that the long-ranged strain field produced by steps and defects induces this sophisticated and intriguing effect.

When a dynamical process is studied by STM, the influence of the tip and the electric field applied to the tunneling gap must be carefully addressed. We measured the time traces of the same single dimer with various tunneling conditions (tunneling current: $I_t = \sim 200$ pA-4 nA, for each condition over 50 000 events were counted) and obtained the interval histograms and autocorrelation functions (not shown), and calculated the transition rates [inset of Fig. 4(c)]. All of them were independent of the tunneling conditions; hence, we conclude that the influence of tip is negligible at typical tunneling conditions.

In conclusion, we have elucidated that the dynamics of the flip-flop motion strongly depends on the local environment and that the activation energy must vary at least 110 meV for dimers belonging to different domains.

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