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Extrinsic structure changes by STM at 65 K on Si(001)

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Using variable-temperature scanning tunneling microscopy to image buckled dimers in a $C(4\times2)$ phase on Si(001) at 65 K under conventional scanning conditions, we have observed symmetric dimers in the $P(2\times1)$ phase and the flip-flop motion of dimers at the boundary of two different phases. Careful investigation shows that higher tunneling currents produce larger areas of $P(2\times1)$ phase and higher flip-flop rates of individual dimers. We have measured and plotted the flip-flop rate as a function of current. The origin of the phase transition and the flip-flop dimer motion are discussed.

The Si(001) surface has attracted much attention over the last 30 years because of its many technological applications. Since the images of Hamers *et al.* in 1986, scanning tunneling microscopy (STM) has played an important role in obtaining detailed information about the Si(001) surface on an atomic scale.[1] Some of the more interesting features of a Si(001) surface are the surface reconstruction by formation of dimers, their row arrangement, and buckling because of Peierls distortion.[2] STM images of dimers at room temperature appear usually as symmetric patterns because of rapid thermal flip-flop motion of the buckled dimers. Asymmetric dimers were successfully imaged by Wolkow *et al.*[3] in 1992 by lowering the surface temperature to 120 K. Since buckling can occur in two orientations, several phases are possible corresponding to different arrangements of alternately buckled dimers. Wolkow showed that the honey comb appearance of the $C(4\times2)$ phase was more stable than the $P(2\times2)$ phase. This result agreed with previous low-energy electron diffraction measurements.[4]

However, recent STM images of Si(001) surfaces at low temperatures have presented novel results, first the observation of the $P(2\times2)$ phase[5] and then the observation of a $P(2\times1)$ phase as composed of symmetric dimers[6] at 6 K. Thus naturally the question arises which phase on Si(001) would be most stable below 120 K. Recent theoretical calculations have shown that the $C(4\times2)$ phase has an energy that is lower by a few mV per dimer compared with that of the $P(2\times2)$ phase.[7] However, to fully understand this issue it might be necessary to include the possibility of extrinsic effects, i.e., tip-to-surface interactions on the Si(001) surface by the STM observations themselves, especially at low temperatures. Such tip-surface interactions have, for example, been observed at 80 K on Ge(001).[8] Furthermore, tip-surface interactions in STM of the Si(001) surface were suggested theoretically in 1993.[9]

In this work, we present an observation of tip-to-surface interactions by demonstrating the variation of STM images of Si(001) surfaces at 65 K under different scanning conditions. We confirmed the two phases, $C(4\times2)$ and $P(2\times1)$ on Si(001), and found that the $P(2\times1)$ phase becomes locally more stable as tunneling current increases. We also present the first proof that flip-flop motion of asymmetric Si dimers at the boundaries of the phases is indeed induced by the STM tip, and demonstrate the dependence of the flip-flop rate on tunneling current. Finally, we discuss the origin of the phase changes and the flip-flop motion.

All measurements were performed in an ultrahigh vacuum chamber at $<10^{-11}$ torr. Antimony-doped, *n*-type surfaces (0.05–0.09 Ω cm) and Boron-doped, *p*-type Si(001) surfaces (0.01–0.02 Ω cm) were annealed by conventional current heating.[10] This produces surfaces of an exceptionally low defect density. The samples were then transferred onto the cryogenic STM stage and cooled down to 65 K. STM imaging was performed for sample biases between $+1.5$ and -2 V and tunneling currents between 25 pA and 1 nA. To find the rate of the flip-flop motion of buckled dimers versus current, we measured the tunneling current with the feedback turned off after positioning the STM tip directly over the brightest point of a dimer in a defect-free area.[11] Two discrete values of tunneling currents can be observed when a dimer flips up and down under an STM tip.[12]

Four images of the same location on a *P*-type Si(001) surface at 65 K under various tunneling conditions are presented in Fig. 1. The surface exhibiting a $C(4\times2)$ phase consists mostly of buckled dimers with only a few symmetric dimer rows; it was imaged with a -1.2 V sample bias and a 25 pA tunneling current as shown in Fig. 1(a). Symmetric dimer rows, marked by arrows, are located at the antiphase boundaries of the two alternate $C(4\times2)$ phases.[13] Buckling is weakened at the boundaries of the two phases and fluctuates even at 65 K.[14] In addition, there are a few dimers that extend from the ledge of an *A*-type step edge. They appear as symmetric dimers in the image; for the time being we will call these ''symmetric dimers of a $P(2\times1)$ phase'' and discuss later whether the $P(2\times1)$ phase consists of symmetric dimers or asymmetric dimers with rapid fluctuation. Surpris-

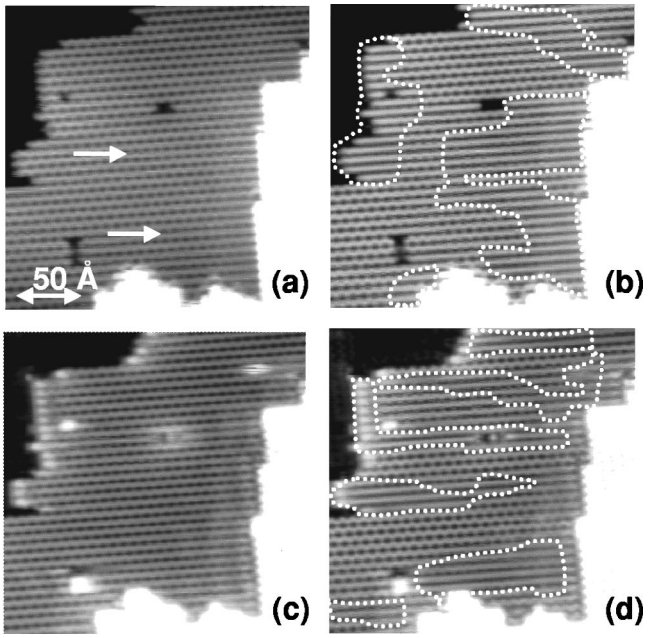

FIG. 1. STM images of the Si(001) surface at 65 K showing the expansion of the $P(2\times1)$ phase in a bed of $C(4\times2)$ phases under increasing current, (a) -1.2 V sample bias with 25 pA and (b) 1 nA. The $P(2\times1)$ phase is surrounded by dotted lines. (c) 1 V sample bias with 25 pA, and (d) 1 nA. The location of the $P(2\times1)$ phases, indicated by dotted lines, is different from that of filled state images. Since carbon-containing molecules show as dark spots (similar to defects) under negative bias of (a) and (b) and as white spots at positive bias in as (c) and (d), a careful inspection of the images seems to indicate that at least some of these features are absorbed molecules, others are simple defects.

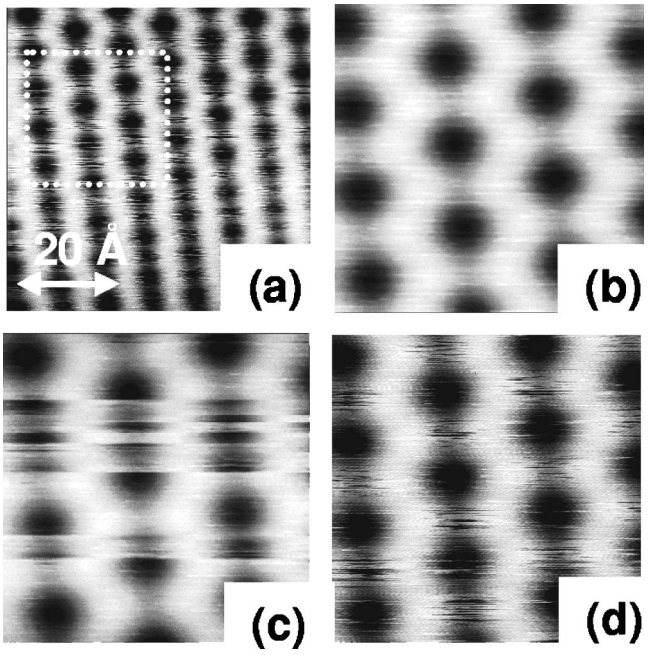

FIG. 2. A set of zoom-in STM images of the Si(001) surface at 65 K that shows STM-induced structure changes: (a) An image from the boundary between the $P(2\times1)$ and $C(4\times2)$ phases with -1.2 V sample bias and 1 nA current. (b) A zoom-in image of the box-area of (a) at 25 pA (c) with 0.1 nA current. It shows the exchange of the alternate $C(4\times2)$ phases. (d) At 1 nA the motion of flip-flops appears as dents.

ingly, a current increase up to 1 nA at the same bias voltage enlarges the area of the $P(2\times1)$ phase as seen in the area surrounded by dots in Fig. 1(b). Ten symmetric dimers are seen to extend from the ledge. Figures 1(c) and 1(d) show the very similar current dependences of the expansion of the $P(2\times1)$ phases under the positive sample bias; however the location of the $P(2\times1)$ phase areas differs from those of the negative sample bias: compare Fig. 1(b) with 1(d). The symmetric dimer rows are longer at positive bias voltages. The domains of the phases are reproducible and reversible, i.e., they are independent of the history of current and bias. However, there is no strong bias dependence of the extension of the $P(2\times1)$ phase for both bias polarities although the STM images show symmetric dimers at voltages higher than $+1.3$ V sample bias because of the imaging of bulk states.[15]

Figure 2(a) shows a filled-state, negative sample bias STM image at the boundary between the $P(2\times1)$ and $C(4\times2)$ phases on a 65 K Si(001) surface. Figures 2(b), 2(c), and 2(d) are zoom-in images of the box in Fig. 2(a). They convey the significant changes that appear under different scanning conditions. A perfect $C(4\times2)$ phase was imaged at a -1.2 V sample bias with a 25 pA tunneling current in Fig. 2(b). However, scanning with a higher tunneling current [0.1 nA, Fig. 2(c)] produces sudden changes in the surface structure although each stripe retains the $C(4\times2)$ phase.[16] It implies that scanning produces an exchange between the two $C(4\times2)$ phases by inverting the directions of all neighboring buckled dimers at a much faster rate than the STM can observe. Interestingly, $P(2\times2)$ phases have never been observed during structure changes. For example, changing the dimer directions in a single row will produce a three row $P(2\times2)$ phase under the STM tip and this phase may be stable at 65 K if the energy difference between $P(2\times2)$ and $C(4\times2)$ is only a few mV per dimer while the energy barrier between these phases is in the order of 0.1 eV per dimer as theoretical calculations have suggested.[7]

Increasing the tunneling current up to 1 nA produces ''dents'' in the scan lines of the up-atoms in the buckled dimers as seen in Fig. 2(d). The appearance of these dents (mostly spike-downs) can be considered to be the result of sequential motions of flopping down and flipping back to up-atoms within a few ms when the STM tip scans over the dimer. When the tunneling current increases further, the number and length of the dents increases and then finally, the dimers appear to be symmetric because all up-atoms are forced into a flop-down position when the STM tip scans over them. Eventually this becomes the $P(2\times1)$ phase that we observed in going from Fig. 1(a) to 1(b). The gradual change in appearance from the $C(4\times2)$ phase to the $P(2\times1)$ phase can also be seen at bottom of the STM image, Fig. 2(a). On the other hand, flipping up of originally down-oriented atoms was rarely found. A similar behavior was observed in empty-state imaging.[17] Again, significant differences were not observed when the sample bias was changed from -0.8 to -2 V and from $+0.8$ to $+1.3$ V.

In this section we discuss the current dependency of the flip-flop rate. Figure 3(a) shows typical examples of the current change as a function of time. Higher (lower) current values indicate that the atom below the STM tip is in the up (down)-position for negative sample bias. On the other hand,

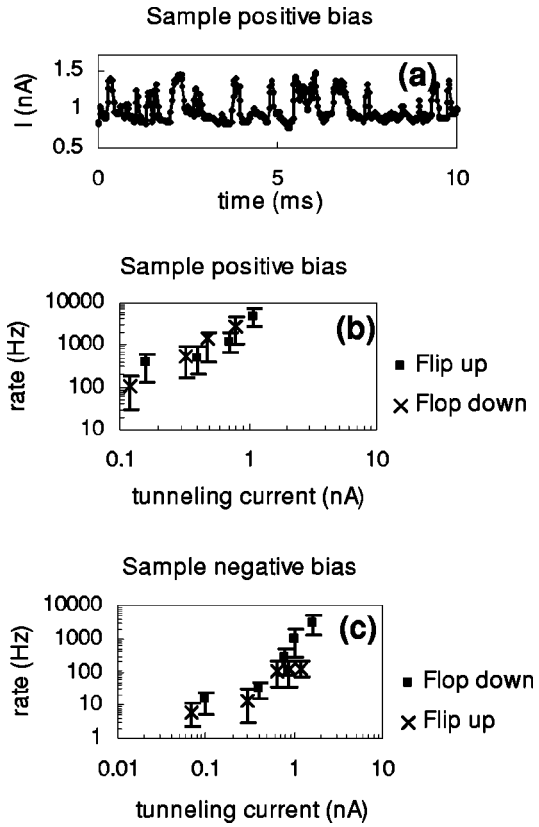

FIG. 3. Examples of current change with time: (a) for positive sample bias. Two discrete values of currents are observed. The rate of the dimer motions as a function of currents for positive sample bias (b) and for negative sample bias (c). The flip-up rates saturate near 1 nA for negative sample bias.

higher (lower) current values indicate down (up)-position of an atom for positive sample biases since the STM tip is imaging empty states. Figure 3(a) shows longer occupational times for measurements at lower currents than at higher currents. It implies that atoms prefer an up-position over a down-position under the STM tip. It also proves clearly that the flip-flop motion is indeed induced by the STM because the occupational times in up- and down-positions would be the same if the flip-flop motion were driven by intrinsic thermal excitations only.

Current dependences of the dimer flip-flop rates are plotted in Figs. 3(b) and 3(c) at both bias polarities and for tunneling currents from 0.1 to 1 nA. The rates were less than 0.005 Hz for tunneling currents of 25 pA at both polarities. Flip-up and flop-down rates must differ in their current dependences because the tunneling currents flowing into atoms in the up-position and atoms in the down-position differ as can be seen in Fig. 3(a). The error bars for these rates were estimated directly from the distributions of the experimental data since the data show a much larger scatter than a Poisson distribution.

Some interesting features can be observed in these plots. For positive sample biases, the flip-flop rates increase approximately linearly with currents. The distribution of the experimental data scatters widely, i.e., from 50 to 800 Hz at a current of 0.32 nA as shown by the error bars. The reason for the wide distributions is the differences between the type of transitions, i.e., the final states. As we show in Fig. 2(c), an exchange between two alternate $C(4\times2)$ phases occurs under the STM tip; however, the final states, i.e., the size of the newly altered $C(4\times2)$ phases cannot be observed by the STM measurements because of limitations in scanning speed. If the final states are different, one can expect to measure different rates for the flip-flop motions. The ratio of the occupational times in the down-position to the up-position is 1:3 at a current of 0.16 nA, 1:1 at 0.4 nA and at 0.7 nA and 1:2 at 1.1 nA.

Again, the rates at lower currents spread over a wide region for negative sample biases. The flop rates increase linearly with current near 0.7 nA while the flip-up rates saturate. It implies that the ratio of the occupation times in the down-position to the up-position increases when current increases. Eventually, the ratio reaches 23:1 at 1.6 nA while the ratio is about 3:1 for less than 1 nA. In other words the STM tip almost ties the atoms beneath the tip into the down position. As a result, the occupational time in the up-position would then become too short to cause any response in the STM feedback loop and the STM could not image atoms in up-positions. We conclude that no contribution of an up-atom imaging can possibly produce the appearance of the $P(2\times1)$ phase areas. The ratio change with currents is different for positive and negative sample biases, however, a similar argument would apply.[18]

This flip-flop motion is a phenomenon that differs from the symmetric appearance of dimers located at the antiphase boundaries of the $C(4\times2)$ regions in Fig. 1(a) and also differs from dimers at room temperature. We also observed an extension of the symmetric dimers and the flip-flop dimer motions under high tunneling currents on a defect-free larger terrace of *n*-type Si(001) at 65 K and *p*-type Si(001) at 78 K (not shown).

What could be the origin of the $P(2\times1)$ phases, the appearance of symmetric dimers and the flip-flop dimer motion? One possible explanation is that the presence of the STM tip reduces the energy barrier for flip-flop motions as Cho and Joannopoulos suggested in their *ab initio* calculations of the total-energy pseudopotential of the tip surface.[9] Furthermore, they suggested asymmetrical occupational times between the down-position and the up-position. Their polarity-independent ratio of the occupational times in the down-position and up-position is 1:1000. It implies that the STM tip ties the atoms into an up-position. In our results the STM tip also ties the atom into the up-position for positive sample bias. However, the ratio depends on polarity and tunneling current and is at most 1:3. Furthermore, it becomes 23:1 at 1.6 nA for negative sample bias as mentioned above. We have to conclude that the STM tip ties the atoms into the down-position for negative sample bias, contrary to the theoretical results.

Another possible explanation could be that the $P(2\times1)$ phases are images of ''bulk states'' instead of surface π states. Buckled up-atom topography in STM images receives its main contribution from π surface states above the up-atoms in filled-state imaging or from π^* surface states above down-atoms in empty-state imaging. It implies that buckled up-atoms cannot be produced by electron shifts from states lower than the π surface states due to the depletion of the π surface states, or by shifts into states higher than π^* states due to the occupation of π^* states. It would occur wherever

electrons cannot be supplied into π states or removed from π^* states fast enough compared with the rate of the tunneling current. We would then expect that a $P(2\times1)$ phase forms wherever the effective area of surface states cannot sustain the tunneling current.[19] In this case, the STM currents would unpin the surface states locally, especially at low temperatures. This may be the reason why the $P(2\times1)$ is cooperative, forms domains, and therefore appears to be determined by nearby local structures like step edges and defects.[20] Furthermore, the local depletion or the occupation of the surface states reduces the Peierls distortion that could lower the energy barrier for flip-flop motions of the buckled dimers. This picture gives a consistent interpretation of the current dependences of the $P(2\times1)$ expansion and their bias independence. But then the recombination rates of the π states for electrons or holes must be of the same or lower order than the electron transfer rates by tunneling currents (10^8-10^{10} Hz). These electron transfer rates are unexpectedly low although the lower carrier densities at lower temperatures do decrease the rates of carrier transportation from surface states into bulk states. This argument implies that $P(2\times1)$ phases on Si(001) dominate at temperatures lower than 65 K, a fact that has been observed experimentally.[6]

In summary, we have observed the local $P(2\times1)$ phase in the $C(4\times2)$ phase on Si(001) at 65 K by STM under conventional imaging conditions. We find tip-surface interactions that switch the two alternate $C(4\times2)$ phases and enlarge the $P(2\times1)$ phase as the STM tunneling current increases. During these phase changes, no $P(2\times2)$ phase was observed. The appearance of the $P(2\times1)$ phase at 65 K is due to the absence of up-atom configurations, a phenomenon different from the appearance of the $P(2\times1)$ phase at room temperature. Finally, we find the dependences of the dimer flip-flop rates versus tunneling currents are nearly linear. Our results show that the STM tip tends to tie the atom beneath the tip into a down-position (up-position) for negative (positive) sample biases.

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[11] In empty state imaging, down-atoms appear buckled up because the location of π^* bond states.

[12] Since the rates strongly depend on the location of the dimer and the tip position over the dimer, two dimers are chosen for each bias polarity and the tip position is readjusted every 30 s.

[13] The $C(4\times2)$ phases actually consist of two phases that differ only by changing all up-atoms in the dimers to down-atoms or vice versa.

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[16] The scanning direction is horizontal.

[17] In this case, the down-atoms appear to be forced into a flip up position, but notice that pinning up or down describes only the STM observations. See the text for further discussion of the underlying phenomena.

[18] The ratio changes nonmonotonically in Fig. 3(b). However, the sample dimer for the ratio measurement in the STM images was asymmetric at 25 pA and appeared symmetric with no up-atom topography at 1.1 nA.

[19] If the single π or π^* states cannot transfer the carriers directly to the bulk states fast enough to sustain the current, the carriers must spread laterally over the surface states.

[20] Carrier recombination rates differ due to local structures. For example see, R. J. Hamers and U. K. Köhler, J. Vac. Sci. Technol. A **7**, 2854 (1989).