

Phase Manipulation between $c(4 \times 2)$ and $p(2 \times 2)$ on the Si(100) Surface at 4.2 K

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(Received 13 February 2003; published 3 October 2003)

Phase manipulation between $c(4 \times 2)$ and $p(2 \times 2)$ on the Si(100) surface has been demonstrated at 4.2 K for the first time using a low-temperature scanning tunneling microscope. We have discovered that it is possible to change the $c(4 \times 2)$ surface into the $p(2 \times 2)$ surface, artificially, through a flip-flop motion of the buckling dimers by using a sample bias voltage control. Also, scanning at a negative bias voltage or applying a pulse voltage can restore the $c(4 \times 2)$ surface. The STM images as a function of bias voltage and tunneling current reveal the interesting dynamics of the buckling dimers on the long debated surface. Our results will show that energetic tunneling electrons are most likely responsible for the observed phase transition from $c(4 \times 2)$ to $p(2 \times 2)$.

DOI: 10.1103/PhysRevLett.91.146103

PACS numbers: 68.35.Bs, 68.37.Ef

One of the recent hot subjects in surface science is concerned with the true atomic configuration on the Si(100) reconstruction surface at very low temperatures below 50 K. There have been several reports observing different surface structures using low-temperature scanning tunneling microscopy (LT-STM) [1–5], low-temperature noncontact atomic force microscopy (LT-NC-AFM) [6,7], and low-energy electron diffraction (LEED) [8]. The two topmost atoms on the Si(100) surface form a dimer with one of two possible asymmetric configurations. This dimerization results in reconstruction surfaces with $c(4 \times 2)$ and $p(2 \times 2)$ periodicities [Fig. 1(a)]. Since Wolkow first performed an LT-STM observation on the surface at 120 K [9], a number of LT-STM studies, cooling temperatures down to 65 K, have been dedicated to finding the ground state structure [10–12]. As a result, the $c(4 \times 2)$ geometry has been accepted as that of the Si(100) surface. In conjunction with advances in LT-STM and LT-NC-AFM, however, lower temperature studies have been performed to show the appearance of the $p(2 \times 2)$ domain [3–6]. The population of the $p(2 \times 2)$ domain observed at very low temperature varies among the reports. Particularly, a recent study by Hata *et al.* [4] has revealed that the area of the $p(2 \times 2)$ phase increases below 40 K and it dominates the *n*-type Si(100) surface at 9 K. They have implied a new ground state structure of $p(2 \times 2)$ on the *n*-type sample. According to the theoretical calculations, energy differentiates between $c(4 \times 2)$ and $p(2 \times 2)$ by only a few meV [13,14]. Thus, the stable phase of the Si(100) surface in the ground state can be of either $c(4 \times 2)$ or $p(2 \times 2)$, or a coexistence of both. Moreover, a very recent analysis by Matsumoto *et al.* using LEED [8] has made this issue more complicated because they have observed an order-disorder phase transition below 40 K. Since there are diversities in experimental results, some unknowns exist with the Si(100) surface reconstruction.

Our recent surveys, using LT-STM imaging below 50 K, have discovered surface structure changes caused

by scanning conditions, such as bias voltage and tunneling current settings. In this Letter, we demonstrate phase manipulation on the Si(100) surface utilizing the precise control of sample bias voltage at 4.2 K. It is possible to intentionally change the $c(4 \times 2)$ surface into the $p(2 \times 2)$ surface by bias voltage control during an empty state imaging, and to switch the $p(2 \times 2)$ domains back to the $c(4 \times 2)$ domains by applying a pulse voltage or by negative bias voltage scanning. Bias

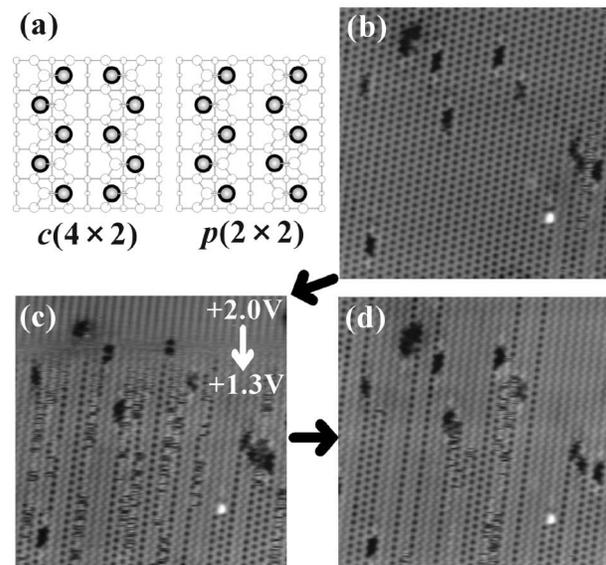


FIG. 1. (a) Top view of the Si(100) surface reconstructions of $c(4 \times 2)$ and $p(2 \times 2)$. (b)–(d) A sequence of $c(4 \times 2)/p(2 \times 2)$ transition observed in the empty state images of the *n*-type Si(100) surface at 4.2 K. (b) Initial $c(4 \times 2)$ dominant surface acquired at a sample bias voltage of +1.3 V, (c) the process of phase transition from $c(4 \times 2)$ to $p(2 \times 2)$. The scan was started at +2.0 V and then the bias voltage was gradually decreased to +1.3 V during the scan, (d) large fraction of the area was $p(2 \times 2)$, recorded at +1.3 V post transition. All images were recorded with a tunneling current of 30 pA.

voltage and tunneling current effects upon the STM image suggest that the mechanism of phase manipulation results from inelastic scattering and transport of energetic electrons in the surface, rather than a tip proximity effect or the local electric field between the STM tip and sample surface. These results will provide a good explanation of the divergence in recent observations, and offer significant information for further exploration of the ground state structure of the Si(100) surface.

Experiments were performed in an ultrahigh vacuum (UHV) LT-STM system. A base pressure of the system was kept below 5.0×10^{-9} Pa. The sample was *n*-type Si(100) wafer (*P* doped, 0.008–0.015 Ω cm). A clean surface was obtained by flashing to 1400 K for 20 s after 12 h of degassing at 900 K. Electrochemically etched tungsten wire was used as the STM tip. All images were acquired at 4.2 K.

A sequence of STM images in Figs. 1(b)–1(d) demonstrates phase manipulation from $c(4 \times 2)$ to $p(2 \times 2)$ by sample bias voltage control. Figure 1(b) confirmed that an initial surface observed at a sample bias voltage of +1.3 V consisted of the $c(4 \times 2)$ phase and some $p(2 \times 2)$ dimers near defects, such as dimer vacancies and a type-*P* defect [3]. A surface scan started at +2.0 V and the bias voltage was slowly decreased to +1.3 V during the scanning [Fig. 1(c)]. The gradual decrease in bias voltage gave rise to a dramatic phase change from $c(4 \times 2)$ to $p(2 \times 2)$. Some dimer rows appeared as an intermediate state of the flickering 2×1 structure because the dimers were alternating their buckling orientations more slowly than those seen in a room temperature image [15]. Another scan at +1.3 V clearly exhibited that a large area of the scanned surface had been changed from $c(4 \times 2)$ to $p(2 \times 2)$ [Fig. 1(d)]. Some $c(4 \times 2)$ dimers still remained at the boundaries between the $p(2 \times 2)$ domains because they were isolated by mismatched buckling orientations at the boundary where two $p(2 \times 2)$ domains met. Several dimers stayed in the $c(4 \times 2)$ structure near defects and their transition seemed to have been blocked by the defects. It is possible to completely stop the flip-flop motions seen in the center of Fig. 1(d) if an observation is made at a lower bias voltage ($\sim +1.0$ V). In order to switch the surface to the $p(2 \times 2)$ phase, it is recommended to keep scanning the surface with a high bias voltage ($\sim +1.5$ V) as long as possible.

The phase transition includes two definitive steps: First, the dimers start the flip-flop motion, and second, the dimers stabilize in the $p(2 \times 2)$ structure. As shown in Fig. 1(c), the flip-flop motions were generated during the bias voltage decrease from +2.0 V. While investigating the minutiae of the phase transition, the surface behavior was recorded as a function of bias voltage. Figure 2 captured the transition process from $c(4 \times 2)$ to $p(2 \times 2)$ through flip-flop motions as the bias voltage was raised. The initial surface at +1.3 V consisted of the $c(4 \times 2)$ dimers and a small area of $p(2 \times 2)$. Flip-flop

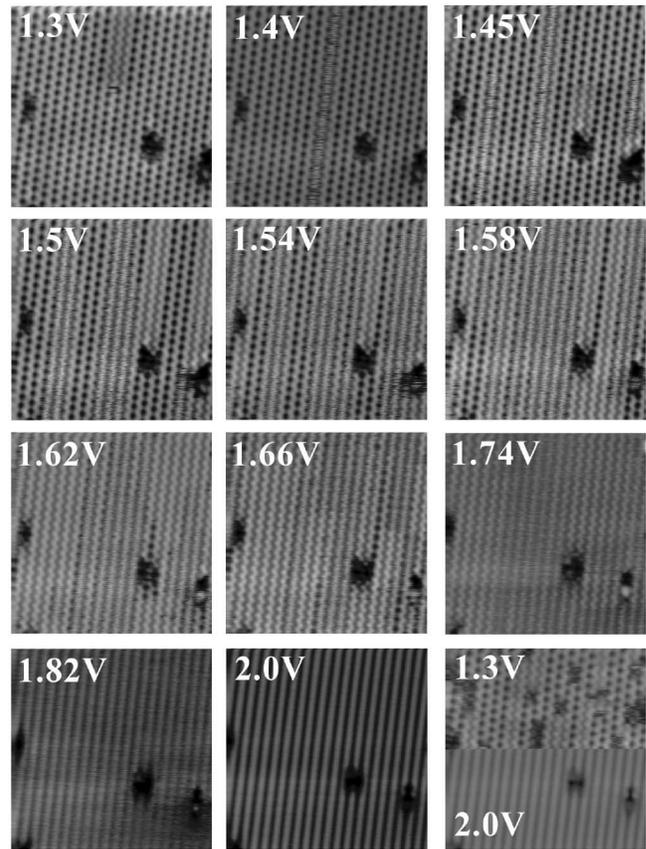


FIG. 2. The empty state images as a function of the positive bias voltage. As the bias voltage was raised, flip-flop dimers increased. The flip-flop dimers preferred to be in the $p(2 \times 2)$ phase when the surface was kept scanning at a higher bias voltage. The bottom-right image confirmed that protrusions appeared above +1.82 V situated between dimer rows. A tunneling current of 30 pA was used for all the images.

motion did not occur at a lower bias voltage below +1.0 V. As the bias voltage was raised, dimers started flipping and formed the $p(2 \times 2)$ domains at 1.4–1.74 V. Further increases of the bias voltage developed protrusions between dimer rows at +1.82 and +2.0 V, which was the result of tunneling to states other than the π^* dangling bond state [16,17]. Such states have a strong contribution to tunneling as seen in the +2.0 V image. At 4.2 K, dimers near defects tended to start the flip-flop motion at a lower bias voltage than those far from defects. Accordingly, the potential height between two orientations of a buckling dimer depends on the surrounding surface structures, such as dimer vacancies and adsorbates.

It should be stressed that the flip-flop dimers have a tendency to develop the $p(2 \times 2)$ structure when they are scanned at a relatively high bias voltage. The $p(2 \times 2)$ domains are more stable than the $c(4 \times 2)$ domains when the surface is excited by bias voltage manipulation. Similar phase changes have been reported on the Ge(100) surface at 80 K [18]. This is explained by the suggestion that the energy of the $p(2 \times 2)$ structure is

intrinsically lower than that of the $c(4 \times 2)$ structure. That is not the case for Si(100) because it is possible to reverse $p(2 \times 2)$ to $c(4 \times 2)$ by exciting the flip-flop motion by scanning at a negative bias voltage or applying a voltage pulse to the surface. Figure 3(b) was recorded at +1.3 V just after a pulse voltage of +2.0 V (50 ms) was applied to the center of the image of Fig. 3(a). Most of the area resumed the $c(4 \times 2)$ structure, although many flip-flop dimers remained. The successive scan confirmed that most flip-flop dimers stabilized in the $c(4 \times 2)$ structure [Fig. 3(c)]. It is important to scan the surface with a low bias voltage, after the flip-flop excitation, to thoroughly restore the $c(4 \times 2)$ surface. A high bias voltage scan will result in reforming the $p(2 \times 2)$ domains. Therefore, we cannot conclude that $p(2 \times 2)$ possesses less energy than $c(4 \times 2)$. In addition, a negative bias voltage scanning will more effectively change $p(2 \times 2)$ into $c(4 \times 2)$.

The flip-flop dimer, or a 2×1 structure seen in STM images, has been explained using the tip proximity effect or by the local electric field between the tip and sample surface. Cho and Joannopoulos [19] have claimed that the tip-surface interaction lowers the energy barrier for flipping, which results in a flip-flop dimer as the surface is scanned. Mitsui and Takayanagi [12] have reported that the tip-surface interaction causes flip-flop motion at 65 K. Also, the effect of the electric field has been calculated to predict that a positive bias voltage scanning will affect dimer structure [20], although other calculations have shown that it has slight influence on the electronic structure of dimers but does not change dimer geometry [21,22]. Our analysis was performed by changing the tip-sample surface distance (tunneling current) to examine the potential of the tip proximity effect and the electric field effect on dimer structure. The bias voltage was fixed at +1.3 V. When the tunneling current was 30 pA, the surface stayed in the $c(4 \times 2)$ phase as seen in Fig. 4. Larger tunneling currents up to 100 pA were tested, but no structural anomalies were observed. Conversely, when a smaller tunneling current (20, 10, or 5 pA) was employed, dimers started the flip-flop motion and aligned into the $p(2 \times 2)$ arrangement. Unexpectedly, the smaller tunneling current scanning transformed the surface even at +1.3 V. If the tip or the electric field effect was

responsible for the flip-flop dimers, these effects should have become weaker as the tip receded from the surface. The reason for the behavior is uncertain, but we can exclude the tip or the electric field effect as a factor in our results. Further examinations of the tunneling current and bias voltage found that the decrease of tunneling current lowered the critical bias voltage for the flip-flop excitation.

Another possible explanation for the excitation of the flip-flop dimer is inelastic scattering of energetic tunneling electrons in the surface. As seen in Fig. 2, a higher bias voltage scan excited flip-flop dimers more frequently. The tunneling current affects the critical bias voltage for flip-flop, but it is not a major factor upon flipping dimers. In fact, when the bias voltage was decreased below +1.0 V, a flip-flop dimer was not recorded, even when the tunneling current was set at 5 pA. These observations suggest that the tunneling electrons provide dimers with enough energy to alternate the buckling orientations. The barrier height to flip a dimer is approximately 0.1 eV [14,19,23], which can be supplied from a typical inelastic energy of the energetic electrons of more than 1.0 eV. At present, inelastic electron scattering will best explain our results of the flip-flop excitation.

The most intriguing behavior of this surface at very low temperature is the appearance of $p(2 \times 2)$. Since the $c(4 \times 2)$ structure typically dominates the surface at 4.2 K while scanned with an adequately low bias voltage, the $c(4 \times 2)$ structure appears more stable than the $p(2 \times 2)$ structure. The $p(2 \times 2)$ domain emerges only when the surface is scanned with a positive bias voltage. Dimers presumably prefer to be in the $p(2 \times 2)$ phase when electrons are injected into the surface. Mitsui and Takayanagi mentioned [12] that injected electrons could spread laterally over the surface state instead of traveling into bulk states. That phenomenon at low temperature is due to electron transport from the surface state to bulk states being slower than electron tunneling from the tip to the surface. Such an assumption allows us to hypothesize upon the transition to the $p(2 \times 2)$ phase in terms of Coulomb repulsion or dimer-dimer interaction. Energy differentiation between $c(4 \times 2)$ and $p(2 \times 2)$ is essentially a few meV [13,14]; thus, once dimers start flip-flop

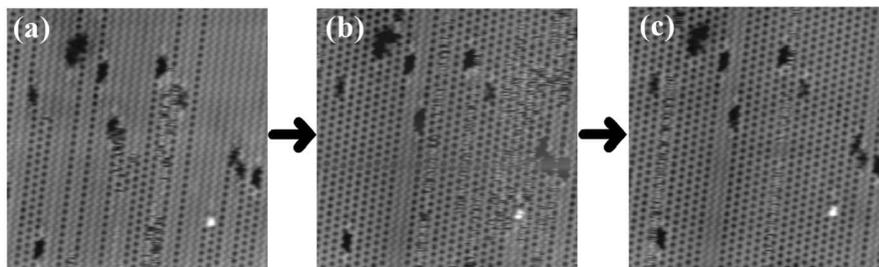


FIG. 3. Reverse transition from $p(2 \times 2)$ to $c(4 \times 2)$. (a) The same image as Fig. 1(d). (b) The flip-flop dimers were excited by applying a pulse voltage (+ 2.0 V, 50 ms) to the center of the image of (a). The tip was fixed at the center of (a) under the tunneling condition with +1.3 V and 30 pA. (c) Another scan confirmed the surface was successively changed back into the $c(4 \times 2)$ structure. All images were recorded with a sample bias voltage of +1.3 V and tunneling current of 30 pA.

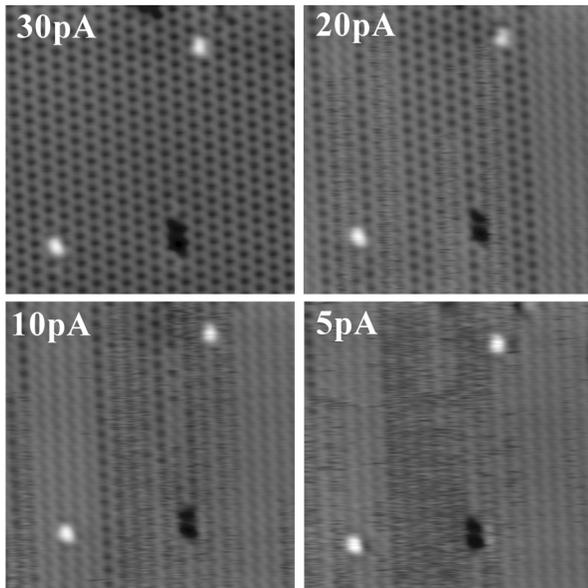


FIG. 4. The empty state images for various tunneling currents. The bias voltage was fixed at +1.3 V for all imaging. As the tunneling current decreased, the area of flip-flop dimers increased. Under the circumstance where the flip-flop motions are excited, the dimers prefer to be in $p(2 \times 2)$.

motion, only slight interactions between dimers should be sufficient for stabilization in the $p(2 \times 2)$ phase. Provided that the injected electrons can spread laterally, the dimers in $c(4 \times 2)$ experience a larger repulsion than in $p(2 \times 2)$, since the lower atoms in the $c(4 \times 2)$ geometry are arranged face to face [Fig. 1(a)]. Reverse transition from $p(2 \times 2)$ to $c(4 \times 2)$ is assured, only when $c(4 \times 2)$ is the most stable upon the neutral surface, as predicted by prior theoretical studies [13,14,24].

At this moment, the reason for the variety in observed structures in the previous reports [2–5,8] has become clear. The $p(2 \times 2)$ domain [3–5] or flip-flop dimers [2] observed in previous STM studies were probably as a result of unintentional manipulation of the dimer configurations. From our study, it is obvious that inappropriate bias voltage will inhibit observing the ground state structure, $c(4 \times 2)$, and will develop $p(2 \times 2)$ domains. Furthermore, the disordered surface detected by the LEED below 40 K [8] was caused by the LEED analysis itself due to much greater energies (52 and 110 eV) of incident electrons into the surface and low beam currents (20 to 500 nA). Because of the large incident energies, the effect of activating flip-flop motion surpassed that of stabilization in $p(2 \times 2)$. The images observed with lower currents of 5 and 10 pA in Fig. 4 showed a large number of flip-flop dimers. We surmise that these images correspond to the disordered surface detected by LEED.

In summary, we have demonstrated phase manipulation between $c(4 \times 2)$ and $p(2 \times 2)$ utilizing sample bias voltage on LT-STM. The phase transition from the $c(4 \times 2)$ structure to the $p(2 \times 2)$ structure can be executed by applying positive bias voltage control. A

relatively high bias voltage scan can drive dimers into the flip-flop motion. Dimers tend to be stabilized in the $p(2 \times 2)$ phase during high bias voltage scanning. The critical bias voltage required to excite the flip-flop dimers decreases when a small tunneling current is used. It is possible to revert the $p(2 \times 2)$ domains back to the $c(4 \times 2)$ domains by scanning using a negative bias voltage or applying a pulse voltage. Our experiment results suggest that $c(4 \times 2)$ is more stable than $p(2 \times 2)$ and the appearance of the $p(2 \times 2)$ domain is related to the effect of energetic tunneling electrons.

This work was performed as part of the Active Nano-Characterization and Technology Project, Special Coordination Funds of the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.

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