Origin of $p(2 \times 1)$ Phase on Si(001) by Noncontact Atomic Force Microscopy at 5 K

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The controversial issue of the origin of the $p(2 \times 1)$ reconstruction of the Si(001) surface observed in recent low temperature scanning tunneling microscopy experiments is clarified here using 5 K noncontact atomic force microscopy. The $c(4 \times 2)$ phase is observed at separations corresponding to weak tip-surface interactions, confirming that it is the ground state of the surface. At larger frequency shifts the $p(2 \times 1)$ phase of symmetric dimers is observed. By studying the interaction of a reactive Si tip with the $c(4 \times 2)$ Si(001) surface using an *ab initio* method, we find that the observed change in the surface reconstruction is an apparent effect caused by tip induced dimer flipping resulting in a modification of the surface structure and appearance of the $p(2 \times 1)$ phase in the image. Using an appropriate scanning protocol, one can manipulate the surface reconstruction at will, which has significance in nanotechnology.

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The Si(001) surface has attracted much attention because of its practical importance in most large-scale integration technology devices that are fabricated on this surface. Since the $p(2 \times 1)$ superstructure was discovered [1], the reconstruction of this surface was extensively investigated both experimentally [1–10] and theoretically [11–13]. Two other phases $c(4 \times 2)$ and $p(2 \times 2)$ were also observed in which the dimers are flipped in opposite directions along the rows which are either in antiphase or in phase with each other [7,8,14]. $p(2 \times 1)$ and $c(4 \times 2)$ structures are shown schematically in Figs. 1(a) and 1(c).

The most widely accepted stable phase is that of asymmetric buckled dimers $c(4 \times 2)$. This has been confirmed by the observation of alternating zigzag rows from scanning tunneling microscopy (STM) [7,8] studies and low-energy electron diffraction LEED patterns at around 100 K [5,9]. The buckling is accompanied by a charge transfer from the lower to the upper dimer atom [11]. This was consistent with the core level photoelectron spectra suggesting that two types of surface atoms exist [6]. The *ab initio* calculations confirmed that the $c(4 \times 2)$ phase is the ground state of the surface, followed by the $p(2 \times 2)$ phase (between which exists a small energy difference) and then the asymmetric $p(2 \times 1)$ phase [12,15]. At room temperature, a fast flip-flop motion is thermally activated, resulting in the symmetric $p(2 \times 1)$ phase as observed in STM images [4].

However, recent STM studies performed at low temperatures (LTs) questioned whether the $c(4 \times 2)$ phase is the most stable phase. For instance, the $p(2 \times 1)$ structure was observed in Ref. [16,17]. It was suggested in Ref. [16] that the origin of the $p(2 \times 1)$ structure is due to the time averaging of the rapid flip-flop motion at 5 K. At the same time, the symmetric $p(2 \times 1)$ structure observed in Ref. [17] at 20 K was attributed to static symmetric dimers stabilized by the ''antiferromagnetic'' dimer-dimer interaction.

Thus, up to now, the appearance of the $p(2 \times 1)$ phase in STM images at LTs remains a controversial issue. From the theoretical study by Kawai [18,19], the $p(2 \times 1)$ phase was suggested to be observed as a result of the rapid flip-flop motion excited by local heating induced by current injection from the STM tip. It is well-known that the following three effects are at work during STM imaging: a bias effect, current injection, and the tip-force interaction. Therefore, from STM studies alone, we cannot identify the origin of the $p(2 \times 1)$ phase since the bias and the current injection effects are always present. In order to eliminate these experimental factors, an investigation by the LT noncontact atomic force microscopy (NC-AFM) [20] would be extremely valuable, because it gives atomically resolved imaging based entirely on the direct tip-surface interaction [21].

In this Letter, we report on the origin of $p(2 \times 1)$ phase on the Si(001) surface by LT-NC-AFM at 5 K. We found that at large frequency shifts the stable $p(2 \times 1)$ phase is observed and that it is caused by the surface dimer flipping during the scan induced by the interaction with the tip. This conclusion is supported by detailed *ab initio* density functional calculations. We also demonstrate the ability of the LT-NC-AFM to modify surface structure and perform controlled manipulation of the surface reconstructions.

The experiments were performed with a homemade LT-NC-AFM apparatus operated in UHV [22]. The cryostat has three shields with the two fold shutters. The AFM unit hangs from the bottom of the liquid helium Dewar, and is surrounded by inner and middle concentric radiation shields connected with the liquid helium Dewar. These shields are surrounded by an outer radiation shield connected with the liquid nitrogen Dewar. Hence, the AFM unit can be cooled down to 5 K and its temperature maintained for 14 h.

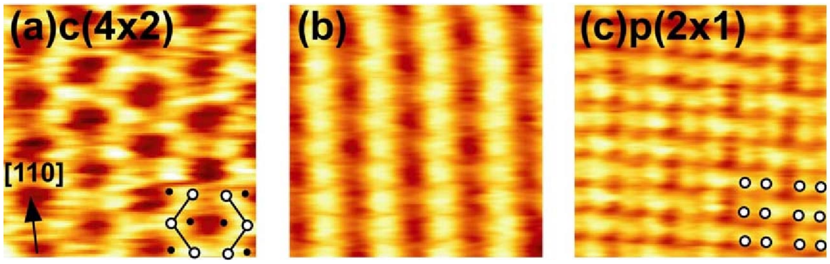

FIG. 1 (color online). NC-AFM topographic images of the Si(001) surface at 5 K observed at (a) $\Delta f = -10$ Hz, (b) -22 Hz, and (c) -30 Hz. In all images the scan area is 3.0×3.0 nm^2. Dimer rows run in the [110] direction are indicated by the arrow. The fast scan direction is from left to right. Open and black circles represent the positions of upper and lower dimer atoms, respectively.

An arsenic-doped n-type Si(001) wafer was used with a conductivity of 0.01–0.025 Ω cm. The sample was cleaned by repeated cycles of flashing at 1200 °C and annealing at 950 °C after prebaking for one night (over 12 hours). During this procedure, the pressure was maintained below 7×10^{-11} Torr. A commercial silicon cantilever with typical 40 N/m spring constant and 171.417 kHz mechanical resonant frequency (n-type, Sb doped Si wafer) was used as the force sensor (Nanosensors, type NCLR-W). In order to remove the native oxide layer and any contamination on the tip, the cantilever was cleaned by Ar$^+$ ion sputtering for 25 minutes. Therefore, we believe that the tip apex is likely to be terminated by the Si dangling bonds. All AFM observations were performed at 5 K and the pressure was maintained below 1×10^{-12} Torr. During the scan the average tip-sample distance was controlled to maintain the same frequency shift Δf and the tip oscillation amplitude was kept at 13.5 nm.

Figure 1(a) shows the NC-AFM topographic image of the Si(001) surface taken at $\Delta f = -10$ Hz when we can assume that the tip-surface interaction is rather weak. Here, the $c(4 \times 2)$ phase (measured fresh on a surface area not scanned before) with the characteristic zigzag pattern is clearly observed. The distance between nearest bright spots of the adjacent dimer rows is about 5.2 ± 0.2 Å, while the separation of the nearest bright spots measured in the direction along the row is about 3.9 ± 0.2 Å, which is consistent with the distance between two nearest dimers of the same row. This result is in a good agreement with the previous AFM study [20].

Figure 1(b) shows a stable topographic image taken at a larger $\Delta f = -22$ Hz when the tip-surface interaction is much stronger. We find that a surface phase is observed with bright lines along dimer rows and flicker noise. The distance between bright lines along dimer rows is about 7.8 ± 0.1 Å, which is in agreement with the distance between the adjacent dimer rows. It is noted that NC-AFM images with flicker noise were observed for the first time, although the same phenomenon has been confirmed by STM studies [16]. Appearance of the flicker noise strongly suggests that surface dimers are frequently flipped by the tip-surface interaction. Notice that the $p(2 \times 1)$ phase was not observed at this frequency shift.

Figure 1(c) shows a topographic image taken at even larger $\Delta f = -30$ Hz in which case a very strong tip-surface interaction is expected. We find that the $p(2 \times 1)$ phase with symmetric dimers is observed at these conditions. For the first time, the appearance of the $p(2 \times 1)$ phase was confirmed by NC-AFM at 5 K without the energy injection effect normally associated with STM experiments. The distance between nearest bright spots corresponding to the same dimer is about 3.0 ± 0.2 Å. This is larger than the distance of 2.4 Å found between two Si atoms of the symmetric dimer in density-functional theory (DFT) calculations. This is explained by the fact that the surface dimers are buckled so that dangling bonds imaged by the tip are tilted; also, the oscillating tip continuously flips the dimers. We shall show in the following that when the tip comes close to the lower dimer atom, a chemical bond is formed between them resulting in a dimer flip [23]. The dimer does not flip back and remains in the flipped position during subsequent tip oscillations since there is not enough thermal energy in the system at 5 K. When during the lateral scan the tip eventually moves to the other atom of the same dimer (which became the lower dimer atom after the dimer flipped), the dimer flips again. This means that each atom of the dimer is imaged equally as the upper atom, and results in the $p(2 \times 1)$ phase with symmetric dimers observed, with the increased apparent distance between the corresponding bright spots as seen in Fig. 1(c). It is always the case that when the tip passes beyond a dimer, the atom that is scanned last is in the upper position.

Thus, when the tip-surface interaction is weak, a stable image is observed; with approach, the stable image gradually changes into an unstable one with flicker noise, and that in turn changes back again to a stable image upon further approach corresponding to a very strong tip-surface interaction.

To explain the observed images, extensive *ab initio* DFT calculations have been performed using the SIESTA code [24] to investigate the interaction of a Si tip with a single dangling bond and the lower and upper dimer atoms of the $c(4 \times 2)$ Si(001) surface. The code utilizes periodic boundary conditions, numerical localized double-zeta polarized basis set, norm-conserved pseudopotentials, GGA [25] density functional, and a single $\boldsymbol{k} = \boldsymbol{0}$ point.

The surface was simulated by a 6-layer slab with 8 Si dimers arranged in two rows, 4 dimers in each, in the surface unit cell. Hydrogen atoms were used to terminate unsaturated Si bonds at the bottom of the slab. We used a ten atom pyramidal Si tip [26,27] that has a single dangling bond coming out of its single apex atom. In all our calculations the four lowest Si atoms of the tip and the two upper layers of the Si surface were allowed to relax. The vertical distance between the tip and surface D_{TS} is defined as the distance between the apex atom and the upper dimer atom *prior* to atomic relaxation.

To study the tip-surface interaction, a tip positioned initially at about 7 Å away from the dimer upper atom, was moved in steps of 0.15 Å towards and then away from the surface. At each point the whole system was relaxed to mechanical equilibrium (until the forces on atoms were less than 0.02 eV/Å) and the tip force was calculated by summing the forces on all fixed tip atoms. This way, the whole tip-surface curve for approach and retraction above the upper dimer atom was calculated. The calculation was then repeated for the lower dimer atom.

The calculated force-distance curves for both dimer atoms are shown in Fig. 2. When the tip is positioned above an upper dimer atom, there is an attractive force between the tip and surface, which at the distance of about $D_{\mathrm{TS}} = 3.3$ Å reaches its maximum value of more than -2.75 nN. At around the same tip-surface separation a chemical bond is formed between the apex Si atom of the tip and the upper atom of the dimer; see Fig. 3 (*left*). Upon further approach the attractive interaction starts to decrease and the dimer becomes symmetrical. Upon retraction, the system follows exactly the same path along the whole trajectory; no hysteresis is observed.

When positioned above the lower dimer atom (Fig. 2) the tip-force curve increases sharply at the distance of $D_{\mathrm{TS}} = 3.6$ Å, at this point the dimer flips to reduce the distance between the tip apex and the Si dimer atoms, and hence to facilitate the formation of a strong chemical bond; see Fig. 3 (right). At further approach and subsequent retraction, the force curve follows nearly the same path as in the case of the upper dimer atom. The bond between the tip and the Si dimer atom remains in place along some part of the tip retraction path after which it is broken, and the dimer remains flipped. Note that the dimer does not return to the ground state due to the calculated energy barrier of 0.1 eV that it is unlikely to be overcome at 5 K. The tip-force curve demonstrates a hysteretic behavior characteristic for dissipation effects, but note that the surface remains permanently deformed. The formation of the tip-dimer chemical bond has also been observed in the previous tight-binding [27] and *ab initio* calculations [23,28].

Thus, when during the lateral scan at high frequency shifts the tip approaches a dimer near the upper atom, the dimer does not flip during the tip oscillations and is imaged as an upper atom appearing as a bright spot. When the tip approaches a lower atom closer than the critical distance, the dimer flips, the lower atom turns into the upper one and during all subsequent tip oscillations is imaged as the upper atom since at 5 K the dimer cannot return to the ground state. Note that the other dimer atom becomes the lower atom after the dimer flips. At sufficiently high frequency shifts the dimer flips during one of the very first tip vertical oscillations, so that during the remaining tip residence time the initially lower dimer atom is imaged as the upper one. This means that both dimer atoms would appear equally as bright in the image and the surface would be seen in AFM as the symmetric $p(2 \times 1)$ phase.

Depending on the particular scan direction, each dimer may be flipped one or more times; i.e., the actual orientation of surface dimers after the scan depends on the particular scanning protocol. For instance, if the fast scan direction is perpendicular to the dimer rows as in our experiments in Fig. 1 and the tip comes to the lower dimer

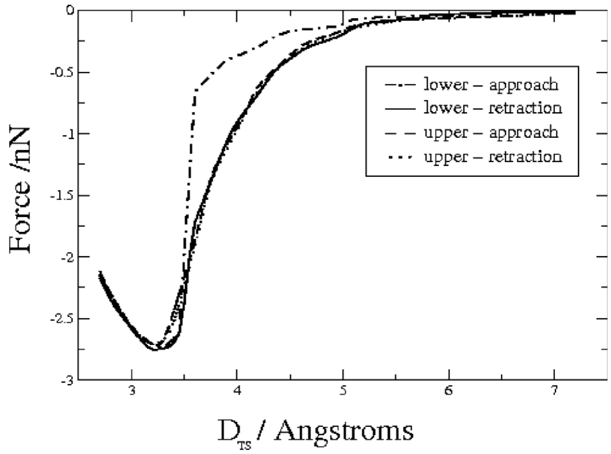

FIG. 2. Approach and retraction tip force-distance curves above the lower and upper dimer atoms calculated using an *ab initio* DFT method.

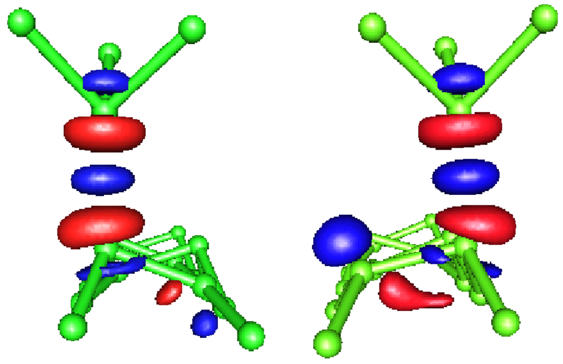

FIG. 3 (color online). Electron density difference plots that show the tip forming a chemical bond with the dimer upper (left) and lower (right) atoms of the $c(4 \times 2)$ surface. The medium gray (red online) contours (depletion) represent a charge difference of -0.02 Å^{-3} while the dark gray (blue online) contours (excess) represent a charge difference of $+0.02$ Å^{-3}. One row of surface dimers and the lower four atoms of the Si tip are shown explicitly.

atom first, the dimer will be flipped twice; if the tip comes first to the upper atom, the dimer will only be flipped ones. Using a Monte Carlo method in which it is decided at random if the dimer is flipped, we have simulated a number of possible scan protocols taking into account continuous dimer flip events, and found that in all cases the image corresponds to the apparent symmetric $p(2 \times 1)$ phase, although the actual positions of surface dimers depend on how the scan is performed.

At small frequency shifts the tip does not come sufficiently close to the lower dimer atom and the dimer does not flip, the surface remains in its initial state. At these conditions, assuming typical values for the van der Waals force [29] and using the standard methods [30], one can calculate the constant frequency shift image. These calculations clearly show that the lower and upper dimer atoms can easily be distinguished: the upper atom appears as bright while the lower as dim spots. This means that different surface reconstructions must be possible to read out by NC-AFM, since each phase is characterized uniquely by the upper atoms (bright spots) pattern. The fact that at 5 K the $c(4 \times 2)$ structure is observed in our NC-AFM experiments at small Δf proves that this phase is indeed the ground state of this surface.

At intermediate values of Δf (intermediate distances of close approach) the dimer flip events happen more rarely due to finite response times of the electronics of the NC-AFM apparatus. Hence, the tip does not come beyond the critical distance to the lower dimer atom during every vertical oscillation. For instance, the particular dimer may be flipped along one lateral traverse of the tip and not along the way back. This should result in a flicker noise in the image and this is indeed what we have observed; see Fig. 1(b).

In conclusion, we have investigated the origin of the $p(2 \times 1)$ phase on the Si(001) surface by NC-AFM at 5 K. For the first time, the $p(2 \times 1)$ phase was observed at conditions corresponding to a very strong tip-surface interaction that affects strongly the buckling direction of asymmetric dimers of the $c(4 \times 2)$ phase. The stable $p(2 \times 1)$ phase is caused by the continuous change of the buckling direction during the scan in which the tip acts as a manipulation (“writing”) device. Using a special scanning protocol at high frequency shifts, one can create a particular dimer pattern on the surface (cf. Ref. [23]). At low frequency shifts the tip performs as a probe that does not damage the surface, “reading” the actual pattern of buckled dimers. This regime can thus be used to image the surface before and after the intrusive scan to check the surface structure change. The observed effect of controlled modification of the surface has general significance for nanotechnology. We also confirm that the $c(4 \times 2)$ is the ground state of the Si(001) surface, and the observed $p(2 \times 1)$ structure in STM experiments at low temperatures is either caused by the tip-surface interaction or current injection effects.

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