## Dimer buckling of the Si(001)2×1 surface below 10 K observed by low-temperature scanning tunneling microscopy

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Using scanning tunneling microscopy (STM), we studied the dimer structure of the Si(001)2×1 surface at low temperature (<10 K). Asymmetric (buckled) dimer structure, locally forming  $c(4\times2)$  or  $p(2\times2)$  periodicity, was observed with positive sample bias voltages, while most of the dimers appear symmetric with negative bias voltages. Our observation indicates that actual dimer structure is asymmetric and that the apparent symmetric dimer observation is due to an artifact induced by STM imaging. Since a transition temperature between the buckled- and symmetric-dimer imaging, which is found to be ~40 K, corresponds to the temperature where the carrier density changes dramatically from intrinsic to saturation range, the apparent symmetric-dimer imaging should be related with the reduced carrier density and ensuing charging effect.

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The Si(001)2×1 surface is one of the most investigated surfaces both experimentally<sup>1-10</sup> and theoretically<sup>11-15</sup> because of technological importance of the surface, which various devices have been fabricated on. Despite extensive studies, the nature of its reconstruction is still a subject of discussion. Recent studies by low-temperature scanning tunneling microscopy (STM) raised a question on its ground-state structure,<sup>7,8</sup> while the ground structure has also been discussed theoretically as a model surface at which so-called *static* and *dynamical* electron correlations play subtle but significant roles on the structural determination.<sup>16–21</sup>

On the surface, a dimer structure is formed for a reduction of the dangling bond density. The dimers are arranged linearly in the  $\langle 110 \rangle$  direction to form a so-called "dimer row" structure with a long-range  $2 \times 1$  periodicity.<sup>1</sup> The unique feature that leads the surface to show a variety of phases is a tilting or buckling of the dimer:<sup>11</sup> the two dimer-composing atoms are located up and down relative to the surface plane. Along the dimer-row direction the asymmetric buckled dimer exhibits an "antiferromagnetic"-like interaction to make a zigzag structure. Interaction between the neighboring dimer rows can be either "ferromagnetic" or "antiferromagnetic," producing a  $p(2 \times 2)$  or  $c(4 \times 2)$  ordering, respectively.<sup>4</sup> A flip-flop motion of the asymmetric dimer is induced by thermal activation or by a proximity effect of the probe tip in STM. The motion can be pinched off near local defects, such as steps and missing dimers.<sup>4,6,10</sup>

According to the generally accepted scenario on a temperature dependence of the structure, an order-disorder phase transition occurs at around 200 K;<sup>22</sup> below the transition temperature the buckled dimers are arranged with the  $c(4 \times 2)$  ordering, and above the temperature the thermally activated dimer flip-flop motion breaks the symmetry to exhibit the 2×1 ordering.<sup>22</sup> Recently, Kondo *et al.*<sup>7</sup> reported STM images taken below the transition temperature showing symmetric dimers, inconsistent with the above-mentioned scenario, and claimed a new ground-state structure. Yokoyama and Takayanagi<sup>8</sup> then showed an evidence of the  $c(4\times 2)$ structure from an analysis of electronic structure obtained by STM at 5 K. Observing symmetric dimer images with STM, they claimed an anomalous flip-flop dimer motion at the temperature.<sup>8</sup> Before their observations, Shigekawa *et al.*<sup>23</sup> demonstrated buckled-dimer STM images around the temperature where Kondo *et al.* and Yokoyama *et al.* observed symmetric dimer images, contradicting each other.

From a theoretical point of view, the subject of buckled vs symmetric dimer has been a hot issue, too,<sup>16-21</sup> since it involves subtle aspects of electron correlation.<sup>16</sup> The buckling of dimer is stabilized by rehybridization of the dangling bonds and accompanying charge transfer from the lower to the upper dimer-composing atoms. In order to discuss its stability, thus, how the Coulomb interaction in the upper atom is screened, which is an issue of dynamical correlation, should be estimated precisely. On the other hand, in the case of the symmetric dimer, the two dangling bonds filled with one electron each, static electron correlation should be included in a discussion of stability against the buckling, as the case of dissociation of hydrogen molecule. Calculations with density functional theory, which adequately treats the dynamical correlation, supports a buckled dimer,14,15 while multiconfiguration self-consistent field calculation, which handles the static correlation, predicts lower energy for the symmetric dimer.<sup>17,19</sup> Recent studies including both correlations seem favorable for buckled dimers,<sup>16,20</sup> but not conclusive yet.18,21

Concerning a technical side of this issue, it has been argued that uncertainty of sample temperature could be the origin of the inconsistent observations.<sup>7</sup> In fact, the sample temperature is often measured on a stage where a sample holder is mounted. Actual sample temperature could be higher than that reported if thermal conductance from the mount through the holder to the sample is not good. In order to solve the undetermined situation, we carried out STM experiments at low temperature, which was measured at the sample site. To avoid uncertainty on the sample temperature, we first measured the temperature with a resistance temperature sensor (Cernox) attached on a dummy sample, and confirmed that the sample temperature during our observation (except that taken intentionally at an elevated temperature) is below 10 K. Our results show apparently symmetric dimer images with negative sample voltages (filled-state images),



FIG. 1. (Color) STM images taken below 10 K with a sample bias voltage of -2.2 V (a) and +1.6 V (b). Tunneling current is set at 38 pA and 55 pA, respectively. The filled-state image (a) apparently shows symmetric dimers, while the empty-state image (b) shows buckled dimers. In an area surrounded by a dashed green line in image (a) [zoomed in (c)] a faint trace of the  $c(4 \times 2)$ structure, alternative array of dark spots between the dimer rows, is observed, as pointed with arrows, indicating an existence of the  $c(4 \times 2)$  periodicity and the buckled dimers there.

as observed by Kondo *et al.*<sup>7</sup> and Yokoyama and Takayanagi.<sup>8</sup> With positive sample voltages (empty-state images), however, buckled-dimer structure was clearly observed, similar to the result reported by Shigekawa *et al.*<sup>23</sup> Our observations support for asymmetric dimer structure at the low temperature and lead us to conclude that apparent symmetric dimer structure in the filled-state images is an artifact induced by STM imaging.

In the present study, we used a commercial STM setup made by Unisoku (USM type), which can be operated under multiple extreme conditions of ultrahigh vacuum (UHV), low temperature (>2.8 K), and magnetic field (<11 T). The base pressure in the STM chamber is  $\sim 1 \times 10^{-8}$  Pa at room temperature. The Si(001)2×1 surface was prepared by a standard method; a small piece of *n*-type silicon wafer (Sb-doped, 0.14–0.07  $\Omega$  cm) oriented to the (001) direction was cut and loaded into a UHV chamber. In the chamber, it was heated at 600 °C for 10+ hours for outgas and was flashed at 1200 °C to make a clean surface. A chemically etched tungsten tip was used as a probe.

Figure 1 shows STM images taken at a temperature below 10 K with negative (a) and positive (b) sample bias voltages. Filled and empty electronic states of the sample surface around the Fermi level are imaged, respectively. The filled-state image [Fig. 1(a)] shows equally spaced linear features, or dimer rows, running in the [110] direction with a separation of 0.77 nm. The linear feature is composed of the cocoon-shaped dimers. In the image most of the surface area is seemingly covered with symmetric dimers. We took filled-state STM images with a bias voltage ranging from -3 V to -1.3 V. Basically symmetric dimers were always observed, except a few buckled ones near step edges or defects (one example is clearly shown in Fig. 2).

The empty state image, presented in Fig. 1(b), shows a remarkable contrast from its counterpart. Almost all area is filled with zigzag dimer rows, supporting for an presence of buckled dimers on the surface. Depending on a correlation of

the zigzag pattern with the neighboring dimer rows, two types of ordering exist: in phase and out of phase, corresponding to  $p(2\times2)$  and  $c(4\times2)$  ordered structure, respectively. At a boundary of the  $c(4\times2)$  and  $p(2\times2)$  phases a transitional motion of phase boundary is observed quite often as a fuzzy-looking region,<sup>23</sup> one example found in the lower part of the image of Fig. 1(b). Changing applied bias voltage from +3 V to +1.6 V does not affect basic feature of the imaging. Theoretical calculations<sup>12,13</sup> suggest the upper (lower) atom in the buckled dimer is observed as a protrusion in the filled (empty)-state images. The lower atoms of buckled dimers are presumably observed in Fig. 1(b).

The characteristic difference in apparent dimer structure between the filled- and empty-state STM images is observed



FIG. 2. (a, b) STM images taken below 10 K on identical area taken with a bias voltage of different polarities. The filled-state image (a) was taken with the sample voltage of -1.5 V and the tunneling current of 42 pA, while the empty-state image (b) was taken with +1.5 V and 42 pA, respectively. (c) A filled-state STM image taken at 47 K. The sample voltage and tunneling current are -2.0 V and 68 pA, respectively.

reproducibly all over the probed area. We also changed the setting tunneling current from 5 pA to 300 pA, but the main feature of the observation did not change in both polarities of the bias voltage. In fact, the contrastive imaging between the filled- and empty-state images was observed on the same place, as is shown in Fig. 2, where (a) and (b) are filled- and empty-state images, respectively. The image taken with a bias voltage of -1.5 V [Fig. 2(a)] shows apparently symmetric dimers, while the other image taken with +1.5 V [Fig. 2(b)] shows buckled dimers. As mentioned before, buckled dimers are occasionally observed in filled-state images, in particular, near step edges or missing dimers. Such buckled dimers can be found at the upper step edges in Fig. 2(a). The observation of these buckled dimers proves that the symmetric-dimer imaging is not due to limited spatial resolution.

The difference in imaging is, however, observed only at low temperature (< 10 K). At an elevated temperature only buckled dimers were observed in both polarities of the bias voltage, basically similar to that observed by Wolkow at the liquid nitrogen temperature (77 K).<sup>6</sup> Figure 2(c) is a filled-state image taken at 47 K and shows buckled dimers only. Transition temperature between the symmetric- and buckled-dimer imaging in filled state images is found to be  $\sim$ 40 K for the sample we used.

At the low temperature (<10 K) the dimer looks symmetric in the filled-state images, while buckled in the emptystate images. Since the same dimer looks in a different manner between the filled- and empty-state images, the difference should not be originated by the properties intrinsic to the surface, such as a new ground state or thermally induced flip-flop motion. It should be caused by STM observation itself. It has been known that in silicon the carrier concentration drops dramatically around 40 K.<sup>24</sup> The carrier in silicon is introduced by thermal excitation from dopants and quenched at low temperature. At 300 K, almost all donor impurities are ionized and the carrier density is saturated at the dopant concentration, but below 40 K it decreases with temperature T in a form of  $\exp(-E_d/2kT)T^{1.5}$ , where  $E_d$  and k are an energy level of dopant states measured from conduction band minimum (CBM) and the Boltzmann constant, respectively. The carrier density goes down to  $\sim 1\%$  of the dopant concentration at 40 K. Since a relaxation process to an extra charge, that is, the screening effect depends on the carrier density, the effect also becomes weak below the temperature. In the STM observation holes or electrons, depending on a polarity of the bias voltage, are inherently injected as tunneling current. We thus speculate that the imaging difference between the filled- and empty-state images at the low temperature is related with the reduced screening effect to the injected charges.

According to photoemission/inverse photoemission studies on the electronic structure of the Si(001)2×1 surface, there are two surface states with an energy level around the Fermi level.<sup>2</sup> At the  $\Gamma$  point, the maximum energy level of the lower surface states ( $\pi$  state) is located below the valence band maximum (VBM) by 0.4 eV, while the minimum of the upper surface states ( $\pi^*$  state) is located within a band gap below the CBM by 0.2 eV.<sup>2</sup> The  $\pi(\pi^*)$  states are occu-



FIG. 3. Schematics of the band diagram near the surface: (a) with negative sample voltage (filled-state imaging) at ambient temperature, (b) with positive sample voltage (empty-state imaging), (c) with negative sample voltage (filled-state imaging) at low temperature (below 40 K), (d) same conditions as (c) with a tunneling current. Injected holes into the sample surface as tunneling current (I) cause lowering of surface potential (II). As a result,  $\pi^*$  states are occupied by electrons, contributing to tunneling current (III).

pied (unoccupied) and thus in usual STM observation the  $\pi(\pi^*)$  states are supposed to be observed in the filled (empty)-state images. In the case of the filled-state imaging, where negative voltage is applied on the sample, the Fermi level is pinned at the bottom of the  $\pi^*$  state, as is shown in Fig. 3(a)<sup>25</sup> At the low temperature, due to the charging by injected holes from the tip to the sample surface [Process I in Fig. 3(d)], surface potential is lowered locally under the tip (Process II). As a result the  $\pi^*$  states are partially occupied by electrons and contribute to electron tunneling (Process III). Since effective tunneling barrier for the electrons in the  $\pi^*$  states is smaller than that of the  $\pi$  states because of its higher energy level, the contribution of the  $\pi^*$  states to the tunneling current is presumably significant. The  $\pi$  states are localized above the upper atom in the dimer, while the  $\pi^*$ states are above the lower atom. Since both the upper and lower atoms of the dimer then contribute to the tunneling current, an symmetric dimer is seemingly observed in the filled-state images, although the dimer itself is buckled. On the contrary, the  $\pi$  states cannot contribute to the empty-state image because the states are in fact surface resonance located below VBM, and thus do not pin the Fermi level [see Fig. 3(b)].

If the observed phenomenon is due to the charging effect, it should depend on the amount of tunneling current. In our case, however, changing in the amount of tunneling current does not affect the imaging. When the sample temperature is below 10 K, the carriers are quenched and the screening effect almost diminishes. In such situation, the charginginduced band bending is presumably saturated by a pinning due to the  $\pi^*$  states, and therefore the amount of the band bending does not depend on the amount of tunneling current. On the other hand, around the temperature where the screening effect is still significant, it is expected that the charginginduced band bending depends on the amount of tunneling current. In such cases, the image contrast of the dimers in the filled-state images should depend on the amount of the tunneling current, as reported by Mitsui and Takayanagi,<sup>9</sup> who carried out STM studies on the surface at 65 K.

If this explanation of the apparent symmetric-dimer observation in filled-state images is correct, some trace of the  $c(4 \times 2)$  or  $p(2 \times 2)$  structures should appear in the images. In fact, for instance, in the zoomed area of the filled-state image shown in Fig. 1(c), a very faint pattern of alternative dark spots between the dimer rows is found. The pattern, fitting well with a periodicity of the  $c(4 \times 2)$  structure, must be a trace of the intrinsic  $c(4 \times 2)$  structure overlapped with the symmetric-dimer appearance. The similar  $c(4 \times 2)$  pattern is also found in other areas of Fig. 1(a) and the filledstate image of Fig. 2(a). It was difficult to detect a trace of the  $p(2 \times 2)$  structure because smaller corrugation is expected for the  $p(2 \times 2)$  structure than for the  $c(4 \times 2)$  structure in STM observation. When the surface is almost covered with the  $p(2 \times 2)$  structure [as in the case of the images shown in Fig. 2(c)] or when spatial resolution of STM imaging is limited, only the apparent symmetric dimer is observed in the filled images. Buckled dimers observed near step edges or missing dimers in filled-state images (cf. Fig.

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2) are presumably due to the reduced charging effect by extra relaxation process related with their local structures.<sup>26</sup>

Recently, there are some efforts trying to detect the structural transition at low temperature below 70 K by photoemission spectroscopy.<sup>27,28</sup> By measuring core-level shifts of Si 2p states, which is sensitive to local arrangement of Si atoms including that composing dimers, these studies conclude no structural transition around the temperature, supporting our arguments.

In conclusion, we studied whether the dimer of the  $Si(001)2 \times 1$  surface is buckled at the low temperature. Buckled dimer structure was observed in the empty-state images, while in the filled-state images most of the dimers look symmetric. The seeming symmetric dimer structure in the filled-state images is due to STM imaging mechanism, presumably induced by the charging effect. These observations imply that no structural transition occurs between the liquid nitrogen temperature (77 K) and 10 K, and that most probably the buckled dimer is the ground-state structure of the surface.

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