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Metastable phase of symmetric dimers on Si(001)

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The reconstruction of the Si(001) surface is reexamined by using first-principles density-functional calculations. We find that a symmetric dimer structure in which symmetric dimers are alternately displaced up and down along the dimer rows is more favored by 21 meV/dimer than the conventional symmetric dimer structure where all the dimers have an identical height. In this metastable $p(2\times2)$ structure, the up and down symmetric dimers accompany the lateral movements of the second-layer atoms: i.e., on the two sides of the dimer the second-layer atoms bonding to the up (down) dimer move equally toward (outward) each other by 0.15 Å. With this predicted symmetric dimer structure we discuss the symmetric dimer phase observed in a recent low-temperature scanning tunneling microscopy experiment.

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Over the past several decades the Si(001) surface has been extensively studied because of its technological importance in the fabrication of semiconductor devices as well as for many fundamental issues of chemical reaction, epitaxial growth, and surface dynamics. The Si(001) surface exhibits a surface reconstruction in which pairs of surface atoms bond to each other, forming dimers.[1,2] It is well established that the ground-state structure of Si dimers is buckled, accompanying a charge transfer from the down atom to the up atom.[3] At room temperature, scanning tunneling microscopy (STM) experiments have shown symmetric dimer patterns which were interpreted as due to thermal activated flipping motion of the buckled dimers.[2,4,5] Such flipping motion becomes frozen at low temperatures below ~120 K, pinning to a $c(4\times2)$ phase where dimers are alternatively buckled along and perpendicular to the dimer rows.[6] Therefore, the surface dynamics causes an order-disorder transition with increasing temperature, leading to the room-temperature (2×1) surface symmetry.[7–10]

However, recent STM experiments performed at low temperatures[11–15] have shown a new aspect which seems not to be consistent with the above picture of the reconstruction of Si(001). Yokoyama and Takayanagi[11] observed a reappearance of symmetric dimer patterns upon cooling down to 5 K. This symmetric dimer image has flicker noise which was interpreted by slow dynamical flip-flop motion of the buckled dimers. As a matter of fact, Hata, Sainoo, and Shigekawa[12] measured the dynamics of the flip-flop motion of the buckled dimers at 70 K and found that the activation energy between the two stable buckling configurations significantly varies for dimers in different domains. Thus, the above two experiments[11,12] argued that the reemergence of the symmetric dimer image at low temperatures would be attributed to reduction of the barrier height for the dimer flipping. Interestingly, using a variable-temperature STM,[16] Kondo *et al.*[13] observed a coexistence of three different phases at 50 K, i.e., (i) the $c(4\times2)$ phase, (ii) the $p(2\times1)$-symmetric phase with streaks, and (iii) the $p(2\times1)$-symmetric phase without streaks. Here, streaks imply the existence of relatively slow flip-flop motion of the buckled dimers, equivalent to flicker noise measured by other STM studies.[11,12,14] Kondo *et al.*[13] also observed that at 20 K the surface is dominantly covered with the third phase. Consequently, they claimed that the apparent symmetric dimers at 20 K, which were imaged as two bright spots per a dimer, are not associated with the flipping motion of buckled dimers, but due to their static symmetric configuration. Since this claim that the ground state of Si(001) consists of symmetric dimers rather than buckled dimers is contrasted with most of the previous theoretical[3,10,17–19] and experimental[6,11,12,14,15] works, the observed symmetric dimer images at 20 K need to be explained.

In this paper we predict a reconstruction of Si(001) where symmetric dimers are alternately displaced up and down along the dimer rows [see Fig. 1(c)]. This $p(2\times2)$-symmetric dimer structure is found to be favored over the conventional symmetric dimer structure of $p(2\times1)$ [Fig. I(a)] by 21 meV/dimer. This $p(2\times2)$ structure has a local minimum with respect to some buckling distortion, indicating a metastable structure. Note, however, that the $p(2\times2)$-symmetric dimer structure is less stable than the buckled dimer structures of $p(2\times2)$ [Fig. 1(b)] and $c(4\times2)$. In view of experimental evidences that the low-temperature $p(2\times1)$ phase is induced by the STM tip,[14,15] the metastable $p(2\times2)$-symmetric phase might be induced by the STM tip. Then, it is expected that a dynamical motion between the up and down dimers within the $p(2\times2)$-symmetric structure easily takes place at 20 K because of a shallow energy barrier between the two kinds of configurations. The rapid up-down motion of symmetric dimers produces an apparent $p(2\times1)$-symmetric phase, where every dimer is simulated to be imaged as two bright spots. This may provide an explanation for the observed $p(2\times1)$-symmetric phase at 20 K, i.e., the above-mentioned third phase.[13]

The total-energy and force calculations were carried out using density-functional theory[20] (DFT) within the generalized-gradient approximation.[21] The Si atom is de-

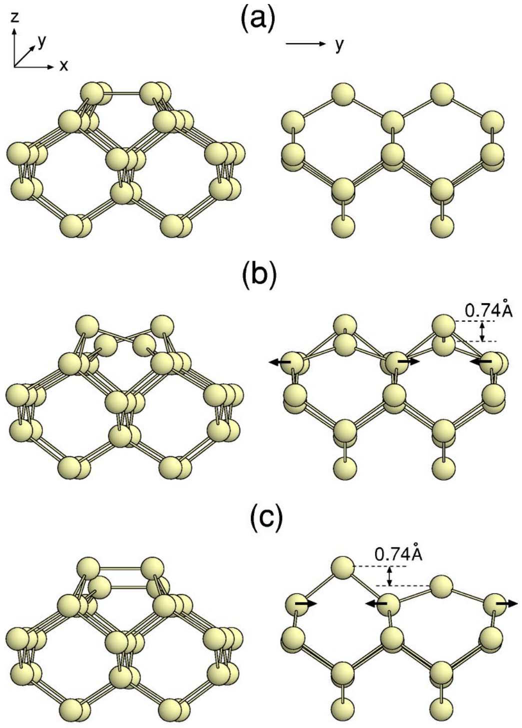

FIG. 1. Optimized structure of the Si(001) surface: the two side views of (a) the $p(2\times1)$-symmetric structure, (b) the $p(2\times2)$-buckled structure, and (c) the $p(2\times2)$-symmetric structure. The arrows in (b) and (c) show pairing patterns of the second-layer atoms. The **x**, **y**, and **z** directions are [110], [110], and [001], respectively.

scribed by norm-conserving[22] pseudopotentials. A periodic slab geometry was employed with 12 atomic layers, and the vacuum spacing between these slabs is about 10 Å. A plane-wave basis set was used with 20 Ry cutoff. The **k** space integration was done with 16 and 32 points in the surface Brillouin zone of the 2×2 and 2×1 unit cells, respectively. All atoms except the two central planes were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr.

We first examine the buckling of dimers of Si(001) within a $p(2\times1)$ periodicity. The buckled dimer structure is found to be favored over the symmetric dimer structure [Fig. 1(a)] by 178 meV/dimer. The buckled dimer structure of $p(2\times2)$ [Fig. 1(b)] in which Si dimers are alternately buckled along the dimer rows is further stabilized by 86 meV/dimer, compared with that of $p(2\times1)$. Therefore, the $p(2\times2)$-buckled structure is more stable than the $p(2\times1)$-symmetric one by 264 meV/dimer. In Table I, we compare our calculated energy differences of various reconstruction structures with previous[10,17–19] DFT results. There are some deviations for the stabilization energy of dimer buckling among several DFT calculations, but all DFT calculations agree that buckled dimers are more favorable than symmetric ones.

TABLE I. Calculated stabilization energy (meV/dimer) of the $p(2\times1)$-buckled (B), $p(2\times2)$-buckled (B), and $p(2\times2)$-symmetric (S) structures relative to the $p(2\times1)$-symmetric structure. All data are given from DFT calculations.

	$p(2\times1)$-B	$p(2\times2)$-B	$p(2\times2)$-S
Inoue *et al.*[a]	169.9	259.3 (260.5)	
Ramstad *et al.*[b]	120±10	168±18 (171±13)	
Lee and Kang[c]	150	220	
Healy *et al.*[d]		225	
This	178	264	21

[a] Reference 10.
[b] Reference 17.
[c] Reference 18.
[d] Reference 19.

The calculated potential-energy barrier ($E_b = 264$ meV) between the two buckled dimer configurations (see Fig. 2) within the $p(2\times2)$ structure allows the flip-flop motion of the buckled dimers. Assuming an Arrhenius-type activation process with the usual attempt frequency of $\sim 10^{13}$ Hz, the flipping rate of the buckled dimers is estimated as $\sim 3.7\times10^{8}$ sec^{-1} at room temperature. Such a rapid flipping motion of the buckled dimers can produce an averaged symmetric dimer image since it takes about 10^{-2} sec to obtain STM image of a dimer. This flipping rate becomes negligible at low temperatures below 70 K. However, recent low-temperature STM experiments[11,12,14,15] observed symmetric dimer images with flicker noise which was interpreted by slow flip-flop motion of the buckled dimers. Our simulated filled-state image [Fig. 3(a)] of the $p(2\times2)$-buckled dimer structure shows a bright spot on top of the up atom of the buckled dimer. As a result, slow flip-flop motion of the buckled dimers produces a change of the position of the bright spot, resulting in the presence of streaks in the STM image. Based on a statistical analysis of the flip-flop motion of the buckled dimers at 70 K, Hata, Sainoo, and Shigekawa[12] estimated a barrier for flipping of about 136±16 meV, smaller than the present and other[10,17–19] DFT results (see Table I). This flipping energy barrier is still too high to explain symmetric dimer images observed in STM experiments at low temperatures below 20 K.[11,13] In this sense, the barrier height for the dimer flipping may be sensitive to the tip-surface interaction through experimental conditions such as bias voltages and tunneling current.[14,15] However, as pointed out

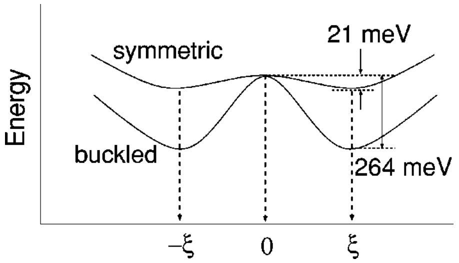

FIG. 2. Double-well potentials of the dimers in the $p(2\times2)$-buckled and $p(2\times2)$-symmetric structures. $\pm\xi$ in the former structure represents the tilt angle of ±18.5° of the buckled dimer, while that in the latter structure is the displaced height (±0.37 Å) for the up and down dimers from the $p(2\times1)$-symmetric structure.

TABLE II. Calculated bond lengths for the $p(2\times2)$-buckled (B) structure [Fig. 1(b)] and the $p(2\times2)$-symmetric (S) structure [Fig. 1(c)]. d_D and d_{12} denote the dimer-bond and back-bond lengths, respectively. The value in parentheses represents the back-bond length associated with the down atom in $p(2\times2)$-B.

		d_D	d_{12}
$p(2\times2)$-B		2.36	2.40 (2.34)
$p(2\times2)$-S	Up dimer	2.55	2.39
	Down dimer	2.32	2.33

by Kondo *et al.*,[13] it is hard to explain their observed symmetric dimer images (without flicker noise) as due to the flip-flop motion of the buckled dimers.

For interpretation of the observed[13] symmetric dimer images without flicker noise at low temperatures, we propose a $p(2\times2)$ structure which consists of the symmetric dimers with alternate up and down displacements along the dimer rows [see Fig. 1(c)]. We find that this $p(2\times2)$-symmetric structure is favored over the conventional $p(2\times1)$-symmetric one [Fig. 1(a)] by 21 meV/dimer. To confirm the stability of the former symmetric structure with respect to dimer buckling, we reoptimized the structure starting from an initial geometry in which the two dimers of the $p(2\times2)$-symmetric structure are alternately buckled by 5° and found it to be converged to the $p(2\times2)$-symmetric structure. This indicates that the $p(2\times2)$-symmetric structure is metastable. In Table II we list the calculated dimer-bond length and the back-bond length of the $p(2\times2)$-buckled and $p(2\times2)$-symmetric structures. We find that the dimer-bond length of the up dimer in the $p(2\times2)$-symmetric structure is 2.55 Å, much longer than that (2.32 Å) of the down dimer. Note that the back-bond length (2.39 Å) of the up dimer is longer than that (2.33 Å) of the down dimer. This back-bond length of the up (down) dimer is close to that of the up (down) atom in the $p(2\times2)$-buckled structure (see Table II). We also note that the height difference between the up and down dimers is 0.74 Å [see Fig. 1(c)], being equal to that between the up and down atoms of the buckled dimer in Fig. 1(b). Thus, it is likely that the local bonding character as well as the bond reordering around Si atoms composing the up (down) dimer in the $p(2\times2)$-symmetric structure are similar to those of the up (down) atom in the $p(2\times2)$-buckled one. It is well known that the underlying mechanism of alternate dimer buckling on Si(001) is a bond reordering (i.e., sp^3- and sp^2-like hybridization for the up and down atoms, respectively) of dangling orbitals by charge redistribution, thereby diminishing repulsive Coulomb interaction between rehybridized dangling bonds.[19]

It is noticeable that in the $p(2\times2)$-symmetric structure the second-layer atoms bonding to the up (down) dimer move equally toward (outward) each other by 0.15 Å [see Fig. 1(c)], as a consequence of the upward (downward) relaxation of the up (down) dimer. Here, the lateral movements of the second-layer atoms have an identical direction on the two sides of a dimer. On the other hand, in the $p(2\times2)$-buckled structure the directions of such lateral movements on both sides are opposite to each other: that is, the second-layer atoms bonding to the up (down) atom move equally toward (outward) each other by 0.11 Å [see Fig. 1(b)]. Therefore, the two $p(2\times2)$ structures induce the different types of strain on the surface. We note that apparent symmetric dimer rows were observed at the antiphase boundaries of the two alternate $c(4\times2)$ phases.[14] Considering that the direction of strains of the second-layer atoms in the $p(2\times2)$-symmetric phase is identical to that of the two alternate $c(4\times2)$ phases along the boundaries, we anticipate a future experiment identifying the presence of the $p(2\times2)$-symmetric structure at those boundaries.

There have been experimental evidences that the low-temperature $p(2\times1)$ phase is induced by the STM tip.[14,15] It was experimentally observed that a buckled dimer is easily flip flopped as the tunneling current increases, implying that the flipping barrier of the buckled dimer can be lowered by the tip.[14,15] A previous theory[23] suggested that the tip-surface interaction would enforce a flip-flop motion, producing a $p(2\times1)$-symmetric configuration in STM images. In this sense, the tip-surface interaction is possibly associated with the $p(2\times1)$-symmetric dimer images observed at low temperatures.[11–15] Although the detailed description for the tip-surface interaction is beyond the present study, the stabilization of the $p(2\times2)$-symmetric structure induced by the tip is examined by a simple model. Here, we assume that one buckled dimer in the $p(2\times2)$ unit cell is transformed to be symmetric by the tip-surface interaction: that is, one dimer is constrained to be symmetric. This assumption is marginally consistent with several experimental evidences[11,12,14,15] where the flipping barrier of buckled dimers is lowered by the tip-surface interaction (therefore reducing the tilt angles of the Si dimers), and is well consistent with the observation[13] of the static symmetric dimer configuration. We optimize the structure of the other dimer within a symmetric or buckled configuration. The height of the constrained symmetric dimer is displaced upward from the equilibrium height of the $p(2\times1)$-symmetric structure [Fig. 1(a)]: this displacement is denoted by Δz. For a given Δz all the atoms are fully relaxed within the $p(2\times2)$ unit cell, except the two central layer atoms and the two Si atoms of the constrained symmetric dimer (but the dimer bond length is optimized). The calculated energies for the two kinds of configurations (i.e., symmetric and buckled configurations of the second dimer) are displayed in Fig. 4 as a function of Δz. We find that the energy curves of the two configurations cross at about $\Delta z_c = 0.22$ Å, therefore indicating that the buckled (symmetric) configuration favors over the symmetric (buckled) one below (above) $\Delta z_c = 0.22$ Å. This result implies that, if the tip-surface interaction is enough to bind a buckled dimer to the tip and transform it into a symmetric configuration, the $p(2\times2)$-symmetric phase will be stabilized at Δz greater than Δz_c. The less stability of the buckled configuration above Δz_c is possibly due to an increase of the reversed strain (which favors the symmetric configuration) in the second-layer atoms [see Fig. 1(b)].

In order to account for the symmetric dimer images (at 20 K) observed by Kondo *et al.*,[13] we estimate the up-down motion of the symmetric dimers within the $p(2\times2)$-sym-

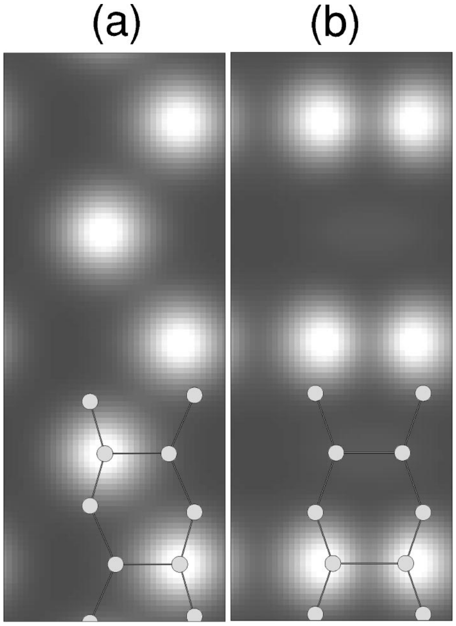

FIG. 3. Simulated filled-state STM image of Si(001): (a) the $p(2\times2)$-buckled structure and (b) the $p(2\times2)$-symmetric structure. These images were obtained by integrating the charge from occupied states within 1.5 eV of the highest occupied state. The images were taken at 3 Å above the outermost Si atom.

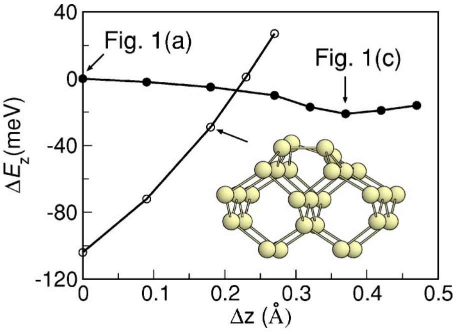

FIG. 4. Energy curves for the $p(2\times2)$-buckled and $p(2\times2)$-symmetric structures where one dimer is constrained to be symmetric with varying the height. The open (solid) circles represent the energies of the buckled (symmetric) configuration. Δz is defined in the text. The energy (meV/dimer) is referenced from the total energy of the $p(2\times1)$-symmetric structure [Fig. 1(a)]. The optimized buckled configuration at $\Delta z = 0.18$ Å is insetted.

metric structure. Using a double-well potential between the up and down symmetric dimer configurations (see Fig. 2), a simple Arrhenius analysis yields the up-down motion with a rate of $\sim 5.2\times10^7$ sec^{-1} at 20 K. We believe that the energy barrier ($E_b = 21$ meV) of this potential is possibly underestimated compared to the actual situation where the observed symmetric dimer is placed under the STM tip. As a result, the above estimated rate of the up-down motion can be an upper limit. Considering that our simulated filled-state STM image [Fig. 3(b)] for the $p(2\times2)$-symmetric structure shows the two bright spots above the two Si atoms composing the up dimer, it is expected that at 20 K every dimer which involves the rapid up-down motion would be imaged as the two bright spots, identical to the STM data of Kondo *et al.*[13] It is notable that at the crossing point Δz_c in Fig. 4 the nucleus positions of the dimer atoms as well as the second-layer atoms in the $p(2\times2)$-symmetric structure differ from those of the $p(2\times2)$-buckled structure. This indicates that the transition from the $p(2\times2)$-symmetric to the $p(2\times2)$-buckled structure does not appear adiabatically as the metastable former structure traverses the crossing point. Therefore, at low temperatures the up-down motion which is coupled with the lateral movements of the second-layer atoms could be allowed without a collapse to the $p(2\times2)$-buckled structure. However, with increasing temperature thermal effect will be dominant to produce that collapse, leading to formation of the $p(2\times2)$-buckled structure.

In conclusion, we have predicted a reconstruction structure of symmetric dimers on the Si(001) surface. This metastable $p(2\times2)$-symmetric structure is found to be favored over the conventional $p(2\times1)$-symmetric structure. With the presence of the $p(2\times2)$-symmetric structure and its dynamics as well as its simulated STM image we tentatively interpret the STM data of the static symmetric dimers observed by Kondo *et al.*[13] However, a further demonstration (e.g., rigorous calculations involving the tip effect) for the stability of the dynamics of the $p(2\times2)$-symmetric structure is necessary to convincingly establish a connection to the observation of Kondo *et al.* We hope that our predictions will stimulate further experimental works for identification of the $p(2\times2)$-symmetric phase which could be formed by the tip-surface interaction or might exist at the antiphase boundaries of the two alternate $c(4\times2)$ phases.

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