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Anomalous flipping motions of buckled dimers on the Si(001) surface at 5 K

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We report on dynamical flipping of buckled dimers on the Si(001) surface at 5 K. A $c(4\times2)$ ordering of the buckled dimers has been observed to fluctuate at 5 K by using low-temperature scanning tunneling microscopy (STM). The flip-flop motion of the buckled dimers on the Si(001) surface exhibits symmetrical appearance in the STM images, independent of sample bias voltages and tunneling current.

The origin and nature of dimer structures on the Si(001) surface is one of the most intensively discussed issues in semiconductor surface physics. From enormous experimental and theoretical studies, it is well established that the basic reconstruction mechanism consists in the formation of buckled dimers,[1] and the 2×1 structure at room temperature is due to thermal activated flip-flop motion of the buckled dimers between their two possible orientations.[2] At low temperatures below $T_c\approx200$ K, scanning tunneling microscope[3–5] (STM) and other experiments[6,7] have shown that the 2×1 structure is transformed into the $c(4\times2)$ structure, which results from an antiphase ordering of the buckled dimers. The structural transformation is described as an order-disorder phase transition with respect to the dimer buckling, and the phase transition behavior has been characterized as an Ising-spin model.[8–11] However, the first principles calculations have predicted that the $p(2\times2)$ configuration, which consists of an out-of-phase and in-phase ordering of the buckled dimers along and perpendicular to the dimer rows, respectively, is also stable for the Si(001) surface at 0 K. Even in the recent precious calculations, the calculated total energies of the $c(4\times2)$ and $p(2\times2)$ structures are very similar in energy (the energy difference is only about 1–2 meV/dimer).[11–14] It is not possible to resolve the energy difference without improving the accuracy of the best calculations. Thus the ground state configuration of the Si(001) surface is still controversial, although the low-temperature experiments have exhibited the $c(4\times2)$ structure.

In this paper, we report on anomalous dynamical properties of the buckled dimers on the Si(001) surface at 5 K. Although most of the dimers are well buckled to make the ordered $c(4\times2)$ structure at 63 K, they appear to be symmetric in STM images at 5 K. Since the tunneling spectra do not change between at 5 K and 63 K, the dimers at 5 K should be buckled with the local $c(4\times2)$ and/or $p(2\times2)$ correlations. Therefore, the symmetric appearance of dimers at 5 K should be due to the flip-flop motion of the buckled dimers.

The experiments were performed with a low-temperature STM in an ultrahigh-vacuum chamber (UHV) with a base pressure less than 1×10^{-9} Pa.[4] Electrochemically W tips were used for the STM probe, which were prepared in UHV by electron bombardment heating. The Si(001) samples (Boron doped with $0.01-0.02\ \Omega$ cm and Antimony doped with $0.05-0.09\ \Omega$ cm) were cut from commercial wafer stocks. After being degassed at 900 K, the Si(001) surfaces were cleaned by thermal flashing at 1400 K. This cleaning procedure completely eliminates surface defects, estimated to be less than 0.5 %, while the high defect density (5–10 %) has been reported for typical clean surfaces.[2] The clean samples were, then, transferred into the low-temperature STM stage. The STM unit (including the tip and sample) is thermally and mechanically connected with a liquid He bath, and shielded by a liquid N_2 bath against room-temperature radiation. Owing to the radiation shield system, the achievable temperature of the STM is about 5 K using liquid He Temperature measurements are achieved by a thermocouple (Au $+0.007$ at. % Fe vs chromel) mounted near the sample holder. All STM images were obtained by a constant-current mode at room temperature, 63 K, and 5 K. Tunneling spectra $[(dI/dV)/(I/V)]$ were numerically derived from I-V characteristics at typical tip-sample separations given by a tunneling current of 100 pA and a sample bias voltage of 1.5 V, which almost represent the local density of electronic states at the surfaces.[15]

At room temperature, most of the dimers appeared to be symmetric in the STM images of the Si(001)-2×1 surface (not shown), which is due to the time average of thermal dimer flipping.[2] By cooling to 63 K, the dynamical flipping of the dimers was mostly frozen. As shown in Fig. 1(a), the buckled dimers were antiferromagnetically ordered on the entire surface, leading to the $c(4\times2)$ reconstruction. Figures 1(b) and 1(c) show the high-resolution STM images of the filled and empty states at 63 K, respectively. The phase of zig-zag pattern in the dimer-row direction changes by 180°, when the bias polarity is changed. The dimer buckling induces the charge transfer of dangling-bond states, which results in a relatively full dangling bond on the upper-side atom of the buckled dimer and empty on the lower-side atom. Thus, the filled-state images probed the upper-side

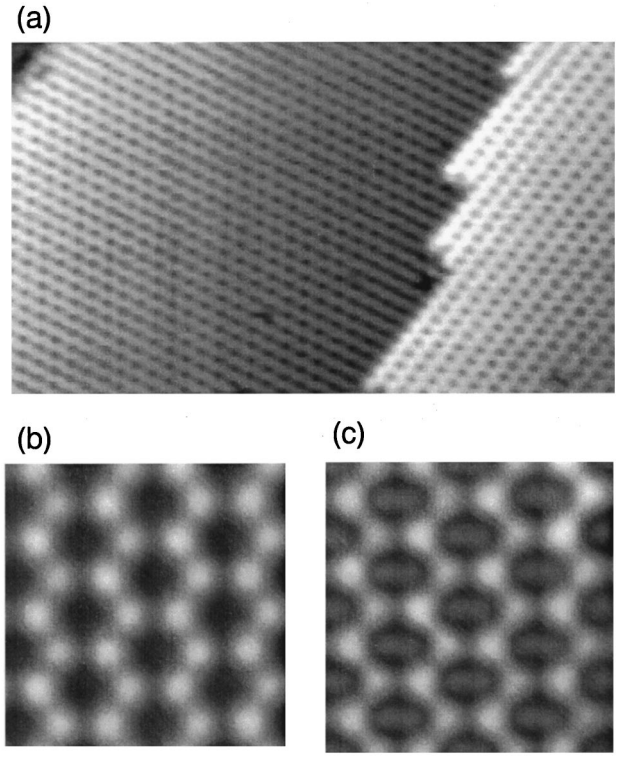

FIG. 1. (a) Filled-state STM image of the Si(001) surface at 63 K, extending over 32×25 nm^2 ($V_s=-1.0$ V, $I_t=100$ pA). The $c(4\times2)$ ordering of the buckled dimers is shown on the entire surface. The symmetric-appearing dimers still remain only at the lower side of the straight S_A step, which is due to the strain field of the S_A step, as reported previously in Ref. 5. (b),(c) The high-resolution STM images of the Si(001)-$c(4\times2)$ surface in filled states ($V_s=-1.0$ V, $I_t=100$ pA) and empty states ($V_s=1.0$ V, $I_t=100$ pA). These STM images extend over 3.1×3.1 nm^2 taken at 63 K.

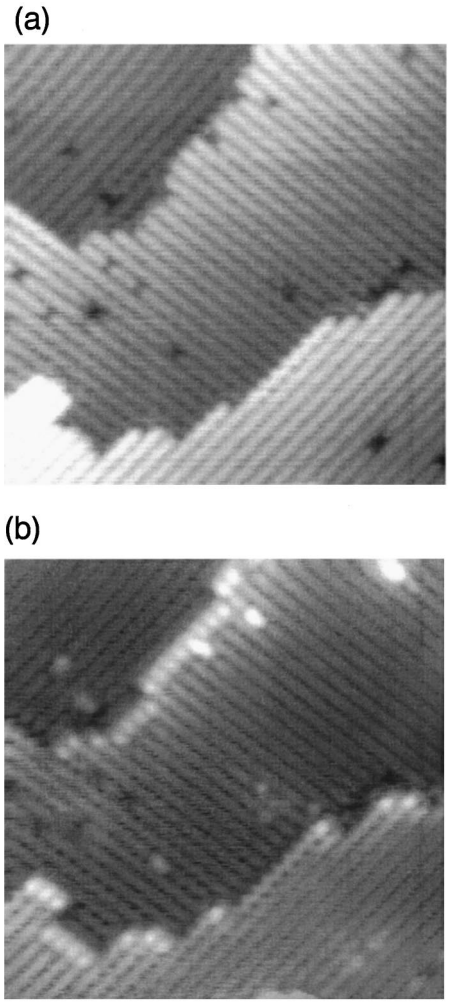

FIG. 2. (a), (b) Filled- and empty-state STM image of the Si(001) surface at 5 K. These STM images extend over 23×23 nm^2, taken at $V_s=-1.0$ V and $V_s=1.0$ V ($I_t=50$ pA), respectively. In both images, most of the dimers appear to be symmetric.

atom, and the empty-state images probed the lower-side atom. These STM images are in good agreement with the calculated STM images for the $c(4\times2)$ buckled dimer structure.[16] Although the $c(4\times2)$ ordering is known to be suppressed by a small amount of defects (even about 1%),[3,17,18] our extremely low-defect surfaces exhibit the complete order of the $c(4\times2)$ phase in this temperature range.

By further cooling down to 5 K, we observed that the buckling of dimers disappeared in the STM images. As shown in both the filled- and empty-state images at 5 K [Figs. 2(a) and 2(b)], most of dimers appear rather symmetric, except for those at the upper edge of the S_A steps and near the kinks. Although the symmetric-dimer images at 5 K are very similar to the 2×1 images at room temperature, the distinguishing features at 5 K are that flicker noise has been observed in both the filled- and empty-state images, and the dimer buckling appears slightly clear in the empty-state images. The flicker noise was not observed in the buckled dimer region of the same images (such as at the upper side of the S_A steps). In addition, such the flicker noise has been also observed at the lower side of the S_A steps even at 63 K, where the flip-flop motion is introduced by the local lattice strain.[5] Thus, the noise should result from slow flip-flop motion of the buckled dimers during the STM scan. The order parameter for the $c(4\times2)$ structure estimated from Fourier transform of the STM images[5] was only 0.25 ± 0.1 at 5 K, while the parameters were 0.1 ± 0.08 and 0.95 ± 0.1 at room temperature and 63 K, respectively. The symmetric dimer images were well reproduced at 5 K, independent of tip and sample conditions. Furthermore, we confirmed such the images on both *p*- and *n*-type Si(001) surfaces at sample bias voltages from -2 V to 2 V with tunneling currents from 5 to 500 pA.

Figure 3 shows the tunneling spectra $[(dI/dV)/(I/V)]$ obtained for the *p*-type Si(001) surface at room temperature, 63 K, and 5 K. Each spectrum has been derived from signal averaging of five I-V characteristics over the terraces. In the spectra, we observed that the peak positions were almost independent of measured positions and tip-sample separations, although their relative heights were slightly changed. For the $c(4\times2)$ structure at 63 K (second curve), the three characteristic peaks at -0.5, 0.6, and 1.3 (±0.05) eV have been assigned as the top of the occupied π_1 surface band, and the bottom and top of the unoccupied π_1^* surface band, respectively.[12–14,16] We observed that these characteristic

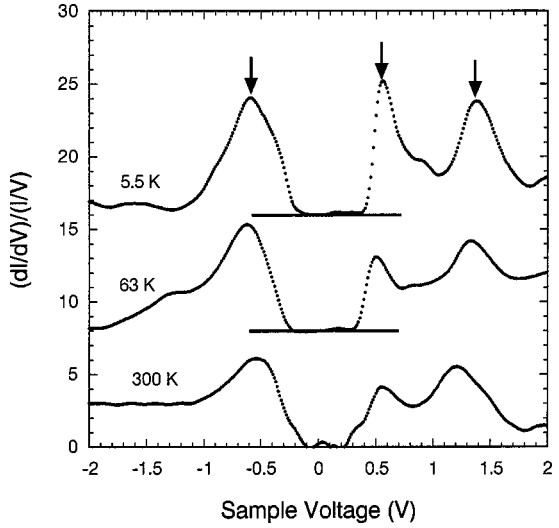

FIG. 3. Tunneling spectra $[(dI/dV)/(I/V)]$ of the Si(001) surface at room temperature (third curve), 63 K (second curve), and 5 K (top curve). At each temperature, the STM tip was fixed at $V_s = 1.5$ V and $I_t = 100$ pA to obtain current-voltage (I-V) curves. These spectra are composed of three identical peaks at $V_s = -0.5$, 0.6, and 1.3 (± 0.05) V.

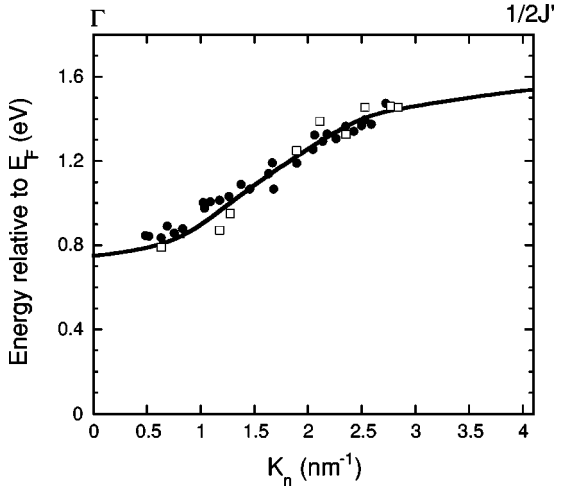

FIG. 4. Plots of the relation between the wave number $k_n(E_n) = n\pi/(L-a)$ of the confined π^* surface electrons and the discrete energy levels E_n, where L is distance between a pair of the Al ad-dimer chains, and $a = 0.45$ nm is the barrier thickness of the Al chain. Circles indicate E_n taken at 63 K, and open squares taken at 5 K. Solid line: calculated dispersion relation for π_1^* surface states by Northrup in Ref. 14.

peak positions were coincident with those at both room temperature and 5 K within ± 0.05 V, as shown in Fig. 3. At room temperature, the electronic structures have been explained as the flip-flop motion having the local $c(4\times2)$ and/or $p(2\times2)$ correlations,[19,20] although the surface exhibits the 2×1 symmetry. Since these characteristic peaks still remain at 5 K, the flip-flop motion with the local $c(4\times2)$ and/or $p(2\times2)$ correlations is also suggested at 5 K.

To study the dispersion relation of the π_1^* surface band at 5 K, we made one-dimensional (1D) quantum boxes on the p–type Si(001) surface. The unoccupied π_1^* surface band of the $c(4\times2)$ structure is known to exhibit a 1D character in the dimer-row direction.[12,13,20] To confine electrons in the 1D π^* surface states, straight chains of Al ad-dimers were used for the potential barrier, which were made by deposition at room temperature.[21,22] The 1D quantum boxes were created in the dimer-row direction between a pair of Al chains, and their quantum properties were directly probed by low-temperature STM, as reported previously.[22] The eigenenergies E_n of the quantum states were obtained from spectral peaks of the tunneling spectra in the quantum boxes, and their wavelength $k_n(E_n) = n\pi/(L-a)$ was determined by the distance L between Al chains and the barrier thickness $a = 0.45$ nm of the Al chain.[22] Figure 4 shows the relation between E_n and k_n obtained at 5 K (open squares). The plots accords well with both the dispersion relation at 63 K (circles) (Refs. 21 and 22) and the calculated π_1^* surface band of the $c(4\times2)$ structure in the $\Gamma - 1/2J'$ line (solid line).[12–14] From these results, we conclude that the local $c(4\times2)$ correlation still exists at 5 K. However, since the calculated dispersion curves for the π_1^* surface band are very similar between the $p(2\times2)$ and the $c(4\times2)$ structures,[12,13] the $p(2\times2)$ correlation cannot be excluded.

The tip-dimer interactions have been suggested by theory,[23–25] which can explain the symmetric appearance of the buckled dimers. However, the tip-dimer interactions should be negligible, since the dimers still appear symmetric even at a very low tunneling current of 5 pA in both bias polarities. In this condition, the tip-sample separation was about 2 Å larger than that for a typical tunneling current of 100 pA. Thereby we consider that the symmetric appearance of the buckled dimers is not caused by the tip effects, but by intrinsic nature of the surface. Another possibility is that the buckled dimers have been changed into the symmetric configuration with $c(4\times2)$ ordering of spins. By calculating the effects of spin arrangements, Artacho and Yndurain have concluded that the dimers are essentially symmetric with a strong spin correlations within them.[26] Although their band structures are very close to those of the buckled dimer structure, we observed the flicker noise in the STM images at 5 K (Figs. 2). The noise should be associated with slow dynamical flipping of the buckled dimers. Recently, similar noise has been detected on the Ge(001) surface at about 200 K, which has been explained by the flip-flop motion during the STM scan.[27]

The dynamical flipping at 5 K should be caused by reduction in the barrier height for the dimer flipping. Although the mechanism is not clear at present, a possible origin seems to be the anharmonic potential effect. Shkrebtii *et al.* have suggested that the dimer flipping is strongly associated with atomic displacements of the second layer atoms, since the flipping motion is coupled to large shifts and large twisting amplitudes of dimers in the dimer row direction.[28] Since this mechanism lowers significantly the barrier with respect to the pure rocking motion of the buckled dimers,[13,28] the elastic property in the subsurface layer should affect strongly the barrier height for the dimer flopping. Due to the anharmonic potential effects, the expansion coefficient of bulk Si is known to become negative at low temperatures (20–120 K) and close to zero below 20 K.[29] Anharmonicity is responsible for important surface processes, such as thermal expansion, reconstructive phase transition, and surface melting. In addition, because of breaking the symmetry, the anharmonic-

ity should be enhanced at surface regions.[30] Accordingly, we believe that important contributions to the reduction of the barrier height arise from the anharmonic potential effects that might induce unexpected atomic displacements in the subsurface layers at 5 K. However, Shigekawa *et al.*[31] observed that most of the dimers were buckled on the Si(001) surface at 6 K, and exhibited coexistence of the $c(4\times2)$ and $p(2\times2)$ domains. In addition, the sequence STM images have shown continuous fluctuations between the $c(4\times2)$ and $p(2\times2)$ arrangements, leading to their conclusion that the $p(2\times2)$ configuration is also stable for the Si(001) surface at 6 K.[31] Although it is controversial why our STM images at 5 K are completely different from Shigekawa's images at 6 K, we suggest that the *C*-type defects remained on their sample surface can freeze the dimer buckling. Due to its asymmetric structure, the *C*-type defect is known to pin the local buckling of dimers even at room temperature.[32] We emphasize that the *C*-type defects have been mostly removed from our sample surfaces by the careful cleaning procedure.

The order-disorder phase transition from the 2×1 to $c(4\times2)$ structures at $T_c\approx200$ K has been also reported for the Ge(001) surface.[33] The negative thermal expansion of Ge is much smaller than that of Si, although it has been observed for bulk Ge at low temperatures.[29] We observed the $c(4\times2)$ ordering of the buckled dimers on the Ge(001) surface at 5 K, similar to at 63 K (not shown). This result indicates that the re-excitation of the flip-flop motion at 5 K is intrinsic nature only for Si, reflecting the difference in the elastic properties between Si and Ge.

In summary, we have observed anomalous dynamical flipping of buckled dimers on the Si(001) surface at 5 K by using low-temperature STM. The static $c(4\times2)$ images at 63 have been transferred into the 2×1 like images. Because the dispersion relation of the π^* surface states were almost identical between at 63 K and 5 K, the 2×1 like images at 5 K should be originated from the dynamical dimer flipping with the local $c(4\times2)$ and/or $p(2\times2)$ correlations. Although the mechanism is not clear at present, we believe that the potential barrier for the dimer buckling has been reduced by anharmonic potential effects in the subsurface layers at 5 K.

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