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Low-temperature scanning-tunneling-microscopy observations of the Si(001) surface with a low surface-defect density

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We have settled a controversy that surface dimers in the Si(001) surface are intrinsically symmetric or asymmetric. Atom-resolved scanning-tunneling-microscopy (STM) images of a low-defect-density (~1%) surface at 144 K give definite evidence for the asymmetric-dimer model. We have identified a local influence of surface defects on buckling of dimers at low temperatures, which was not clarified in previous STM observations at 120 K.

It has been known that room-temperature (RT) scanning-tunneling-microscopy (STM) images[1–3] indicate symmetric-appearing dimers in the major part of the Si(001) surface exhibiting a 2×1 low-energy electron-diffraction (LEED) pattern, although Chadi had predicted in an empirical tight-binding calculation that symmetric dimers are unstable in comparison with buckled (i.e., asymmetric) ones.[4] Actually, asymmetric-appearing dimers are also observed with RT STM at limited regions, in the vicinity of defects or step edges.[1–3] A recent calculation incorporating spin effects concluded that symmetric dimers are most stable.[5,6] In this view (referred to as the symmetric-dimer model), dimers are essentially symmetric, while buckling is induced locally by defects and steps.

On the other hand, a LEED study revealed a reversible structural transformation at ~200 K,[7] as predicted by total-energy minimization calculation.[8] At low temperatures (LT's), the surface exhibited a $c(4\times2)$ LEED pattern. Recent detailed experimental[9] and theoretical[10,11] studies concluded that the transformation is an order-disorder transition with respect to the arrangement of buckled dimers. That is, at LT's "antiferromagnetic"[12] ordering of buckled dimers caused by a dimer-dimer interaction in a dimer row and a row-row interaction results in the $c(4\times2)$ LEED pattern, while "paramagnetic"[12] disordering of buckled dimers leads to the 2×1 pattern at RT. The $c(4\times2)$ structure is found to be the most stable arrangement of buckled dimers by first-principles total-energy calculations.[10,11] In this view (referred to as the asymmetric-dimer model), symmetric-appearing dimers observed with RT STM have been attributed to the time average of a flip-flop motion of Si atoms in buckled dimers allowed by thermal excitation.

Therefore, it is controversial whether dimers are intrinsically symmetric or asymmetric. It has been expected that STM observations at LT's will resolve this issue. LT STM images have been taken by Wolkow.[13] It was found, however, that both buckled and symmetric-appearing dimers exist on terraces even at 120 K. Only about 60% and 80% of the surface consists of buckled dimers in Figs. 2 and 3 of Ref. 13, respectively. Therefore, Wolkow[13] expressed that *the observation at 120 K of an increase in the number of buckled dimers, at the expense of symmetric-appearing dimers, is consistent only with the asymmetric-dimer description.* A reason for this expression came from high defect densities (5–10 %) on the surface. That is, the major part of the surface might appear as buckled-dimer regions, supposing defects induce buckling in many places on terraces. In addition, out-of-phase interferences of buckling induced by neighboring defects might result in formation of many domains of symmetric-appearing dimers, as mentioned in Ref. 13. In the above view, intrinsic buckling is not always necessary. Therefore, it seems that the controversy still remains. In addition, it is not clear what kind of defect induces buckling at LT's and how the defect does it.

In the present study, atom-resolved STM images of the Si(001) surface having a low defect density at 144 K give definite experimental evidence for the asymmetric-dimer model. The previous LT STM study[13] could not exclude the symmetric-dimer model. We have found that about 95% of the surface exhibits buckled dimers with a $c(4\times2)$ arrangement. We have revealed that surface defects affect buckling of dimers only locally and that they have nothing to do with the extensive formation of the $c(4\times2)$ arrangement. The present paper suggests that a defect-free surface will exhibit a complete $c(4\times2)$ arrangement of buckled dimers at LT's.

Experiments were performed by using a variable-temperature STM (JEOL JSM-4500VT), which allows 15–1500-K dynamic observation in an ultrahigh vacuum condition (5×10^{-9} Pa). A STM stage was designed drift free, so the sample drift rate can be minimized by less than 0.01 nm/s at low and high temperatures. A cryostat is mounted on the STM chamber and can operate for several hours without filling liquid helium. The Si(001) surface was cleaned by flashing to 1250 °C after a one night degas at 450 °C.

A STM image of the Si(001) surface at 144 K is shown in Fig. 1. This was taken at a sample bias of −2.0 V with a tunnel current of 0.1 nA. Figure 1 covers an area of 30×30 nm^2 and includes 49 dimer rows. The dimer rows are numbered as indicated in Fig. 1. At the central part, about 80 dimers are seen along a row within the frame. In Fig. 1, there are several bright protrusions on rows 8, 14, 17, 20, 21, 26, 36, and 39–41, which did not used to be observed at RT.

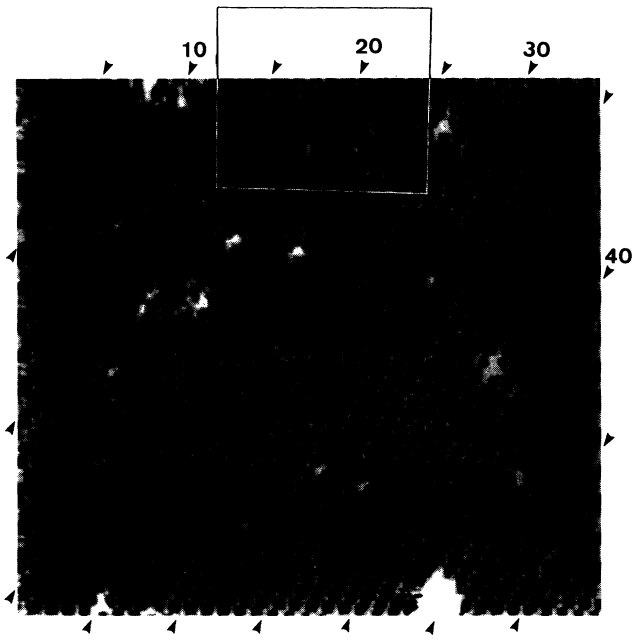

FIG. 1. Low-temperature STM image of the Si(001) surface at 144 K. Dimer rows are numbered. Sample bias is -2.0 V.

Since the number of the protrusions increases with time, these are assigned to be adsorbates from a residual gas due to LT's. However, the quality of this image is much better than those in Ref. 13, becuase the defect density ($\sim 1\%$) is much lower. The low defect-density surface provides a very different image of the surface from Figs. 2 and 3 in Ref. 13 as follows. First, 95% of dimers in the surface appear asymmetric. Second, buckled dimers form the $c(4\times 2)$ arrangement, but they do not form the $p(2\times 2)$ domain. Third, there are a small number of regions of symmetric-appearing dimers. They continue for 10–40 dimers in a row, but formation of symmetric dimers is not transmitted to adjacent rows. They are seen in rows 10, 14, 19, 21, 23, 26, 29, 31, 32, 35, 39, 40, and 46.

We observed in RT STM images that symmetric-appearing dimers prevail on terraces except in the vicinity of some defects, as in the literature.[1–3,13] We can conclude straightforwardly that symmetric-appearing dimers seen in RT images change into buckled ones upon cooling, because most of the dimers appear symmetric and asymmetric in RT and LT STM images, respectively. This change can be well explained by the asymmetric-dimer model as pointed out by Wolkow. At LT's the flip-flop motion of Si atoms in buckled dimers is frozen, whereas at RT the motion is allowed by thermal excitation resulting in symmetric-appearing dimers in STM images. The change cannot be explained by the symmetric-dimer model as discussed below in detail, which is the most important part of this paper. The transformation from 2×1 to $c(4\times 2)$ is assigned to be the order-disorder transition of arrangement of buckled dimers. The critical temperature of the transition is at least higher than 144 K. In the LEED observations[7,9] and first-principles calculations,[10,11] the temperature was 200 and 320 K, respectively. The present conclusion is consistent with the suggestion of the previous LT STM study[13] and in good agreement with the LEED observations[7,9] and first-principles calculations.[10,11]

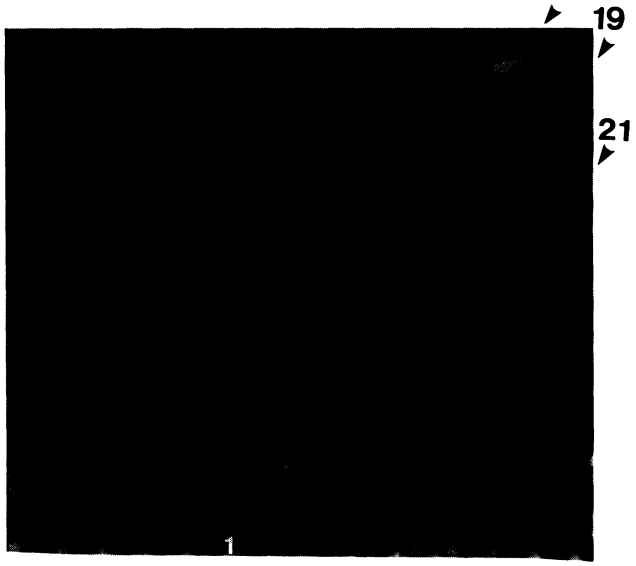

FIG. 2. Low-temperature STM image of a symmetric-appearing dimer region in row 19, enlarged from the central top part outlined in Fig. 1. In row 19, dimers are numbered from the bottom-most. Nos. 7 and 8 correspond to the type-C defect (Ref. 3). A reason for formation of a symmetric-appearing dimer region in row 21 is uncertain, because the region continues out of the frame.

If surface defects induce the buckling of dimers observed in Fig. 1, the symmetric-dimer model cannot be ruled out. We have to clarify the role of defects in the buckling of dimers. As described below, however, we can definitely exclude the symmetric-dimer model by analyzing the effect of the type-C defect denoted previously by Hamers and Köhler.[3] In Fig. 1, there are a small number of symmetric-appearing dimer regions. Some[14] of them (8 in the 13 regions mentioned above) are formed in the vicinity of the type-C defect and localized in each dimer row with 10–20 dimers length, as typically seen in row 19 in a more qualified STM image of Fig. 2. This image is enlarged from a part outlined at the central top of Fig. 1. We number dimers in row 19 from the bottom-most. The protrusions at No. 7 (a brighter protrusion)[15] and No. 8 (a darker protrusion) in Fig. 2 correspond to the type-C defect. That two adjacent protrusions appear as buckled dimers tilted to the same side is one of the characteristics[3,13,16] of the type-C defect.[17] Similar symmetric-appearing dimers are seen in rows 10, 14, 23, 26, 29, 32, and 40 in Fig. 1, and each row always includes one defect. Figure 3 provides another atom-resolved LT STM image of such a combination of the type-C defect and symmetric appearing dimers, in rows 26, 29, and 32. The symmetric-appearing dimers always start from the darker-protrusion side, continue 10–20 dimers, and gradually recover the buckling. In the brighter-protrusion side, dimers are buckled to be the $c(4\times 2)$ order. It should be noted that a single defect does not induce asymmetric dimers but induces symmetric-appearing ones at LT's. This suggests that defects do not play an important role in the buckling of dimers observed in Fig. 1.

The type-C defect is always observed in RT STM images[3,13,16] as one of two typical surface defects[18] on Si(001). Its RT STM image and illustration are shown in

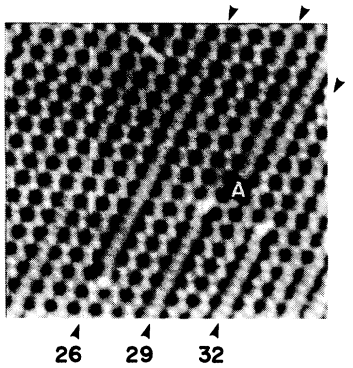

FIG. 3. Low-temperature STM image of the type-*C* defect in rows 26, 29, and 32. *A* indicates the type-*B* defect denoted previously in Ref. 3.

Figs. 4(a) and 4(b), respectively. The protrusions of the type-*C* defect [No. 12 and No. 13 dimer positions from the left edge in Fig. 4(a)] are indicated with two dotted circles in Fig. 4(b). It should be noted that dimers next to the type-*C* defect, i.e., Nos. 11 and 14, are buckled to the same side but opposite side with respect to the protrusions of the type-*C* defect. Along the dimer row, buckling continues from the defect towards both sides for about five dimers as illustrated in Fig. 4(b). Therefore, the type-*C* defect plays a role of a "phase shifter" by a half wavelength along the dimer row. This is a typical feature of the type-*C* defect.

The appearance of symmetric-appearing dimer regions observed in LT STM images [the image of row 19 with adjacent rows is reproduced in Fig. 4(c) from Fig. 2 for comparison, together with its schematic illustration along row 19 shown in Fig. 4(d)] can be explained by the feature of the type-*C* defect, as indicated in Fig. 4(e). Two competing sequences of the buckling of dimers are depicted; in *one side* [the right-hand side in Fig. 4(e)] of the defect, one sequence (shown with broken circles and broken zigzag lines) induced by the type-*C* defect is *out of phase* with the other sequence (shown with open circles and solid zigzag lines) induced by adjacent rows due to the antiferromagnetic ordering, whereas the former sequence is *in phase* with the latter in *the other side* (the left-hand side). That is, out-of-phase contributions from the two origins cancel buckling in dimers in the right-hand side of the defect, which results in formation of a symmetric-appearing dimer region there. We can thus explain the reason why the symmetric-appearing dimers are formed and also why they appear only in the one side of the defect.

The local influence[19] of the type-*C* defect on the buckling of dimers is evidenced by the short propagation of the symmetric appearing dimers at LT's [see Figs. 4(c) and 4(d) again]. In addition, it is clear that the effect of the type-*C* defect is not transmitted to adjacent rows. These two facts are clear evidence for the following: the driving force to form the antiferromagnetic order, being the most thermodynamically stable structure, is much stronger than that of the type-*C* defect to induce buckling of nearby dimers. Suppose only the type-*C* defects induce buckling of dimers on the surface, namely, suppose the thermodynamic driving force is not important, dimers in both sides of the defect would be buckled with the out-of-phase way at LT's. We do not observe such an out-of-phase boundary near the defects. We conclude that the type-*C* defects only give a local influence upon the buckling of dimers and that the symmetric-dimer model is definitely excluded.

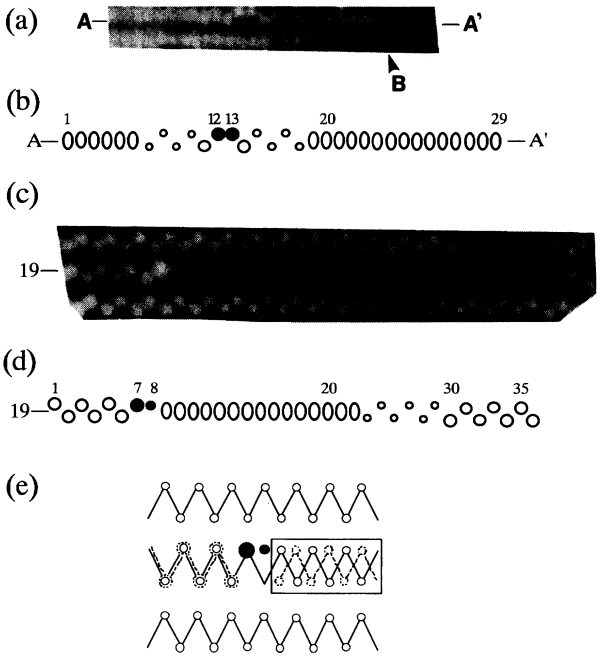

FIG. 4. (a) Room-temperature STM image of the type-*C* defect (Nos. 12 and 13 protrusions from the left edge) in the row AA'. Sample bias is -2.0 V. *B* denotes the type-*B* defect (Ref. 3). Note that the type-*C* defect induces buckling in adjacent dimers in both sides, whereas the type-*B* defect does not. (b) Schematic illustration (top view) of the dimer row along the line AA' in (a). Dotted circles are the type-*C* defect. Large and small open circles depict strongly and weakly buckled-up atoms, respectively. With increase of the distance from the defect, dimers appear symmetric as depicted by beanlike shapes. (c) Low-temperature STM image of the type-*C* defect in row 19 reproduced from Fig. 2. (d) Illustration (top view) along dimer row 19 in (c). Notations are the same as in (b). (e) Illustration along row 19 with adjacent rows for showing two competing sequences of the buckling of dimers induced by two origins; solid zigzag lines with open circles represent one sequence of buckling induced by adjacent rows, and broken zigzag lines and broken circles represent the other sequence of buckling induced by the defect shown by dotted circles. Open and broken circles represent buckled-up atoms, and zigzag lines connect buckled-up atoms for a guide. In the left side of the defect the two sequences are in phase, while in the right side they are out of phase resulting in a symmetric-appearing dimer region outlined by a rectangle.

Finally, we comment briefly on the previous experimental[13] and theoretical[10,11] studies. In Fig. 2 of Ref. 13, we find the combination of the type-*C* defect and symmetric-appearing dimers discussed in the present paper, at the fifth row from the left bottom. The existence of many defects resulted in the formation of a large area of symmetric-appearing dimers there. In the theoretical calculation, effects of defects were considered, but these did not have the feature of the type-*C* defect indicated in this paper.

In conclusion, we have observed STM images of the Si(001) surface having a low density of surface defects at 144 K. It is found that most of the dimers appear asymmetric

and that asymmetric (i.e., buckled) dimers are ordered to be a $c(4\times2)$ arrangement. We observe only a small number of symmetric-appearing dimer regions localized in the one side of the type-C defect along the dimer row. We have revealed that the defects effect the buckling of dimers only locally and that they have nothing to do with the extensive formation of the $c(4\times2)$ arrangement. It is concluded that surface dimers are intrinsically buckled independent of temperature.

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[11] K. Inoue, Y. Morikawa, K. Terakura, and M. Nakayama, Phys. Rev. B **49**, 14 774 (1994).

[12] "Antiferromagnetic" means that buckling of dimers is arranged to be like the antiferromagnetic order in the two-dimensional spin system, assuming that left-atom up and right-atom up in a buckled dimer correspond to up and down spins. "Paramagnetic" means that the arrangement of buckled dimers is disordered like the paramagnetic phase in the spin system above.

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[14] We consider that other symmetric-appearing dimer regions may be induced by the adsorbates.

[15] Such a brighter protrusion cannot be ascribed to the adsorbate, because its number density does not increase with time.

[16] A. Kobayashi, F. Grey, E. Snyder, and M. Aono, Phys. Rev. B **49**, 8067 (1994).

[17] Actual atomic structure of the type-C defect has not been understood. At low temperature Wolkow did not describe this defect (Ref. 13).

[18] The other kinds of defects observed usually on Si(001) are the A- and B-type defects for single- and double-missing dimers, respectively, denoted in Ref. 3. We identify these defects also at 144 K in Fig. 1 and especially at A in Fig. 3, as observed in Ref. 13. These defects behave similarly as they do at room temperature, namely, as if they have nothing to do with the buckling of surrounding dimers as seen at A in Fig. 3.

[19] The short propagation of symmetric-appearing dimers induced by the type-C defect at LT's is consistent with the short propagation of asymmetric-appearing dimers at RT shown in Figs. 4(a) and 4(b). This short influence upon buckling is another feature of the type-C defect.

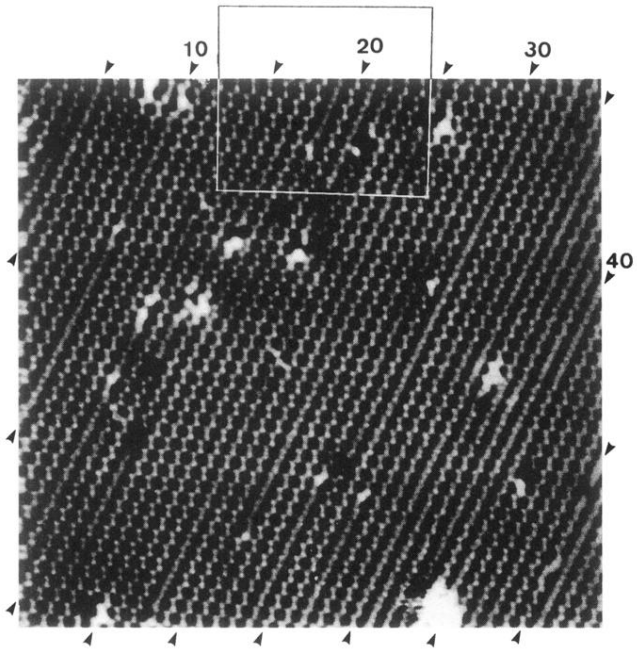


FIG. 1. Low-temperature STM image of the Si(001) surface at 144 K. Dimer rows are numbered. Sample bias is −2.0 V.

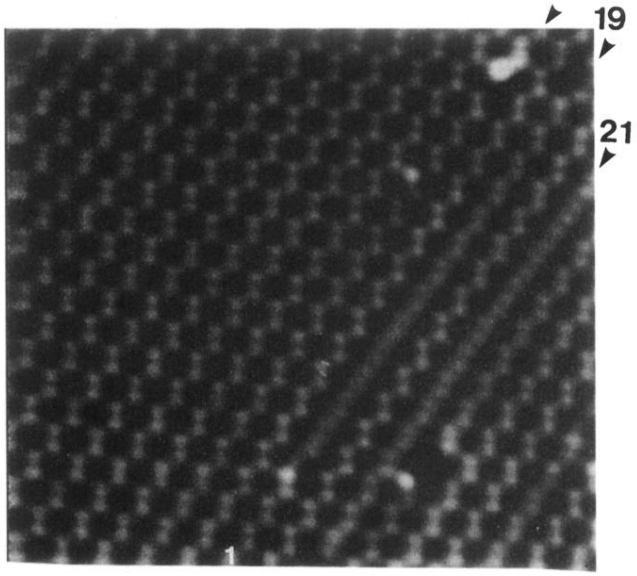
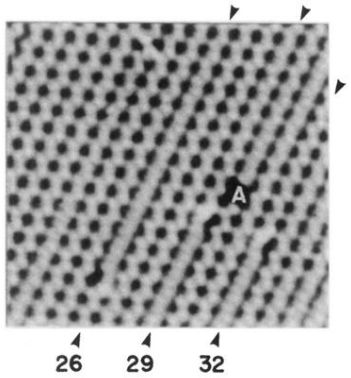


FIG. 2. Low-temperature STM image of a symmetric-appearing dimer region in row 19, enlarged from the central top part outlined in Fig. 1. In row 19, dimers are numbered from the bottom-most. Nos. 7 and 8 correspond to the type-*C* defect (Ref. 3). A reason for formation of a symmetric-appearing dimer region in row 21 is uncertain, because the region continues out of the frame.



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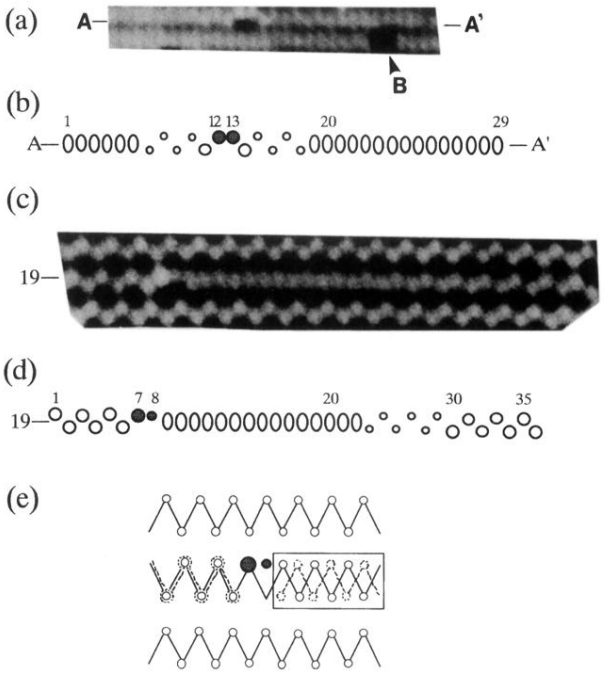

FIG. 4. (a) Room-temperature STM image of the type-*C* defect (Nos. 12 and 13 protrusions from the left edge) in the row AA'. Sample bias is -2.0 V. *B* denotes the type-*B* defect (Ref. 3). Note that the type-*C* defect induces buckling in adjacent dimers in both sides, whereas the type-*B* defect does not. (b) Schematic illustration (top view) of the dimer row along the line AA' in (a). Dotted circles are the type-*C* defect. Large and small open circles depict strongly and weakly buckled-up atoms, respectively. With increase of the distance from the defect, dimers appear symmetric as depicted by beanlike shapes. (c) Low-temperature STM image of the type-*C* defect in row 19 reproduced from Fig. 2. (d) Illustration (top view) along dimer row 19 in (c). Notations are the same as in (b). (e) Illustration along row 19 with adjacent rows for showing two competing sequences of the buckling of dimers induced by two origins; solid zigzag lines with open circles represent one sequence of buckling induced by adjacent rows, and broken zigzag lines and broken circles represent the other sequence of buckling induced by the defect shown by dotted circles. Open and broken circles represent buckled-up atoms, and zigzag lines connect buckled-up atoms for a guide. In the left side of the defect the two sequences are in phase, while in the right side they are out of phase resulting in a symmetric-appearing dimer region outlined by a rectangle.