Jahn-Teller Distortion in Dangling-Bond Linear Chains Fabricated on a Hydrogen-Terminated Si(100)-2 × 1 Surface

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Length-dependent charge redistribution in dangling-bond (DB) linear chains fabricated on a hydrogen-terminated Si(100)-(2 × 1) surface is analyzed by using scanning tunneling microscopy and first-principles calculations. The second-layer Si atoms are displaced alternately to form pairs with charge redistribution, which is explained by the Jahn-Teller distortion in an artificial pseudomolecule. In a short even-numbered (DB) structure, an unpaired second-layer Si atom exists and behaves as a soliton accompanied by the flip-flop motion of the structure. We point out that the odd-even problem, the edge effect, and the finite length of the DB structures are indispensable to understand the relaxation in the structures. [S0031-9007(99)09114-0]

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Total-energy lowering in pseudo-one-dimensional structures by charge redistribution is one of the exciting topics in solid-state physics. The Jahn-Teller distortion [1] in finite-length molecular systems and the Peierls instability [2] in one-dimensional metal systems are two typical examples. Scanning tunneling microscopy/spectroscopy (STM/STS) [3] and atom manipulation [4] have provided a new method for investigating artificial one-dimensional structures. A hydrogen-terminated Si(100)-2 × 1-H monohydride surface [5] has been used as a substrate for fabricating atomic-scale structures by forming dangling-bond (DB) structures using STM [6]. Metal-atom structures were fabricated by selective adsorption of Ga [7], Al [8], and Ag [9] atoms on DB structures.

In this Letter, we report on the first observation of the Jahn-Teller distortion in pseudo-one-dimensional DB structures on the Si(100)-2 × 1-H surface. The atomic geometry and the charge density of DB structures are characterized by low-temperature ultrahigh vacuum STM, and the origin of the charge redistribution is discussed based on the first-principles theoretical calculations. The odd-even problem, the edge effect, and the finite length of the DB structures must be taken into account in order to explain the experimental observations.

The sample was cut from an As-doped Si(100) wafer (n-type, 7 to 18 mΩ cm). The methods for preparing the hydrogen-terminated surface and the W tips were described elsewhere [7,10]. The experiments were performed at low temperature (96 to 110 K) achieved by liquid nitrogen and a temperature-controlling shutter. The base pressure of the STM chamber was 7×10^{-11} Torr. Hydrogen atoms were extracted by moving the tip at a speed of 5 nm/s along a Si dimer row, typically at a sample bias voltage (V_s) of +2.8 V and a tunneling current of 0.9 nA. The STM images were obtained at V_s of −2.0 or +2.0 V and at a constant tunneling current of 20 pA.

Figure 1(a) shows a gray-scale filled-state STM image of a DB structure fabricated at 96 K [5,10]. An atomically flat terrace made of diagonally running dimer rows is observed and cocoon-shaped Si dimers are resolved. The topographic maxima (white protrusions) are associated with the DBs. The hydrogen-terminated dimers are observed to be approximately 0.1 nm lower in height than the DBs because the surface states of the Si dimers are passivated [5]. The DB structure is composed of only unpaired DBs [Fig. 1(b)] and the DBs are imaged off-center of the dimer row, whereas a paired DB [Fig. 1(b)] would be imaged in the center [7].

The DB structure in Fig. 1(a) has eight protrusions; however, it is fifteen dimers long. Figure 1(e) shows the cross-sectional views of a thirteen-DB structure (defined as a DB linear-chain structure made of thirteen unpaired DBs). The higher DBs seen in the filled-state image are observed to be lower in the empty-state image. The DBs are thus imaged bright in the filled-state image only *alternately* [Fig. 1(d)].

The relaxation of a DB structure composed of infinite unpaired DBs along the dimer row was treated in the recent first-principles calculations by Watanabe *et al.* [11]. They showed that surface-state bands exist as a result of DBs and that the DB structure is unstable in the presence of Peierls distortion, which is a periodic lattice distortion accompanied by a redistributed periodic charge called charge density waves (CDW). The calculated height modulation of the first-layer Si atoms was 0.016 nm, and the lateral displacement of the second-layer Si atoms was 0.002 nm [inset of Fig. 1(e)]. The second-layer Si atoms are displaced toward the right or left alternately and they

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tend to pair up. A relatively long DB structure such as the one in Fig. 1(a), can be modeled by a periodic unit structure, and its distortion is well treated by the instability in one-dimensional metal resulting in Peierls distortion. These STM observations and theoretical considerations lead us to conclude that a charge redistribution and a lattice distortion are taking place in these DB structures, and hence result in the alternate topographic peaks.

To examine short DB structures, we fabricated two-, three-, four-, and five-DB structures. Figures 2(a)–2(c) show gray-scale filled-state STM images. Cross-sectional views of filled-state STM images in Fig. 2(d) reflect the redistribution of the charge. In this case, we would not use the calculations where an infinite DB structure is assumed [11]. In order to reveal the origin of the charge redistribution, we performed first-principles calculations dealing a large unit cell. In the calculation, the Si(100)-2 × 1-H surface was represented by a slab model consisting of five layers of Si atoms whose DBs were terminated by hydrogen. A periodic 4 × 8 supercell (two dimer rows with eight dimers each) was used. Relaxed atomic geometries and electronic structures were calculated within the local density functional approach, using the exchange correlation term of the Ceperley-Alder form [12] and an ultrasoft pseudopotential proposed by Vanderbilt [13]. Electronic and ionic degrees of freedom were optimized by using the conjugated gradient method [14]. Wave functions were expanded in a plane-wave basis set with an energy cutoff of 10 Ry. Details of the calculations are published elsewhere [15].

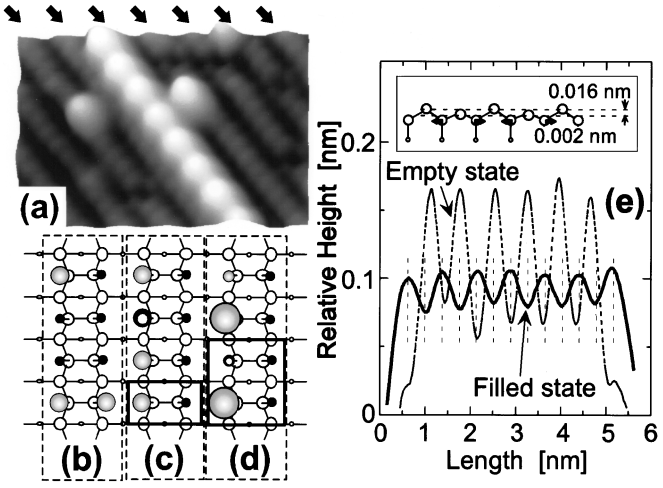

FIG. 1. (a) A low-temperature (96 K) STM image (gray-scale three-dimensional view) of a DB structure fabricated on the Si(100)-2 × 1-H surface (7 nm × 4 nm). The black arrows show the center of the Si dimer rows. (b)–(d) Schematic views of DB structures on the Si(100)-2 × 1-H surface. Blank and filled circles denote Si and H atoms, respectively. Half-tone circles denote DBs, where the size reflects the apparent height observed by STM. An unpaired (top) and paired (bottom) DB are defined as shown in (b). A DB structure made of unpaired DBs before and after relaxation are shown in (c) and (d), respectively. The 2 × 1 and the new 2 × 2 unit cells are shown by the black boxes. (e) Cross-sectional views of a thirteen-DB structure observed at V_s of −2.0 V (filled state) and +2.0 V (empty state). The inset shows a cross-sectional view of the calculated results of infinite-DB structure [11]. Open circles denote Si atoms and dashed lines show the center of up and down Si atoms.

In the odd-numbered DB structures (three- and five-DB structures), distinct alternate peaks are observed in the filled-state images, and edge DBs are observed as protrusions [Figs. 2(a) and 2(c)]. The difference in the apparent height between the edge DBs and the center DB in the three-DB structure is approximately 0.01 nm [Fig. 2(d)]. In an empty-state STM image of the three-DB structure, the center DB appeared to be 0.01 nm higher than the edge DBs [thin line in Fig. 2(d)]. Our calculation of the three-DB structure showed a remarkable qualitative agreement with the STM images. Figure 3(a) shows the contour map of the calculated filled density of states for the most stable configuration. Closeups for filled and empty states are shown in Figs. 3(b) and 3(c), respectively. The Fermi energy is pinned by a half-filled surface-state band, and an almost unity charge of the center DB is transferred to the edge DBs. In contrast, the center DB has higher empty states. The vertical displacement of the first-layer Si atoms is accompanied by a lateral relaxation in the second-layer Si atoms resulting in the pair formation [Fig. 3(d)]. A rough estimate of the height difference between the edge DBs and the center DB in a STM image gives a value of 0.01–0.02 nm [16] and agrees with the observation.

When the second-layer Si atoms pair up, the back bond angle becomes smaller [Fig. 3(d)], which lowers the DB energy [17]. The numerical calculations suggest that the DB character of the center Si atom becomes more p-like

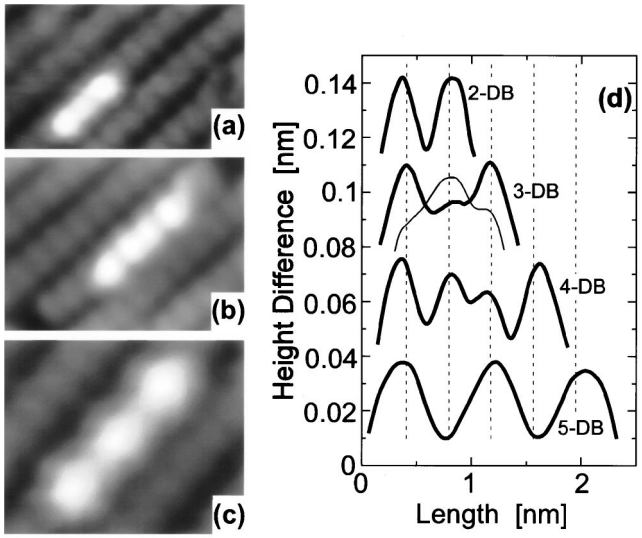

FIG. 2. Filled-state STM images of (a) three-, (b) four-, and (c) five-DB structures and (d) cross-sectional views obtained from the filled-state images of two-, three-, four-, and five-DB structures. A cross-sectional view of the empty-state image for the three-DB structure is also shown by a thin line in (d). The curves are arbitrarily offset vertically.

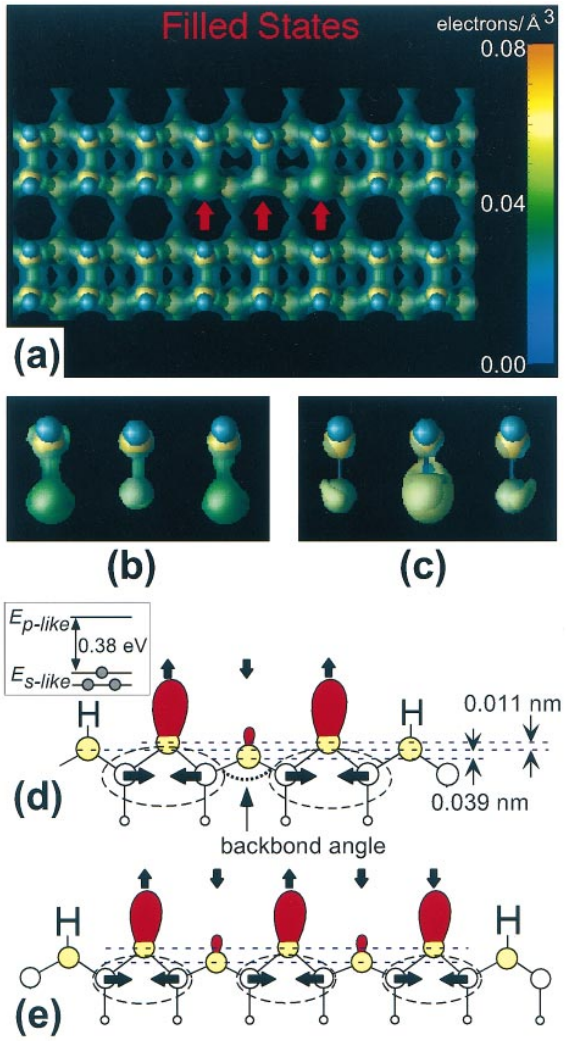

FIG. 3(color). (a) A calculated contour map of the filled-state (−2.0 eV) local density of states for a three-DB structure, which is calculated by integrating the charge from Fermi energy E_F to $E_F - 2.0$ eV. Yellow and blue spheres represent Si and H atoms, respectively. Red arrows indicate the position of DBs. Close up views of filled (−2.0 eV) and empty (+2.0 eV) density of states for three dimers with DBs are shown in (b) and (c), respectively. The number of states used for integration is 68 and 31 for the filled- and empty-state image, respectively. (d) A ball-stick model of the three-DB structure showing displacement patterns of the first- and second-layer Si atoms indicated by the arrows. The yellow and blank circles denote the first- and second-layer Si atoms, respectively. The amount of charge in the DBs are schematically expressed by the red ovals. The dotted ovals show the paired second-layer Si atoms. Dashed horizontal lines show the center of up and down Si atoms with DBs relative to the unrelaxed Si atoms. The inset shows the energy level diagram at the Γ point in wave-vector space associated with the three-DB structure. Filled circles stand for electrons. The second-layer Si atoms are displaced 0.0016 nm laterally to form pairs. (e) A ball-stick model of the five-DB structure showing displacement patterns of the first- and second-layer Si atoms shown by the arrows.

because the back bonds of the Si atom become more sp^2-like. In contrast, the DBs of the edge Si atoms become more s-like because the back bond of the Si atoms becomes p^3-like. Since the s-like orbital with the energy of $E_{s\text{-like}}$ is energetically more favorable than the p-like orbital ($E_{p\text{-like}}$), the center DB ends up with nearly empty charge. The calculated energy levels at the Γ point of wave-vector space showed the energy difference of 0.38 eV between $E_{s\text{-like}}$ and $E_{p\text{-like}}$.

If we consider only the energy gain by charge transfer between the DBs in the three-DB structure, we could also imagine a configuration where the DBs at both ends would be empty. In our calculation, however, we found that the configuration is metastable and has 60 meV higher energy (20 meV per DB) than the most stable configuration [Fig. 3(d)]. We regard the origin of the energy difference as an edge effect, which may be explained by the relaxation of surface stress in the neighboring Si dimers and/or Coulomb repulsion in the DB charges. Details will be published elsewhere. The present numerical calculations assume a periodic arrangement of the DB structure. However, the 4×8 cell is large enough for us to regard the calculated DB structure as an isolated three-DB structure.

These scenarios on the relaxation of the three-DB structure can be well described by a Jahn-Teller distortion in an artificial pseudomolecule composed of three silicon atoms with DBs and four second-layer Si atoms. Pairing of the second-layer Si atoms are common in all the odd-numbered DB structures. The second-layer Si atoms all form pairs. We were able to interpret the STM images of seven- and nine-DB structures in a similar way. In the short odd-numbered DB structures, we predict that the edge DBs will always be observed as peaks and inner DBs will always be observed as alternate peaks.

We now describe even-numbered DB structures. In the filled-state image of the two-DB structure, the height difference between the DBs was less than 0.001 nm. However, the calculated result suggests a buckled atomic configuration, resulting in an inequivalent charge distribution. There are two configurations in mirror symmetry, with a calculated flip-flop barrier of 82 meV (41 meV per DB), which is the energy difference between the relaxed structure and the structure with no distortion. A frequent flip motion, induced even at 100 K, results in the equivalent height of DBs observed by STM. The flip-flop can be explained by the exchange of a lone second-layer Si atom that is not forming a pair. The recombination of a pair in the second-layer Si atom effectively shifts the position of the lone second-layer Si atom. The motion is analogous to a soliton in polyacetylene [18] or phason on a Si(100) surface [19]. The motion of the lone Si atom reduces the effective barrier height of flipping, as is the case in the soliton in a CDW system. The details will be discussed elsewhere [20].

In the four-DB structure, the DBs located at both ends are seen to be higher than the inner two DBs in the filled-state image. Our calculation suggests that two equivalent most stable configurations exist in mirror symmetry

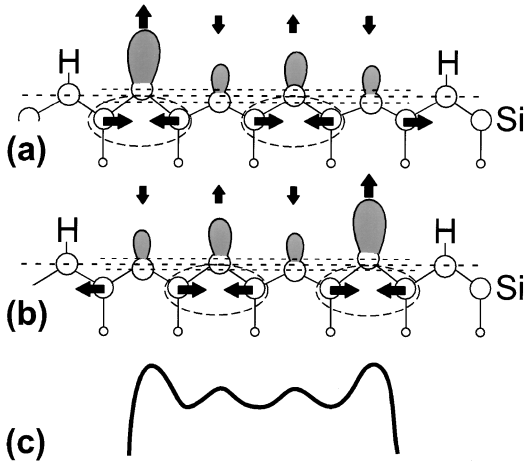

FIG. 4. Ball-stick models of the four-DB structure showing two possible displacement patterns in a mirror symmetry [(a) and (b)]. Blank circles denote Si atoms and gray ovals denote charges in DBs. The dotted oval shows the paired second-layer Si atoms, and the horizontal dashed lines show the center of the first-layer Si atoms. (c) An expected STM cross-sectional view after considering the flip-flop motion between the two displacement patterns shown in (a) and (b).

[Figs. 4(a) and 4(b)]. We consider again that the frequent flip-flop motion occurs between the two configurations. Because of the flip-flop motion, the average atom height expected for the STM image is higher at the edge DBs and lower at the inner two DBs [Fig. 4(c)]. This explanation well interprets the STM results. The barrier height for flip-flop motion is estimated to be 154 meV, which is low enough for the flipping at 100 K if we assume a preexponential factor of 10^{13} s^{-1}. The details regarding the small difference in the DB heights of the inner two DBs in Fig. 2(d) are not yet clear. A possible explanation is that a stress field associated with surface defects or underlying impurities may affect the soliton (lone second-layer Si-atom) motion and thus may determine the average height differences.

The energy gain of two-, three-, four-, and five-DB is calculated to be 41, 47, 69, and 61 meV per DB, respectively. We also performed a calculation on the energy gain in an infinite DB chain using a 4×8 supercell and obtained the energy gain of 54 meV per DB [15]. The energy gain is closely related to the amount of charge transfer and the edge effect. The origin of the length dependence of the energy gain in detail is under investigation. We predict that the DB structure would be fluctuating near the soliton position if a much longer (such as made of more than 20 DBs) even-numbered DB structure is made. It is very interesting to note that this phenomenon is analogous to the well-studied solitons in polyacetylene [21] in a sense that the soliton motion determines the structure.

In conclusion, we have described how DB structures made of unpaired DBs figure out the most stable configurations depending on their length. The second-layer Si atoms are displaced alternately and form pairs. However, the finite-length and odd-even problem prevent the DB structures from taking the simple pairing symmetry. The length-dependent charge redistribution is explained by the Jahn-Teller distortion and soliton motion in DB structures. The results imply that this stabilization can also be found not only in DB structures but also in other artificial one-dimensional atomic structures.

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