Chain-left isomer of the π-bonded chain reconstruction at the Ge{111}2×1 surface

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The phase in the alternation of up and down atoms along the chain shifts at type-*B* boundary between π-bonded chain 2×1 reconstructed domains. However, no shift was observed at some domain boundaries in empty state scanning tunneling microscope images. The no shift was attributed to the domain boundary between Pandey's original chain-right reconstruction and its chain-left isomer.

The π-bond chain structure[1] has been widely accepted as a model of the 2×1 reconstruction at the cleaved (111) surfaces of Ge and Si.[2–6] As shown in the side view of Fig. 1(a), the atoms in the surface layers arrange as alternating five- and seven-members rings in this reconstruction. At the top surface, the highest and the second highest atoms of the seven-members rings construct the zigzag chain extending toward the $[1\bar{1}0]$ direction. The zigzag chain has an upward tilt along the $[11\bar{2}]$ direction[1,3–6] and causes the double periodicity along the $[11\bar{2}]$ direction. Meanwhile, Takeuchi *et al.* have recently proposed the existence of the isomer [Fig. 1(b)] of this reconstruction.[7,8] In the isomer, the tilt angle of the zigzag chain is reversed with respect to Pandey's original model [see the side view of Fig. 1(b)]. Following Takeuchi *et al.*, we call Pandey's original π-bonded chain structure and its isomer as chain-right and chain-left structure, respectively. These two structures have the same energy within the precision of the first principle calculation. In experiments, many 2×1 domains appear at the Ge(111) surface upon the cleavage.[9] Thus, we expected that some domains have the chain-left reconstruction.

In this study, we examined the existence of the chain-left isomer by detecting the shift of the arrangement of up and down atoms at the 2×1 domain boundaries. The simplest domain boundaries related to the chain-left isomer are those that have been proposed by Takeuchi *et al.*[7] Figure 2(a) shows his proposal. In the figure, the tilt angle of the zigzag chain is reversed in the left side. As a result, a boundary appears between the chain-right and chain-left reconstructed domains. In the figure, the arrows, which are separated by a unit length along $[1\bar{1}0]$, match the position of the down atoms (large closed circles) in the zigzag chain in the right side, whereas they match the position of the up atoms (large open circles) in the left side. Namely, the boundary with the chain-left isomer causes the phase shift in the alternation of up and down atoms in the zigzag chain. At the same time, the line linking up atoms in the chain along $[1\bar{1}0]$ (not shown in the figure) shifts by the width of the zigzag chain [1.17 Å (Ref. 10)] along $[11\bar{2}]$ at the boundary. However, this shift (1.17 Å) is smaller than the space between the zigzag chain (6.92 Å) and is less remarkable. Therefore, we believe that the detection of the shift in the alternation of up and down atoms at the boundary is the best way to examine the existence of the chain-left isomer.

Other types of domain boundaries could be also caused by the chain-left isomer at the Ge(111) surfaces. Because of the translational and rotational symmetry of the Ge(111) surface, a shift by the unit length along $[11\bar{2}]$ and a rotation at every 120° are allowed for the π-bond chain reconstruction. These symmetries cause type-*B* domain boundary at which the π-bond chains are parallel but stagger by a unit length, and type-*A* boundary at which the π-bond chains rotate by 120° at the Ge(111) cleaved surfaces for Pandey's original π-bonded chain reconstruction.[9] The chain-left isomer introduces variations to these type-*B* and type-*A* domain boundaries. Type-*B* boundaries between chain-right domains and between the chain-left and chain-right domains are illustrated in Figs. 2(b) and 2(c). At the cleaved surfaces, type-*B* boundary runs obliquely in respect to the zigzag chain.[9] In the figures, the boundary runs from the upper right to the lower left. The chain-right domain meets the chain-right domain in Fig. 2(b), while the chain-left domain meets the chain-right domain in Fig. 2(c). In Fig. 2(b), arrows match the position of down atoms in the right side, whereas they match the position of up atoms in the left side. Namely, the phase of the up and down atoms alternation shifts at the intrinsic chain-right/chain-right type-*B* boundary. Meanwhile, in Fig. 2(c), arrows match the position of the down atoms in both sides. Therefore, no shift is characteristic of the type-*B* boundary between chain-right and chain-left reconstructed

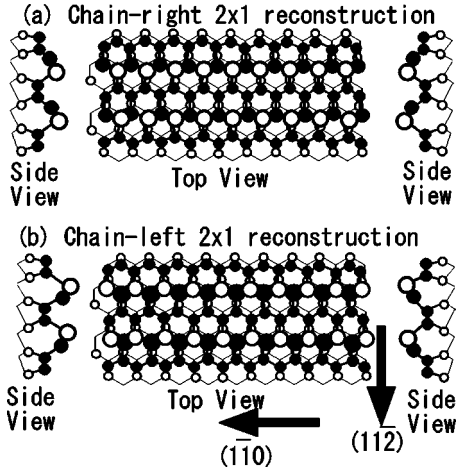

FIG. 1. Models of chain-right (a) and chain-left (b) reconstruction. Top view and side views are illustrated for both reconstructions. The up and down atoms in the topmost zigzag chains are indicated by large open and closed circles. In the chain-left reconstruction, the tilt angle of the zigzag chain is reversed to that of the chain-right reconstruction.

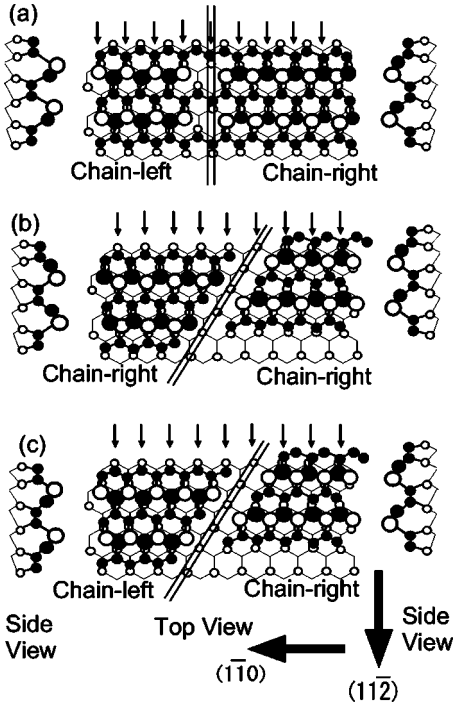

FIG. 2. 2×1 domain boundaries. (a) Boundary of Takeuchi *et al.* The chain-left reconstructed 2×1 domain meets the chain-right reconstructed 2×1 domain at the boundary indicated by a pair of lines. The arrows match the position of up atoms (large open circles) in the chain-left domain, whereas the arrows match the position of down atoms in the chain-right domain. (b) Type-*B* boundary between chain-right 2×1 domains. The π-bond chains are parallel, but stagger at the boundary. The arrows match the position of up atoms in the left domain, whereas the arrows match the position of the down atoms in the right domain. (c) Type-*B* boundary between the chain-left and chain-right 2×1 domain boundaries. In this case, the arrows match the position of down atoms in both domains.

domains. The chain-left isomer also modulates the stagger of the line linking up atoms along $[1\bar{1}0]$ at the type-*B* boundary as in the case of the boundary of Takeuchi *et al.* However, this modulation (1.17 Å) is smaller than the space between the zigzag chain (6.92 Å) and is less remarkable.

As well as at type-*B* boundary, the chain-left isomer causes a variation in type-*A* boundary. However, the adatom arrangement is usually disordered at the egde of type-*A* boundary,[9] and the detection of the characteristics due to the chain-left isomer is difficult. Thus, we do not give a detailed consideration about the variation of type-*A* boundary with the chain-left isomer.

In the π-bonded chain reconstruction, the buckling induced charge transfer happens from down to up atoms in the zigzag chain. Thus, up atoms are imaged in the occupied state scanning tunneling microscopic (STM) image, while down atoms are imaged in the empty state STM image. However, the shift in the alternation of the up and down atoms at the boundary is detectable in observing only up or down atoms. In this respect, we explored the chain-left reconstructed domains by paying attention to the shift at the boundary of Takeuchi *et al.* boundary and no shift at type-*B* boundary in the alignment of the protrusions along $[1\bar{1}0]$.

In the experiment, the sample with dimensions of $7\times5\times0.2$ mm^3 were cut from *p*-type Ge(111) wafers. After introducing guiding grooves for the cleavage, the sample was loaded into an ultrahigh vacuum (UHV) apparatus equipped with the sample cleavage device and the STM unit. Details of the experimental apparatus has been described elsewhere.[9,11] In UHV, the sample was cleaved as to expose its $(1\bar{1}1)$ plane, which is crystallographically equivalent to the (111) plane. The 2×1 reconstruction at the cleaved surfaces was observed by using STM. The pressure during the cleavage and the STM observation was less than 1×10^{-8} and 8×10^{-9} Pa, respectively. STM images are shown with a conventional gray scale keyed to the surface height. To clarify the phase shift in the alternation of atoms at the 2×1 domain boundaries, we tried to take high-resolution STM images in which the up or down atoms were resolved as separated protrusions.

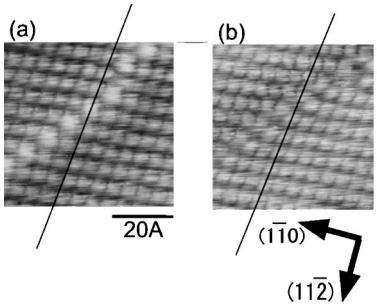

FIG. 3. STM images of type-*B* boundary at the Ge(111)2×1 surface. 70×70 Å^2. (a) Occupied state image. $V_s=-0.56$ V. $I_t=0.66$ nA. (b) Empty state image. $V_s=0.30$ V. $I_t=0.66$ nA. Lines are drawn to guide the eyes to judge the shift in the alignment of the protrusions at the boundary.

In STM observations, all the boundaries were accompanied with the stagger or the rotation of the chains. The boundary of Takeuchi *et al.*, which associates with the shift in the alignment of the protrusions but does not associate either the stagger or the rotation of the chain, was not found. Namely, all the boundaries were type-*B* or type-*A*. No boundary of Takeuchi *et al.* appeared.

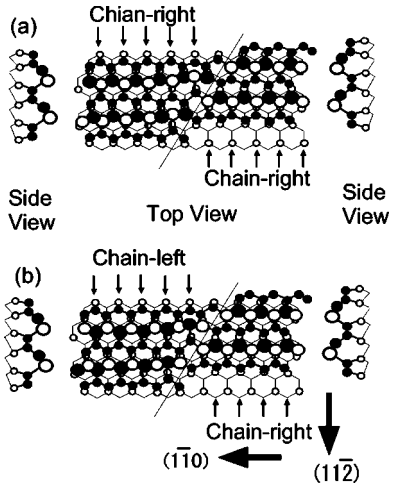

FIG. 4. Models of the atomic arrangement of the type-*B* boundaries observed in Fig. 3. (a) corresponds to the occupied state STM image of Fig. 3(a) in which the up atoms were imaged as the protrusions. (b) corresponds to the empty state STM image of Fig. 3(b) in which the down atoms were imaged as the protrusions.

At some type-*B* boundaries, no shift in the alignment of protrusions characteristic of the chain-left/chain-right boundary were observed in six of ten high-resolution empty state STM images, though the shift was always observed in all six high-resolution occupied state STM images. The polarity dependence of the shift in the STM observation was outstanding. Even at the same type-*B* boundary, the empty state image showed no shift whereas the occupied state showed the shift. Figures 3(a) and 3(b) are the occupied and the empty state STM image of the same type-*B* boundary. In the figures, π-bond chains run from upper-left to lower-right. The chains staggered at the type-*B* boundary running from the upper-right to the lower-left. As indicated by the thin line, the alignment of the protrusions shifted in the occupied state image whereas the alignment did not shift in the empty state image. In the occupied state image, the chain in the right side domain connected to the chain in the left side domain through a kink. Meanwhile, the chain connected rather smoothly in the empty state image.

The no shift of the alignment of the protrusions, which was observed in empty state STM images, evidences the existence of the domain with the chain-left reconstruction. Judging from the no shift at type-*B* boundaries in empty state STM images, several tens percent of domains had the chain-left reconstruction. The size of the chain-left domains were ~ 100 nm on an average, and was not different from that of the chain-right domains. However, as shown in Fig. 3, the same type-*B* boundary showed the shift in the occupied state STM image. This suggests that the chain-left/chain-right type-*B* domain boundary easily converts to the chain-right/chain-right one by the charge extraction during the occupied state STM observation. This point is briefly addressed in the following.

In Fig. 4, we show the model of chain-right/chain-right type-*B* domain boundary that we have proposed previously.[9] At type-*B* boundary, the π-bonded reconstruction lasts to the very edge as observed in STM. Thus, the staggered zigzag chains are regarded to be connected in a smooth manner over the boundary. In the model, the up atom at the end of the zigzag chain (the large open circle) in the right side domain bonds to the atom of the underlayer (the small closed circle) of the left side domain instead of its lacking down atom in the left side. As well, the down atom (the large closed circle) at the end of the chains in the left side domain bonds to the atom of the underlayer (the small closed circle) in the right side domain instead of its lacking up atom in the right side. By these bondings, the π-bond chain reconstruction lasts to the very edge of the boundary without creating dangling bonds. This is consistent with the stability of type-*B* boundary against the structural transition of 2×1 to $c(2\times8)$ at Ge(111) surfaces.[9]

By reversing the alternation of up and down atoms in the left side domain, the structure changes to the chain-left/chain-right type-*B* domain boundary as shown in Fig. 4(b). Figures 4(a) and 4(b) are consistent with the alignment of the protrusions at the boundary observed in the occupied and empty state STM images of Figs. 3(a) and 3(b), respectively. By following the up-atom sites from left to right at the chain-right/chain-right boundary [Fig. 4(a)], we find a kink at the boundary as observed in the occupied state image [Fig. 3(a)]. On the other hand, the down-atom sites in the left side connect rather smoothly to those in the right side at the chain-left/chain-right boundary [Fig. 4(b)] as observed in the empty state image [Fig. 3(b)].

At the boundary, the only difference between Figs. 4(a) and 4(b) is the site of the end atom of the chain in the left side. The end atom takes the down-atom site in Fig. 4(a) whereas it takes the up atom site in Fig. 4(b). However, by making the end atom take the up site, the phase in the alternation of the up and down atoms shifts concertedly in the left side domain. Thus, the structural change from chain-right to chain-left reconstruction is regarded to be triggered by the down to up site change of the atom at the end of the zigzag chain in the left side domain. At present, we do not know the reason why the charge extraction during the occupied state STM observation caused the downward shift of the end atom of the chain in the left side domain. However, it is sure that the bonding of the end atom to the atom in the underlayer of the counterpart domain introduces stress with the distortion of the back bonds to the boundary. On the other hand, the energy of the dangling bond state of the end atom is strongly affected by torsion of the back bonds.[12] Thus, the position of the end atom is determined in a balance of the torsion of the lattice and the energy of dangling bond state. Tentatively, we regard that the change in the site of the end atom is due to the change in the balance between the lattice and electronic energy, which could be easily modified by the STM observation.

In summary, we investigated the existence of the chain-left isomer of the Pandey's 2×1 reconstruction at the Ge(111) surfaces. In some empty state STM images, we observed no shift in the alignment of the protrusions at type-*B* boundary. Since the no shift is characteristic of the chain-left/chain-right boundary, it evidences the existence of the 2×1 domains with chain-left isomer of the Pandey's π-bonded reconstruction. However, the shift was always observed in the occupied state STM images. This suggests that the chain-right reconstruction converts to the chain-left reconstruction easily by the tip-induced effect. In the analysis with the structural model, we proposed that this structual transition was induced by the down to up site change of the end atoms of the π-bonded chain.

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