

Model for *C* defect on Si(100): The dissociative adsorption of a single water molecule on two adjacent dimers

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The origin and atomic structure of *C*-defect on Si(100) have been unambiguously identified. Two pairs of enantiomorphic protrusions of *C*-defect have been observed by low-temperature scanning tunnelling microscopy (STM). These are attributed to the dissociative adsorption of a single water molecule on two adjacent dimers. Two unreacted dangling bonds on these dimers have different electronic states which are visualized in unoccupied state STM images.

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Defects on the surface play a crucial role in not only chemical reaction, thin-film growth but also electronic properties at the surface and interface. One of the long-standing unsettled problems in surface science is the origin and atomic structure of *C* defects commonly observed on the Si(100) surface. By means of scanning tunnelling microscopy (STM), the *C* defect appears as a depression and a bright protrusion at 300 K in the occupied and unoccupied state images, respectively. The *C* defect was initially ascribed to the half missing dimer defect.¹ In addition to *C* defects, the *A*- and *B*-type defects were observed as depressions in both occupied and unoccupied state images. The *A*- and *B*-type defects have been ascribed to the single and double dimer vacancy, respectively.¹

Different proposals have been reported regarding the origin of the *C* defect. Those proposals can be classified into three different models. (i) The intrinsic vacancy model: the *C* defect originates from the removal of only one Si atom in the second layer² or the removal of surface Si atoms.^{1,3} (ii) The subsurface impurity model: a substitutional B (boron)⁴ or two silicon atoms weakly bound to the layer beneath⁵ is the possible origin of the *C* defect. (iii) The extrinsic adsorbate model: the *C* defect is due to the molecular adsorption of two H₂O molecules⁶ or dissociative adsorption of H₂O molecules.^{7,8} Although no consensus has been reached yet about the origin of the *C* defect, some important features commonly observed by STM clearly support the extrinsic model. The concentration of the *C* defect strongly depends on the sample preparation condition. If the background pressure in vacuum is kept very low, the concentration of the *C* defect can be drastically reduced. Very recently, Nishizawa *et al.* have reported that the number of *C* defects increased with the elapsed time after cleaning the surface.⁸ Based on the residual gas analysis and surface infrared spectra, they have proposed that the *C* defect is caused by the dissociative adsorption of two water molecules.⁸

In this paper, we report the STM investigation on *C* defects and adsorption of water on Si(100) at 80 and 300 K. By virtue of the alternate buckled dimer arrangement on Si(100)*c*(4×2) at low temperature (<200 K), the registry of the *C* defect is clearly identified. In addition, two pairs of enantiomorphic protrusions of *C* defects are observed in the high-resolution unoccupied state images. The number of *C* defects was increased by the water exposure on Si(100) at

both room and low temperature. These results unambiguously indicate that the *C* defect is caused by the dissociative adsorption of a single water molecule on the same side of two adjacent dimers.

The Si(100) substrate was obtained from the cut of Si wafers (boron doped, resistivity=0.1 Ω cm, and phosphorous doped, resistivity=0.05 Ω cm). The clean surface was prepared by repeated flashing at 1500 K under UHV with a base pressure better than 1.5×10^{-8} Pa. Using a cryopump, a thus prepared clean surface contained <1% defects. The sample was cooled down to 80 K using liquid N₂. Gaseous water molecules were introduced through a pulse-valve doser.

Figures 1(a) and (b) are the STM images of the Si(100) surface in the unoccupied ($V_{sample}=1.4$ V) and occupied ($V_{sample}=-1.9$ V) states at 300 K, respectively. Both images were recorded almost at the same scanning area. The parallel rows of dimer on upper and lower terraces are clearly observed in both images. In Fig. 1(a), the individual constituent atoms of the dimer are also clearly resolved. Because of the rapid flip-flop motion of the dimer, the time-averaged STM image of the dimer looks symmetric. Some zigzag structures are also observed where the flip-flop motion of the dimer is frozen.⁹ The bean-shaped bright protrusions adjacent to a depression in Fig. 1(a) are the *C* defects. A typical *C* defect in unoccupied and occupied state images is enclosed by the circle. A zoomed-in image of the *C* defect in the occupied state is shown in the inset of Fig. 1(b). The *C* defect consists of two protrusions, indicated by two arrow heads (termed as “odd atoms” hereafter), on the one half and depression on the other half of two adjacent dimers in a row. Note that the appearance of two odd atoms strongly depends on the sample bias, i.e., two odd atoms appear much brighter than the dimers on the clean terrace at low bias.¹⁰ It is clear that the bean-shaped protrusion and the adjacent depression of the *C* defect in the unoccupied state image [Fig. 1(a)] correspond to the two odd atoms and the depression of the *C* defect in the occupied state image [Fig. 1(b)], respectively. The appearance of the *C* defect in both unoccupied and occupied state images is in agreement with the previous work.¹ Some depression sites observed in both images are the missing dimer defects.¹

Figure 2(a) shows the STM image of the clean Si(100)*c*(4×2) surface in the unoccupied state containing

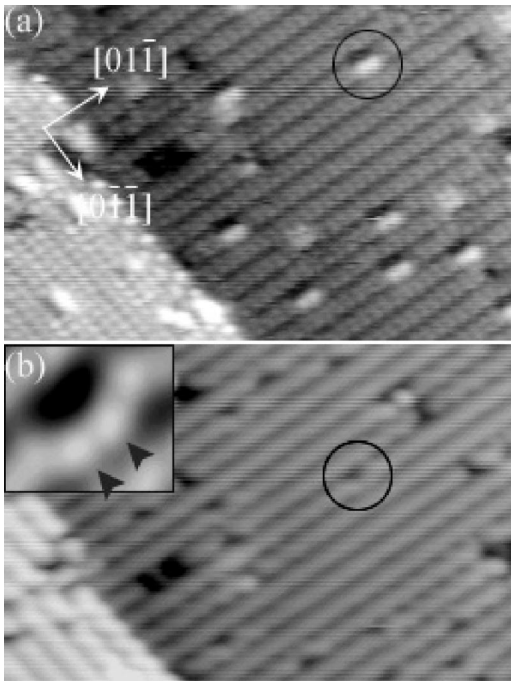


FIG. 1. STM images at the same area of clean Si(100) in (a) the unoccupied and (b) the occupied states at 300 K. Scan area is $15 \times 10 \text{ nm}^2$ for both images. For (a), $V_{\text{sample}} = 1.4 \text{ V}$, $I = 0.13 \text{ nA}$ and for (b), $V_{\text{sample}} = -1.9 \text{ V}$, $I = 0.13 \text{ nA}$. A typical C defect is enclosed by the circles. A zoomed-in C defect in the occupied state is shown in the inset where two protrusions on two adjacent dimers are clearly seen and the other half of the dimers is depressed.

several C defects at 80 K. The flip-flop motion of the dimer is frozen at 80 K and the $c(4 \times 2)$ structure resulting from the alternate arrangement of buckled dimers is clearly observed. It is noted that a partial charge transfer from the lower atom to the upper atom of the dimer occurs, and thereby the occupied and unoccupied surface states are localized preferentially at the upper and lower atoms of the buckled dimer, respectively.¹¹ Hence the STM images in the unoccupied and occupied states reflect the distribution of lower and upper dimer atoms of the Si(100) $c(4 \times 2)$ surface, respectively.

In Fig. 2(a), the bright protrusions marked by U, U', D, and D' are the C defects. Some dark sites observed in the image are the missing dimer defects.¹ Each C defect looks like an asymmetric teardrop-shaped protrusion. By close inspection, one can distinguish four different orientations of C defects as indicated by U, U', D, and D'. The U and U' (D and D') are the mirror image of each other (enantiomorphic) where the mirror plane is parallel to the $[011]$ direction ("perpendicular mirror plane" hereafter). The U and D (U' and D') are also enantiomorphic where the mirror plane is parallel to the $[0\bar{1}\bar{1}]$ direction ("parallel mirror plane" hereafter). The asymmetric teardrop shape of the C defect is found to be independent of the scan direction and the dopant of the silicon substrate. *By the inspection of the hundreds of C defects on Si(100) $c(4 \times 2)$, we have found that any of the C defects at low temperature can be categorized into one of the four types.*

A zoomed-in image of the C defect (D') together with the

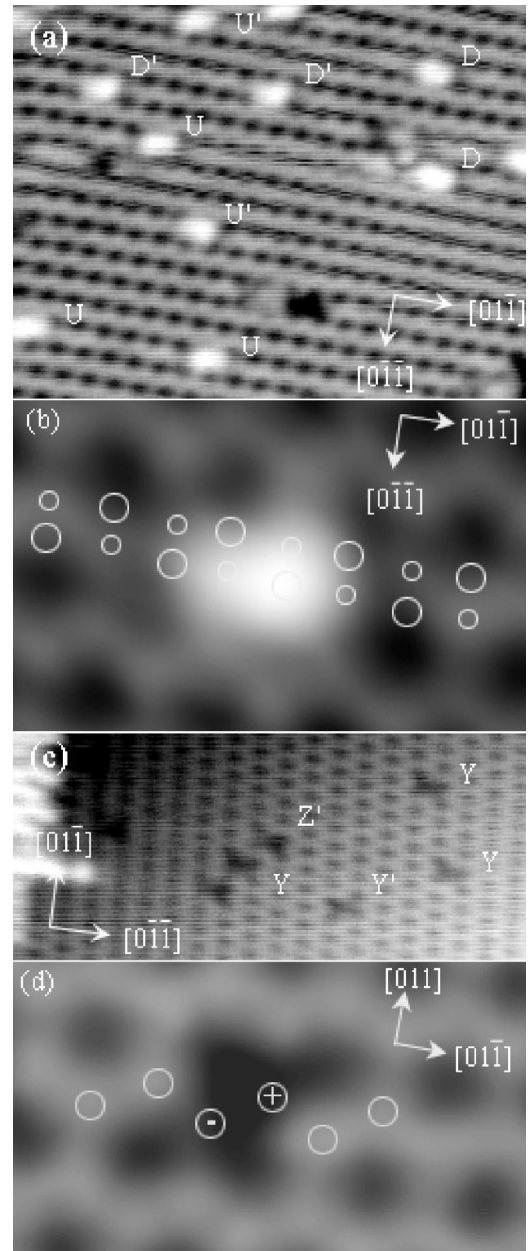


FIG. 2. STM images of clean Si(100) $c(4 \times 2)$ at 80 K. For (a), $V_{\text{sample}} = 1.0 \text{ V}$, $I = 0.1 \text{ nA}$ and scan area = $20 \times 15 \text{ nm}^2$. The asymmetric teardrop-shaped protrusions are C defects. The protrusions are marked by U, U', D, and D' depending on its position and the direction of asymmetry. The registry of a C defect in the unoccupied state is shown in (b). The STM image in the occupied state is shown in (c). Cross shaped dark depressions are the C defects. The protrusions are marked by Y, Y', and Z' depending on the relative position of up-dimer atoms. A zoomed-in C defect in the occupied state ($V_{\text{sample}} = -1.5 \text{ V}$, $I = 0.19 \text{ nA}$) together with the registry on the upper atoms is shown in (d).

registry of dimer atoms on Si(100) $c(4 \times 2)$ is shown in Fig. 2(b). The bigger and smaller open circles represent the positions of the upper and lower dimer atoms of the buckled dimer, respectively. It is clear in Fig. 2(b) that the "head" and "tail" of asymmetric teardrop-shaped protrusion are located at the upper and lower atoms of two adjacent dimers

along the $[0\bar{1}1]$ direction, respectively.

Figure 2(c) shows the STM image of the clean Si(100) $c(4\times 2)$ surface in the occupied state containing several C defects at 80 K. The C defects appear as cross-shaped depressions at 80 K [Fig. 2(c)] which are different from that observed at 300 K [Fig. 1(a)]. It can be detected that in each apparently cross-shaped depression, two upper atoms along the $[0\bar{1}1]$ direction are involved where one is completely missed and another is slightly depressed compared with the upper atoms on the clean surface. A zoomed-in image of the C defect with the registry on the dimer atoms is shown in Fig. 2(d) where the “+” and “-” marked circles indicate the position of completely missed and slightly depressed upper atoms, respectively. Depending on the arrangement of two upper atoms in the cross-shaped depression, we can distinguish three different orientations of C defects in Fig. 2(c) as indicated by Y, Y', and Z'. The Y and Y' are enantiomorphic with respect to the “perpendicular mirror plane.” The Y' and Z' also enantiomorphic with respect to the “parallel mirror plane.” One can predict another orientation of the C defect, the mirror image of Z' with the perpendicular mirror plane, which is not observed unfortunately within this scanning area. We have determined that the completely missed upper atom and the tail of the asymmetric teardrop protrusion in the occupied and unoccupied state images, respectively, lie on the same dimer site.

In order to confirm the origin of the C defect, we have performed the controlled experiment of water adsorption on the Si(100) surface. The concentration of the C defect was increased from 0.75% to 1.85% when the Si(100) $c(4\times 2)$ surface was exposed to one pulse shot of water molecules (~ 0.02 langmuir) at 80 K. The increased number of C defects due to water adsorption was also observed at room temperature. These results clearly support that the C defects observed on Si(100) are extrinsic and caused by water adsorption in agreement with the previous report.⁸

Several investigations on the water adsorption on Si(100) by infrared (IR) and electron energy loss spectroscopy (EELS) have revealed that water dissociates on the Si(100) surface and Si-H and Si-OH species are formed.^{12–16} Theoretical calculations have suggested that there is no energy barrier for the dissociative adsorption of water molecule on Si(100).^{17–19} A lone pair of water molecule initially interacts with the electron deficient lower atom of the buckled dimer followed by the dissociation. The dissociated OH and H fragments are expected to bond with the lower atom and the electron-rich upper atom, respectively.^{17–19} These reacted upper and lower atoms can be located on the same dimer or adjacent two dimers in a row. In the case of dissociation on the same dimer, both atoms of the dimer are occupied by H and OH species. Hence the depression on the whole single dimer site is expected in both occupied and unoccupied state STM images. However, it is obvious from Figs. 1 and 2 that two adjacent dimers are involved in a C defect and thus the C defect is not created by water dissociation on the same dimer although it might occur.

In the case of water dissociation on two adjacent dimers, two unreacted atoms with free dangling bond should still remain at the same side. The two odd atoms in the inset of

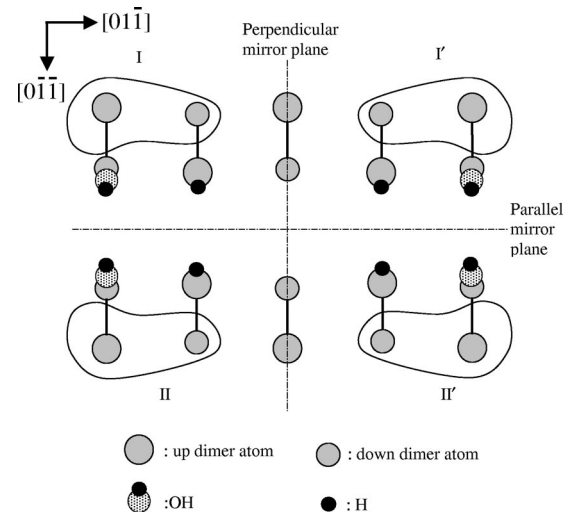


FIG. 3. The proposed model of C defect with four enantiomorphic configurations. The H and OH species are located on the up and down atoms of buckled dimers, respectively. The bright protrusions observed in Fig. 2(a) are schematically shown by asymmetric teardrop-shaped area. The perpendicular and parallel mirror planes are shown by dotted lines.

Fig. 1(b) and the bean-shaped protrusion in the Fig. 1(a) are ascribed to two dangling bonds on the two adjacent reacted dimers. The depressed side adjacent to two odd atoms and the bean-shaped protrusion correspond to the OH and H reacted sites. Thus the room-temperature STM images suggest that the C defect is created by the water dissociation on the same side of two adjacent dimers. At low temperature (80 K), the dangling bond on the OH reacted dimer is found brighter than that on the H-reacted dimer in the unoccupied state image resulting into the asymmetric teardrop protrusion [Fig. 2(b)].

The water dissociation on two adjacent dimers on Si(100) $c(4\times 2)$ would give four different configurations as shown in Fig. 3. Since the electronic states of unreacted upper and lower atoms of two reacted dimers should be different, four different images (the configurations I, I', II, and II' in Fig. 3) can be recognized by STM at low temperature. Based on the preferential adsorption of OH on the down dimer atom,^{17–19} one can correlate the configurations of OH and H species on Si(100) $c(4\times 2)$ I, I', II, and II' (Fig. 3) to the protrusion U, U', D, and D' [Fig. 2(a)], respectively.

The completely missed and slightly depressed upper atoms in Figs. 2(c) and (d) can be ascribed to the H-reacted atom and the unreacted atom (dangling bond) of OH reacted dimer, respectively. These observations may agree with the optimized structure of OH and H adsorbed dimers as determined by Akagi,²⁰ where the OH reacted dimer becomes almost nonbuckled and the H reacted dimer is still buckled. The electronic state of unreacted atom on the nonbuckled OH-reacted dimer is expected to be different from the clean dimer atoms.

Recently, Nishizawa *et al.* have proposed a structural model for the C defect where two water molecules are dissociated on two adjacent dimers and two adsorbed OH species are bonded at the same side of these dimers.⁸ In their

model, all the four dangling bonds of two adjacent Si dimers are occupied by OH and H species; the depression at two adjacent dimers is expected in both occupied and unoccupied state STM images. However, their proposed model can neither explain the present STM images of *C* defect at 300 and 80 K including two pairs of enantiomorphic protrusions nor the metallic properties.¹

The unreacted atoms with free dangling bond in the *C* defect are expected to play an important role in the electronic properties of the surface. These half filled states make the *C* defect metallic.¹ In addition, the reactivity of these free dangling bonds may be different from those of the clean surface. For example, CO and O₂ are preferentially adsorbed near the *C* defect on Si(100) at low temperature.^{21,22}

In conclusion, we have investigated the *C* defects on Si(100) by STM at 80 and 300 K. At 80 K, two pairs of

enantiomorphic protrusions of the *C* defect are observed in the unoccupied state image. The number of *C* defects was increased by the water exposure on Si(100) at both room and low temperatures. These results unambiguously show that the *C* defect is extrinsic and caused by the dissociative adsorption of a single water molecule. The dissociated H and OH species adsorb on the same side of two adjacent dimers leaving two unreacted atoms; four different local configurations are possible on Si(100)*c*(4×2) and in fact two pairs of enantiomorphic protrusions are observed by the present STM study.

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