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Structure Transformation of the C Defects Observed at Low Temperature (80 K)

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The dynamical characteristics of the C defect at low temperature (80 K) were studied by sequential scanning tunneling microscopy observations. We found that the C defect frequently transforms into a another type of defect termed as the C_2^{LT} defect. In addition, the reversal C_2^{LT} to C defect structural transformation was observed which implies that the C_2^{LT} defect is a metastable state of the C defect. The observed structural transformation was completely different from that observed at room temperature. We interpret that structural transformation associated with a change in the phase of the defect is suppressed at low temperatures because it disturbs the ordering of the surrounding buckled dimers.

KEYWORDS: scanning tunneling microscopy, scanning tunneling spectroscopies, surface electronic phenomena, silicon, surface defects

Defects are one of the most serious problems of the Si(001) surface. The first scanning tunneling microscopy (STM) observation of a clean Si(001) surface carried out by Tromp *et al.*[1)] at room temperature, showed the existence of a rather large number of atomic-scale defects on the surface. Subsequent, STM observations of clean Si(001) surfaces consistently showed a certain amount of defects, which were classified into three types, termed "A", "B", and "C" defects by Hamers and Kohler.[2)]

Among these, the C defects are the most important. When the filled states are probed, the C defects appear to be two adjacent Si atoms missing along the dimer row direction and are observed as bright protrusions in the empty states.[2,3)] Other reported characteristics of the C defects are as follows. Tunneling $I-V$ measurements on the C defects show a metallic feature.[2,4–6)] Regarding the rather high concentration of C defects, they were supposed to be the prominent cause of Fermi level pinning.[2)] Furthermore, it has been reported that the C defects influence the site of adsorption. For example, it is reported that the C defects are sensitive to oxidation.[4,7)]

The C defect is also known to strongly influence the configuration of the surrounding dimers.[8)] At room temperature, the main part of the dimers are observed in a symmetrical configuration in the STM images,[1)] though dimers adjacent to the C defects are frequently observed as buckled.[1,2)] At room temperature, buckled dimers are induced by the C defects. When the temperature of the sample is lowered below 200 K, a symmetric⇔buckled phase transition occurs and the majority of dimers are observed in a buckled configuration.[9)] It is generally accepted that the flip-flop motions of the dimers are frozen at low temperatures below 200 K and buckled dimers are observed in the STM images.[9)] In this article, low temperature means a temperature below 200 K. Whether the surrounding dimers are buckled or not is a factor which requires serious consideration. Tochihara *et al.*[8)] have shown that the C defects influence the configuration of the surrounding dimers differently at low temperatures. They showed that dimers at one side of the C defects appear buckled while those at the other side appear symmetrical at low temperatures (140 K).[8)] Symmetrical dimers are induced by the C defects at low temperatures.

Recently, Zhang *et al.*[3)] reported an interesting dynamical characteristic of the C defects at room temperature. They reported the observation of a frequent structural transformation of the C defect into another defect in two sequentially acquired STM images. The new defect was termed the C_2 defect and was considered to be a variation of the C defect. Appearance of the C_2 defect in the STM image is similar to one of the individual protrusions of the C defect transferred to the opposite side of the dimer row. Foregoing studies have shown that the reverse transition, a $C_2 \rightarrow C$ structural transformation exists, which suggests that the C_2 defect is a metastable and excited state of the C defect.[10)] It should be noted that these structural transformations were observed at room temperature, and at low temperatures the C defects might show different dynamic features as was the case for their static characteristics.[6)]

In this article, we report the observation of the structural transformation of the C defects by STM at low temperature (80 K) which yields new insights to our understanding of the C defects. A completely different structural transformation from that reported at room temperature was observed at low temperature which we interpret is induced by the difference in the configuration of the surrounding dimers at room and at low temperatures.

Standard procedures were employed to fabricate the clean surface. Si samples were phosphorus-doped at a conductivity of 0.005 Ω cm. After the sample was prebaked at ∼700°C for one night, it was flashed once to 1250°C for 30 s, followed by annealing at 700°C for another 30 s. The base pressure was kept below 5×10^{-8} Pa during the flashing. Electrochemically etched tungsten tips were used for the STM measurements.

Through continuous observations of identified C defects over a long period, we studied the structural transformation of the C defect in detail. A set of subsequent STM images is displayed in Figure 1, showing the structural transformation of the C defects at 80 K, a temperature far below the critical temperature of the symmetric⇔buckled phase transition. Figures 1(a) and 1(b) show the filled ($V_s = -0.8$ V) and empty ($V_s = +0.6$ V) states of the initial surface, respectively. Note that the surface bias ($V_s = +0.6$ V, -0.8 V) is significantly lower than the typical bias (-2 V). The surface bias is a very important factor which should be treated with care

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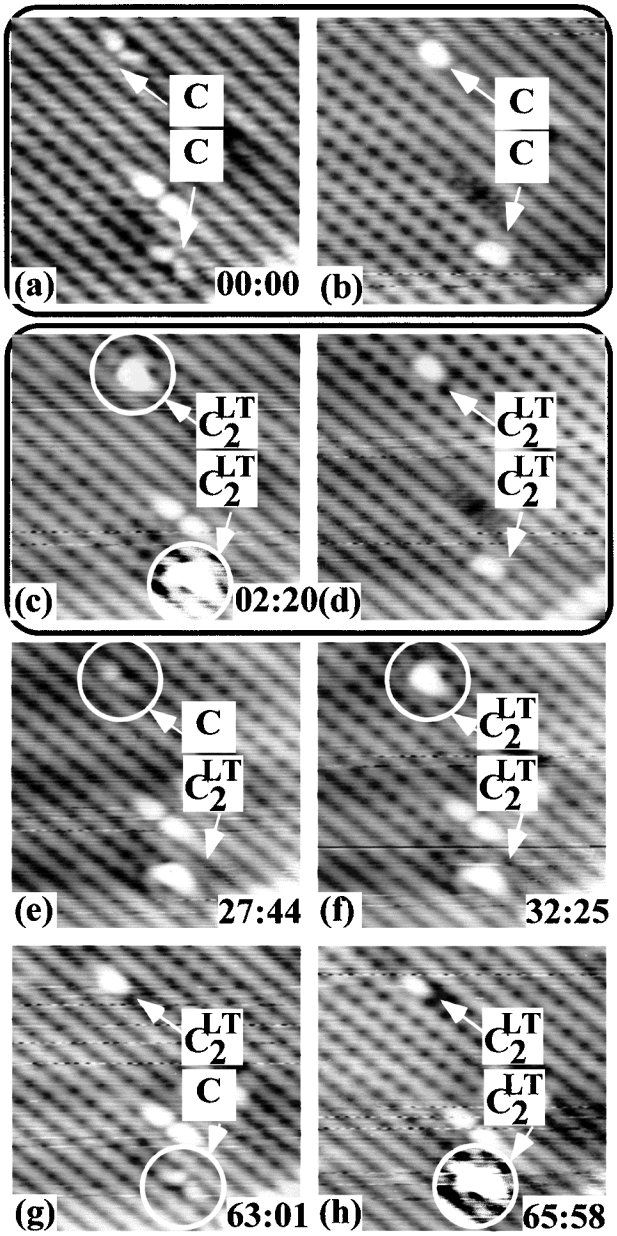

Fig. 1. A series of STM images showing the structural transformation of the C defect at 80 K. The sequence of events is (a)→(c)→(e)→(f)→(g)→(h). These images were taken at a surface bias of −0.8 V, thus they are images of the filled states, except (b) and (d) taken at +0.6 V, and show the empty states of (a) and (d), respectively. The time displayed indicates the duration in minutes and seconds from the end of scanning Fig. 1(a) to the end of scanning each image. Two C defects are observed in the images, as indicated by the arrows. Each circle in the images represents a single structural transformation of the C defects. Scale: 10 nm × 10 nm. Tunneling current=1 nA.

when studying the structural transformation of the C defect at low temperatures as discussed below. Two C defects are observed in these images, as indicated by the arrows. Since the surface bias is lower than usual the C defects appear in the filled states as two protrusions that is slightly brighter than the surroundings with a depression in the other side, a result that is in accordance with the intense local density of states near the Fermi energy of the C defects.[4–6] After 2 min, the first structural transition occurred and both of the C defects transformed into different structures, which we term as C_2^{LT} defects, as indicated by the circles in Fig. 1(c), an STM image of the filled state. Figure 1(d) is the corresponding STM image of the empty state ($V_s = +0.6$ V). The C_2^{LT} defect appears as a single very bright protrusion in the low-biased filled-state STM image, similar to the appearance of the C defect in the empty states. It should be noted that the appearance of the C_2^{LT} and C defect in the empty-state STM images are practically indistinguishable, hence the structural transformation would not be noticed only if the empty states were continuously observed. After 27 min, the second transition was observed, as shown in Fig. 1(e). A reversal procedure of the first transition occurred and the C_2^{LT} defect in the upper region of Fig. 1(c) transformed into a C defect, as indicated by the circle. Observation of the reversal C_2^{LT}→C defect transition is very important, since it directly shows that the C→C_2^{LT} defect transition is not an irreversible and one-way structural transformation but instead implies that the C_2^{LT} defect is a metastable and excited state of the C defect at low temperature. Both the C→C_2^{LT} and the reversal C_2^{LT}→C transition of defects were observed frequently, as shown in the subsequent STM images where each circle indicates an individual structural transformation. During the observation, the C defect in the upper region in Fig. 1(e) was again excited into a C_2^{LT} defect (Fig. 1(f)), and the C_2^{LT} defect in the lower region in Fig. 1(e) recovered to a C defect (Fig. 1(g)) and was again excited to a C_2^{LT} defect (Fig. 1(h)). The results show that the C defect is easily excited into a metastable C_2^{LT} state. Note that every C_2^{LT} defect observed exhibited the same features in the STM images.

We found that the appearance of the C_2^{LT} defect in the STM images has a very interesting and complex dependence on the surface bias. One striking feature is that the appearance of the C_2^{LT} defect is not confined to a single dimer row but crosses over to the adjacent dimer rows in the filled-state STM images at typical surface biases. A series of STM images of a single C_2^{LT} defect, taken with different biases at 80 K are displayed in Fig. 2. At −0.8 V (Fig. 2(a)), the C_2^{LT} defect appears as a white protrusion, although a close inspection reveals that the shape of the protrusion is irregular when compared to the white protrusion observed in the empty state (Fig. 2(e)), and has a small projection which is indicated by an arrow. This projection grows larger as the surface bias is increased, as shown in Fig. 2(b), an image taken at $V_s = -1.0$ V. Here, the size of the original protrusion in dimer row (2) has decreased while the projection in the adjacent dimer row (1) has grown into a new protrusion. At $V_s = -1.2$ V, this feature becomes clearer, and the new protrusion in dimer row (1) and the original one in dimer row (2) become comparable in intensity and size. At this stage, the appearance of the defect is not confined in a single dimer row but crosses over two dimer rows. At higher voltages the situation becomes more complicated and at $V_s = -1.5$ V, a surface bias close to the typical value used, only the new protrusion in dimer row (1) remains, while the original protrusion in dimer row (2) transforms into a structure which resembles a zigzag buckled dimer having a slightly stronger intensity than the surroundings. Note that the protrusion observed in the empty states is always located in dimer row (2). Such a complicated dependence of the appearance on the surface bias has rarely been reported and implies that the electronic structure of the C_2^{LT} defect is very complicated.

The observed structural transformation at a low temperature is similar to that observed at room temperature in the

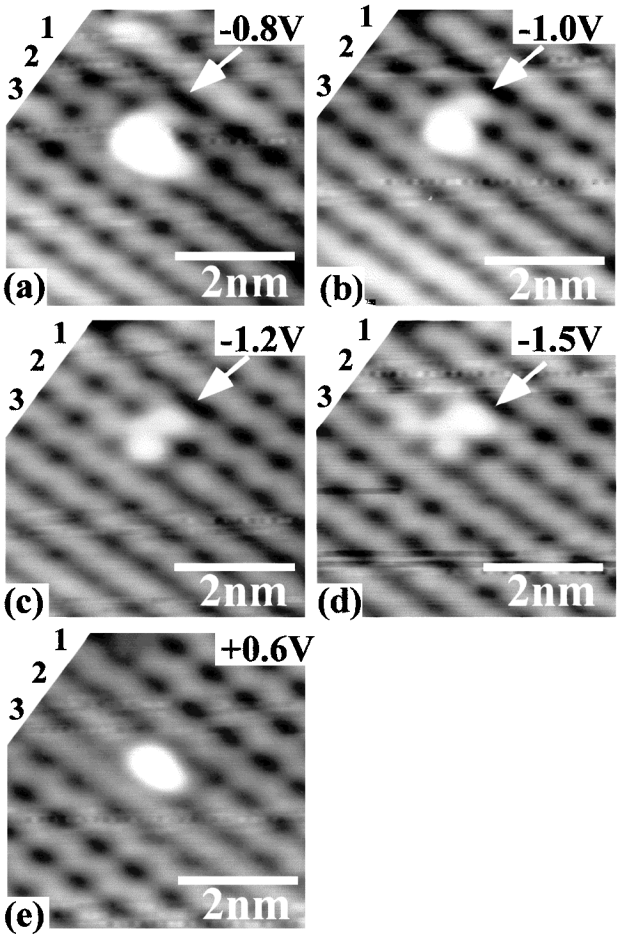

Fig. 2. A series of STM images showing the peculiar voltage dependence of the appearance of the C_2^{LT} defect at 80 K. The surface bias is displayed in the upper-right region of each image. Note that (a) to (d) are images of the filled state while (e) is an image of the empty state. Dimer rows (1) to (3) are numbered. Tunneling current=1 nA.

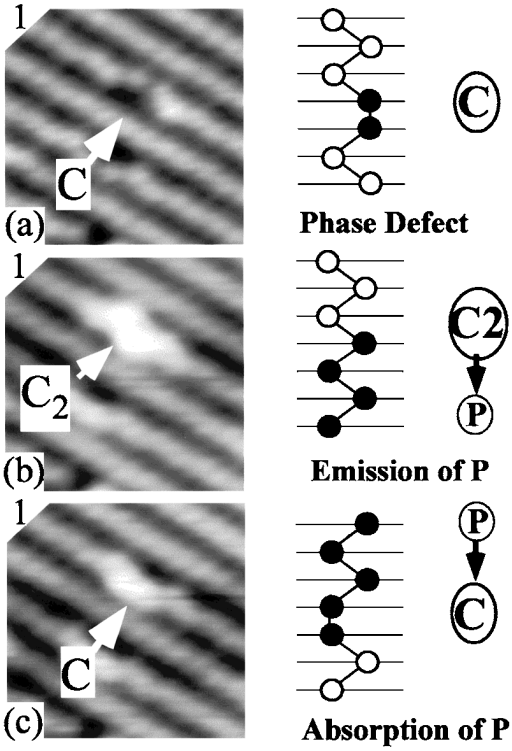

Fig. 3. A series of STM images showing the structural transformation of the C defect at room temperature. Tunneling conditions $V_s = -1.0$ V, $I = 1$ nA. The C defect, indicated by an arrow in (a), changes into a C_2 defect in (b) and reverses to the C defect in (c). Schematics in the middle row show the stick and ball structures of the C and C_2 defects. The black circles represent the C and C_2 defects, the gray circles the dimers which flipped to the opposite configuration during the transition. Note that the C defect is a phase shifter while the C_2 defect is not. The phase shifter ingredient is carried in and out by a P defect, and the gray circles show the direction of migration because the dimers will flip to the opposite configuration when a P defect migrates over them (ref. 11). Accompanying the structural transformation of the C→C_2 defect, a P defect was released and migrated downwards. On the other hand, accompanying the structural transformation of the C_2→C defect, a P defect was absorbed in the defect which came from upward as schematically shown in the right-hand side figures.

sense that the C defect is excited into a particular structure (C_2^{LT} and C_2 defect) which can also reverse the C defect. However, the appearance of the excited structures is completely different. At room temperature, the C_2 defect is similar to a zigzagged buckled dimer which has a slightly stronger intensity than its surroundings as shown in Fig. 3(b), and shows no bias dependence. For comparison, we have presented an example of the C→C_2 and the reversal C_2→C defect transition in Fig. 3. In the following, we present a possible explanation for the difference in the excited states observed at room and low temperatures.

Even though the practical atomic structure of the C defect is not known, schematically it can be considered to represent two adjacent dimers buckled in the same direction (ferromagnetic ordering), thus disorganizing the antiferromagnetic ordering of the buckled dimers at low temperature. Thus, the C defect acts as a phase shifter in a complete set of buckled dimers at low temperatures, although it does not at room temperature, because high-ordering does not exist among dimers at room temperature. Tochihara *et al.*[8] have proposed that the C defect influences the configuration of the surrounding dimers at low temperatures because it is a phase shifter. Whether a particular structure acts as a phase shifter or not is a factor which has to be treated with great care at low temperatures although it is not so important at room temperature.

In this sense, it is important to note that the C_2 defect is not a phase shifter. Therefore, accompanying the C→C_2 and the reversal C_2→C defect transition, the C defect switches from a phase defect to a defect which is not a phase shifter, and vice versa. The phase shifter ingredient is carried out/in from the C/C_2 defect by another phase shifter termed as the P defect. The P defect has been defined as two adjacent buckled dimers aligned in the same direction, thus it is, by definition, a phase shifter.[11] When a P defect migrates along a dimer row, the buckled direction of the dimers switches to the opposite configuration. Taking this into consideration, we can deduce the direction of migration of the P defect, as shown in the right-hand schematics in Fig. 3 for the structural transitions displayed in Fig. 3.

At low temperatures, the birth and migration of a P defect along the dimer row will cause a dramatic change in the configuration of the surrounding buckled dimers. Indeed, when a C defect is artificially perturbed by the STM tip at low temperatures, its phase shifter ingredient is converted into a P defect and accompanied to its migration, a large scale phase transition of the surrounding buckled dimers is induced.[12] Such a dynamic change accompanied with the C→C_2^{LT} and C_2^{LT}→C

defect transition was not observed in our experiments. We interpret that the observed difference in the structure of the excited states of the C defect between low and room temperature is caused by the difference in whether or not the excited states can easily damp out the phase shifter ingredient into a P defect to the surrounding dimers. In other words, at low temperature, the C defect cannot easily switch between a phase and a non-phase defect whereas at room temperature this is possible.

In conclusion, we have observed the structural transformation of the C defect at low temperature (80 K). Frequently, the C defect transforms into a different defect, termed as the C_2^{LT} defect. As well, a reversal $C_2^{LT} \rightarrow C$ structural transformation occurs, which implies that the C_2^{LT} defect is a metastable and excited state of the C defect. Appearance of the C_2^{LT} defect has a very unique dependence on the surface bias in the filled-state STM images, although it remains similar to the C defect in the empty-state images. The difference between the structural transformation observed at low and room temperature illustrates the close and complex relationship between the C defects and the configuration of the surrounding dimers.

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