Role of corner holes in Si(111)-7×7 structural formation studied by HBO_2 molecular irradiation and quenching

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By using the characteristic of the HBO_2 molecules, which initially react preferentially with the center adatoms in the unfaulted half units of the 7×7 structure, stability of corner holes in Si(111) structure was studied by scanning tunneling microscopy. The 7×7 structure began to break from the areas below step edges. Along the boundaries between 7×7 and the disordered areas including the $\sqrt{3}\times\sqrt{3}$ phase, the structure of the corner hole in the 7×7 structure was observed to be maintained. A similar structure was also observed on a quenched Si(111) surface. The results obtained indicate that corner holes play an important role in the formation mechanism of the 7×7 structure. In fact, structures in which a dimer-adatom-stacking fault structure was considered to be formed from a corner hole were observed on a quenched Si(111) surface. [S0163-1829(97)03507-8]

It is well established that the Si(111) surface forms the DAS (dimer-adatom-stacking-fault) structure, and that the 7×7 structure is the most stable of the DAS structures.[1] Since the DAS structure consists of a few surface layers and is very complicated, the stability and formation mechanism of the structure has been attracting considerable attention. According to recent scanning tunneling microscopy (STM) studies on quenched and high-temperature Si(111) surfaces, dimers in the second layer were confirmed to play an important role in stabilizing the DAS structure.[2–6] In addition to the characteristic, nucleation of faulted half units at the shared corner holes was observed in triangular domains of 1×1 area in a quenched Si(111) surface.[6] Since corner holes are related to the structure of the stacking fault formed in a 7×7 unit, the observed results suggest that corner holes play an important role in stabilizing the 7×7 structure. A model in which oxygen atoms serve to form and stabilize corner holes was proposed by Ohdomari.[7] However, to our knowledge, the role of corner holes has not been clarified yet.

In order to clarify the mechanism for stabilizing the 7×7 structure, it is necessary to study the breaking process of the DAS structure, in addition to the analysis of its formation process. One possible way is to observe the structural change caused by chemical reaction of the surface with atoms or molecules. However, in general, atoms and/or molecules react preferentially with and disturb the faulted half units in-

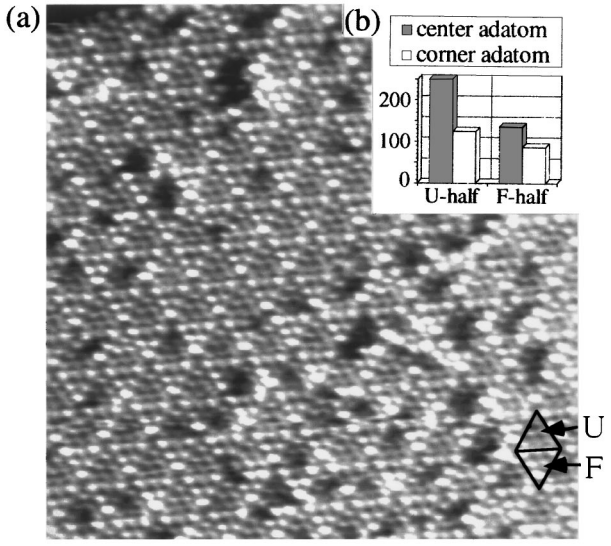

FIG. 1. STM images of Si(111) surface after HBO_2 irradiation for 3 min at 750 °C. Tip bias voltage V_t and tunneling current I_t are 1.0 V and 1.0 nA, respectively. The number of the reacted adatoms are shown in the inset.

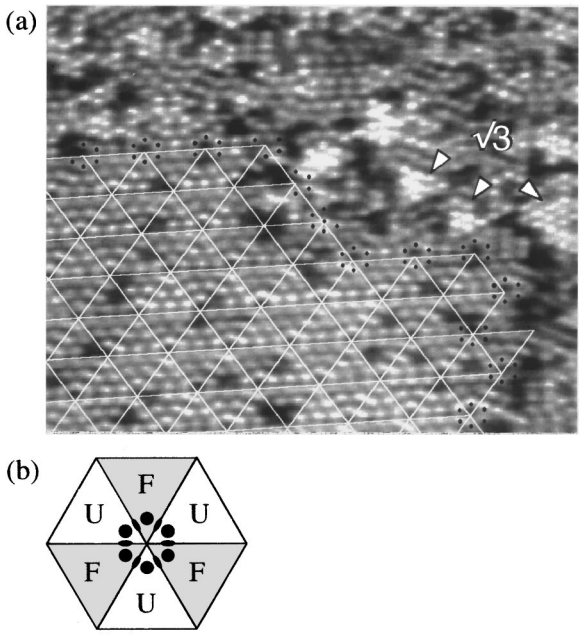

FIG. 2. (a) STM image of Si(111) surface after HBO_2 irradiation for 5 min at 750 °C, which includes 7×7 and disordered areas introduced by HBO_2 irradiation ($V_t=-1.0$ V and $I_t=1.0$ nA). Corner adatoms forming corner holes of the 7×7 structure at the boundary are indicated by dots. (b) Schematic structure of a corner hole in the 7×7 structure. Ellipses represent dimers, and faulted and unfaulted half units are indicated by *F* and *U*, respectively.

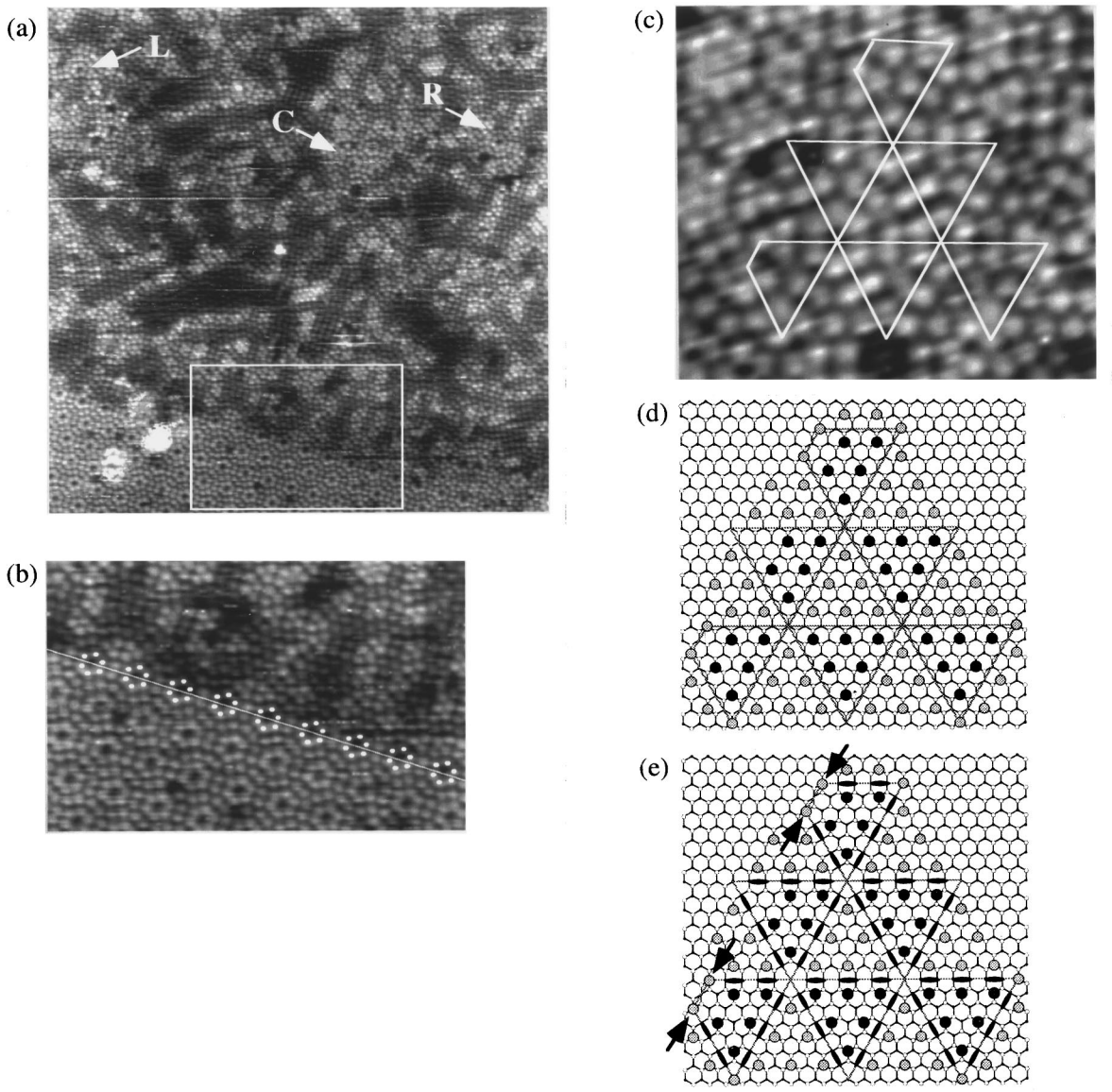

FIG. 3. (a) STM image of quenched Si(111) surface ($V_t=-2.0$ V and $I_t=0.3$ nA). Corner adatoms forming corner holes of 7×7 structure at the boundary are indicated by dots. (b) Magnification of the rectangular area in (a). (c) Magnification of the 7×7 fragment indicated by *C* in (a). Two schematic models for the structure shown in (c); without [(d)] and with [(e)] stacking faults.

cluding the stacking faults.[8] Since, with STM, we have to analyze the underlayer structure through observation of the top-layer adatom structure, such a disturbance hampers detailed analysis of the structure of the faulted half units upon breaking the 7×7 structure.

According to recent results obtained by STM,[9] a uniform $\sqrt{3}\times\sqrt{3}$ structure was formed by irradiation of HBO_2 molecules onto a Si(111)-7×7 surface at ~750 °C. In its initial stage, HBO_2 molecules were found to react preferentially with the unfaulted half units of the Si(111)-7×7 structure. Therefore, even after partial breakdown of the 7×7 structure, it is expected to be possible to analyze the structure of stacking faults including the role of corner holes in the stabilization of the 7×7 structure.

In this work, we present the results of STM observation of the initial structural change from the Si(111)-7×7 phase to the ordering Si(111)- $\sqrt{3}\times\sqrt{3}$ phase formed by HBO_2 molecular irradiation. The results obtained on a quenched Si(111) surface are also discussed.

Phosphorus-doped *n*-type Si(111) ($\rho=0.4\sim1\ \Omega$ cm) substrates were chemically cleaned and degassed at ~500 °C before being subjected to flash heating in order to form the 7×7 structure. For HBO_2 molecular irradiation, after confirming that a clean 7×7 structure had been obtained, HBO_2 molecules were irradiated onto the surface with the substrate temperature kept at ~750 °C. The HBO_2 cell temperature during irradiation was kept at ~800 °C. All STM observations were performed at room temperature using an electrochemically etched W tip. The base pressure was $\sim1\times10^{-10}$ Torr and the pressure during HBO_2 irradiation was $\sim2\times10^{-8}$ Torr.

Figure 1(a) shows a STM image of a surface formed after HBO_2 irradiation for 3 min. The Si(111)-7×7 structure remained, but some half units of the 7×7 structure became dark. The number of reacted adatoms on the terrace around the imaged area is shown as a bar graph in the inset of Fig. 1(a) [Fig. 1(b)]. As shown in Fig. 1(b), HBO_2 molecules

initially react preferentially with the center adatoms in the unfaulted half units, the details of which will be presented elsewhere.[10] Since HBO_2 molecules react preferentially with the center adatoms in the unfaulted half units, the stability of the corner holes and the stacking fault structure is expected to be analyzed after partial breakdown of the 7×7 structural area as mentioned above.

Figure 2(a) shows a STM image obtained after irradiation of HBO_2 molecules for 5 min, which includes the remaining 7×7 and introduced disordered areas. The 7×7 structure was broken from the areas below step edges on the surface. Some $\sqrt{3}\times\sqrt{3}$ structural islands were formed in the disordered area as indicated by arrows.

As indicated by dots in Fig. 2(a), corner holes remain along the boundary between the 7×7 and the disordered areas. Preferential reaction of HBO_2 molecules with the center adatoms in unfaulted half units made this observation possible. The observed result indicates that the structure of a corner hole is stable compared to other parts of the 7×7 unit. Since a corner hole has a symmetric structure as shown in Fig. 2(b), the existence of a complete corner hole may balance the strain around it. Such stabilization mechanism may be related to the dimer-adatom pairing mechanism proposed by Payne,[11] in which a combination of a dimer with two adjacent adatoms reduces surface energy. In a previous STM observation at ~600 °C, corner holes were not completed at the boundary, which indicates that the structure of the isolated corner hole at the boundary is not stable enough at the temperature.[5]

In order to compare the result obtained in the breakdown process of the 7×7 structure with that in the 7×7 formation process, a quenched Si(111) surface was observed by STM. Figure 3(a) shows a STM image of a Si(111) surface obtained by quenching from 1200 °C. When the disordered area is narrow, it is considered to be difficult to study the stability of isolated corner holes. Therefore, as shown in Fig. 3(a), wide disordered area with 7×7 domains was searched for and investigated. In addition to 7×7 domains, domains consisting of $c(2\times8)$ and other structures also exist. However, no $\sqrt{3}\times\sqrt{3}$ structural domains were formed on the quenched surface, as expected.

Figure 3(b) shows a magnification of the rectangular area in Fig. 3(a). Similar to the surface formed by HBO_2 irradiation shown in Fig. 2(b), corner holes exist at the boundary between the 7×7 and disordered areas as indicated by dots in Fig. 3(b). Since corner holes were observed at boundaries in both the breakdown [Fig. 2(a)] and formation [Fig. 3(b)] processes of the 7×7 structure, they are considered to play an important role in the stability and the formation mechanism of the 7×7 structure.

As indicated by arrows in Fig. 3(a), three fragments of DAS structural islands exist. A magnification of the central one indicated by C in Fig. 3(a) is shown in Fig. 3(c). Schematics of the two structural models of Fig. 3(c) are shown in Figs. 3(d) and 3(e), in which the model in Fig. 3(d) does not have stacking faults, but that in Fig. 3(e) does. Both models can reproduce the observed structure well. However, in consideration of the number of dangling bonds in each model, the model with stacking faults shown in Fig. 3(e) is more possible. If the observed fragments of the 7×7 structure in Fig. 3(c) are a quenched structure formed during the formation process as shown in Fig. 3(e), frontier areas with excess dangling bonds exist along the boundary between the normal and the stacking fault areas as indicated by arrows in Fig. 3(e); stacking faults are formed from a corner hole by recombining the Si-Si bonds one by one. With this assumption, the formation of a corner hole is considered to serve as a trigger for 7×7 structural growth. As is observed in Fig. 2(a), corner holes were stably observed also in the breakdown process of the 7×7 structures, which supports the mechanism. Oxygen atoms may play a role to form and stabilize a corner hole as proposed by Ohdomari.[7]

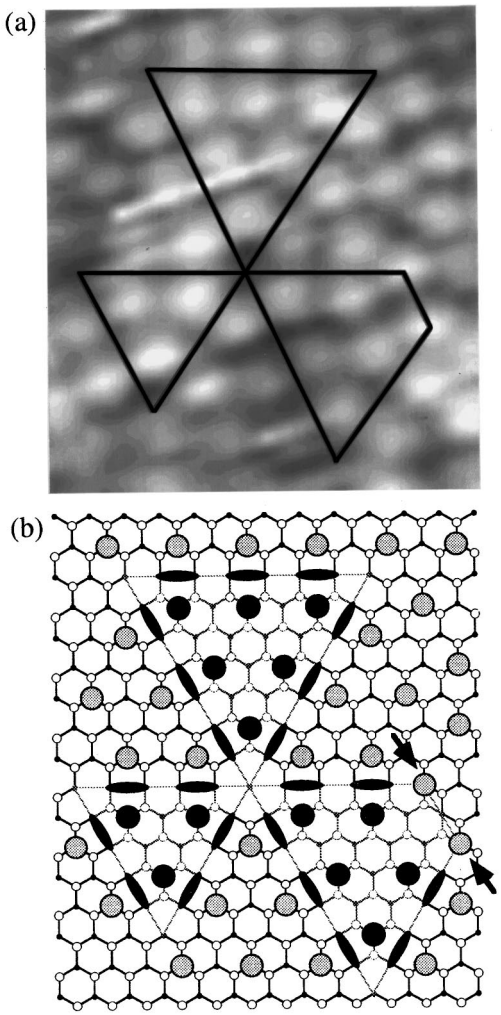

FIG. 4. (a) Magnification of the 7×7 fragment indicated by *L* in Fig. 3(a). (b) Schematic of the structure of (a).

When formation of a corner hole serves as a trigger for 7×7 structural growth, fragment of DAS structural island with one corner hole is expected to exist. Figure 4(a), a magnification of the area indicated by *L* in Fig. 3(a) shows an example. Schematic of the structural model of Fig. 4(a) is shown in Fig. 4(b), in which the structure of stacking faults is assumed similar as that in Fig. 3(e). As is shown in Fig. 4, DAS structure is growing from a corner hole. Since adatoms were always observed in the area with stacking faults as shown in Figs. 3 and 4, the dimer-adatom pairing mechanism proposed by Payne[11] is considered to play an important role to stabilize the DAS structure from the beginning of its formation process.

Fragment structure of the faulted halves is similar in both Figs. 3(c) and 4(a) as the frontiers of the area with stacking faults are indicated by arrows, which agrees well with the process that formation of a faulted half unit is triggered from a corner hole and ends at the other corner hole by recombining the Si-Si bonds one by one as mentioned above.

Stability of the faulted half units of the DAS structures has been known.[3,5,6] Here, as shown in Fig. 4, a 5×5 structure is formed from a corner hole. Similar formation process of a 9×9 structure exist at the fragment of DAS structure indicated by *R* in Fig. 3(a). These results may indicate that corner holes play a similar role in all DAS structures.

In conclusion, corner holes were observed to remain at the boundaries between 7×7 and disordered areas on the Si(111) surfaces formed by HBO_2 irradiation and quenching. The observed results indicate that corner holes play an important role in the stability and formation mechanism of the 7×7 structure. Structures of the DAS fragments formed by quenching were explained well with this model.

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