

Mechanisms and energetics of site hopping and chemical reactions of O₂ molecules at Si(111)-7×7 surfaces

I.-S. Hwang, R.-L. Lo, T.T. Tsong *

Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan, ROC

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Abstract

With continuous-time imaging using a variable-temperature scanning tunneling microscope (STM), we observe the dynamic behavior of a bright species, which we believe to be single O₂ molecules on Si(111)-7×7 surfaces. We have found the hopping motion of this molecular species between neighboring adatom sites, which is mediated by two intermediate states. A model is proposed to explain the detailed mechanism of the site hopping. Using Arrhenius plots, we determine the activation energies of different hopping paths and the relative binding energies of different states. We also observe the chemical reaction process of two adsorbed O₂ molecules to form an atomic species. Our results reveal that the hopping motion and chemical reactions of oxygen molecules depend strongly on the configuration of dangling bonds at the surface and the oxygen bonding. This study provides a direct view of molecular dynamics at a solid surface. © 1998 Elsevier Science B.V.

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1. Introduction

The way in which molecules adsorb and react on crystalline surfaces is an important subject in surface chemistry [1–3]. So far, experimental results have mainly been obtained through non-microscopic techniques, such as ultraviolet photo-electron spectroscopy (UPS), electron energy loss spectroscopy (EELS), electron-stimulated desorption (ESD), etc. These methods are helpful in providing information about the electron energy level, chemical bonding, and bonding geometry. On real surfaces, however, several factors could complicate the measurements and analyses of

traditional experimental results. First, there are often simultaneously several species present at different adsorption sites, especially on reconstructed semiconductor surfaces, where the configurations of surface atoms and dangling bonds are rather complicated. These adsorbed species may migrate on the surface, and sometimes they undergo more than one possible reaction. Second, identification of intermediate states is essential in understanding surface kinetics, but they often have a very low concentration and a short lifetime [3]. Thus, it is difficult for traditional methods to isolate them for measurements. Third, step edges or surface defects can further complicate the situation because the chemical bonding there differs from that of a perfect surface. Currently, microscopic description of surface kinetics has heavily

* Corresponding author. Fax: (+886) 2 7888933;
e-mail: phtsong@ccvax.sinica.edu.tw

relied on postulate and theoretical calculations, with which experimental measurements are interpreted. Using scanning tunneling microscopy (STM) [4,5], it is now possible to image individual molecules on surfaces and resolve their adsorption sites at the atomic scale. However, almost all STM experiments were conducted at room temperature. In this work, we demonstrate the ability of variable-temperature STM in the investigation of surface dynamic processes on the atomic level. Individual atomic and molecular events are directly observed, and the activation energies and energetics of different states are determined quantitatively, which provide a new insight in the study of surface chemistry.

The initial stage of chemisorption of O₂ molecules on Si(111)-7×7 surfaces has been one of the most studied systems in surface science, partly due to the fact that the growth of silicon oxide thin films is an important process in the semiconductor industry. Despite great efforts using many experimental techniques and theoretical calculations [5–29] in the past three decades, it is still unclear how O₂ molecules adsorb on to the surface, how many different states are there, the atomic configurations and the corresponding energetics, the pathway of reaction, etc.

In order to understand how O₂ molecules adsorb on Si(111)-7×7 and the assorted dynamic phenomena occurring on this surface, one has to know the atomic structure and the dangling bond configuration of the Si(111)-7×7 reconstruction [30], which is illustrated in Fig. 1. Each 7×7 unit cell consists of a faulted and an unfaulted half-cell. These half-cells are separated by dimer rows and corner holes. The two halves can be determined experimentally by taking filled-state STM images, with the faulted half appearing slightly brighter than unfaulted half [31]. Each half has six Si adatoms. Three of them occupy the corner sites (indicated with a “C”), and the other three occupy the edge sites (indicated with an “E”). Thus, there are four inequivalent adatom sites, and they are indicated as faulted corner (FO), faulted edge (FE), unfaulted corner (UO), and unfaulted edge (UE) sites. Each adatom has a dangling bond on the top. Some of the second-layer rest atoms (marked with a “+” sign) also have a dangling

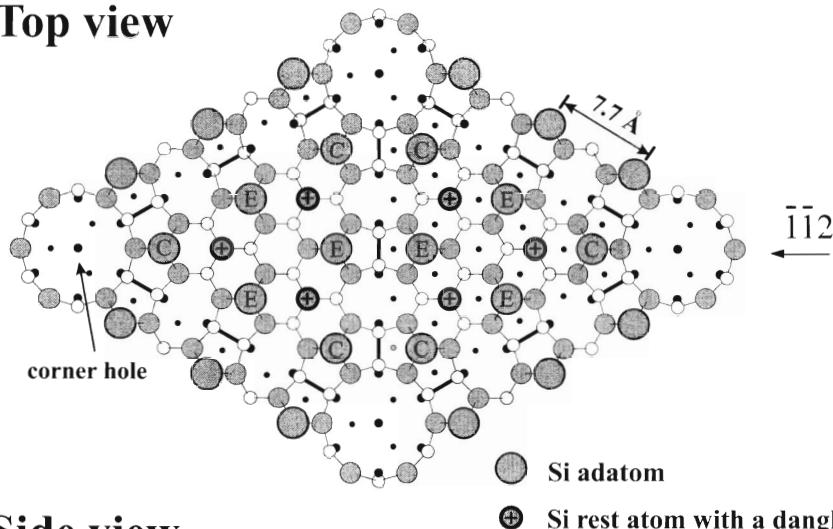
bond, and they are located at the center of three surrounding adatoms, as shown in the top view model. As we shall see, these dangling bonds play an important role in the adsorption of O₂ molecules as well as in the hopping process.

It has been known that an incoming O₂ molecule interacts first with Si adatom dangling bonds [17,19,20,25–27] and adsorbs on top of an adatom [22] at room temperature. Besides, the O–O axis has been found to be approximately parallel to the surface [14]. The para–paul–grif model (Fig. 2) proposed by Schubert et al. [20], based on extended Hückel tight-binding calculations, agrees well with the above experimental results. Moreover, the predicted peaks of electronic density of a state near 4 and 7 eV agree well with UPS measurements [9,14,17,19,20,25–28]. Thus, the above model has been generally accepted as the atomic configuration for the major molecular state. Note that the para, paul, and grif configurations are atomic structures at 0 K. At finite temperatures, the bond angles and bond lengths are less defined due to thermal vibrations. Therefore, we would simply use the paul configuration to represent the major molecular state, because these three configurations are basically the same in the temperature range in which we are interested.

Previous room-temperature STM studies show that the adsorption of oxygen molecules produces two stable species at the adatom positions of Si(111)-7×7 [16–18,28,29]. One appears brighter than Si adatoms (referred to hereafter as the B site) and the other one appears dark, just like a missing adatom (referred to hereafter as the D site). Recent STM studies by Martel et al. [29] and Dujardin et al. [28] showed that most of the reaction products are B sites at a very low exposure. Further incoming oxygen molecules can react with B sites, resulting in the formation of D sites. Thus, the ratio for the number of D sites to the total number of reacted sites increases with oxygen exposure. By combining STM and UPS measurements, Dujardin et al. proved that B sites are the major molecular species [28].

A second molecular state was reported recently by Comtet et al. using UPS measurements [26,27]. This state has a characteristic peak at 5.1 eV below the Fermi level. It exists in small concentrations

Top view



Side view

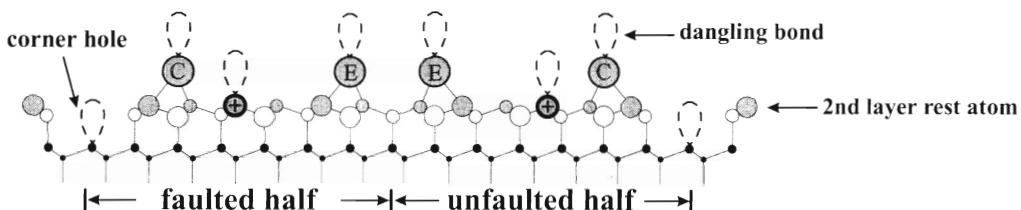


Fig. 1. The dimer-adatom-stacking fault (DAS) lattice for Si(111)-7×7. It consists of a faulted and an unfaulted half-cell. Each half has six adatoms. Three of them occupy the corner sites (indicated with a "C") and the other three occupy the edge sites (indicated with an "E"). There are 19 dangling bonds in total for each 7×7 unit cell: 12 for adatoms, six for rest adatoms, and one inside the corner hole.

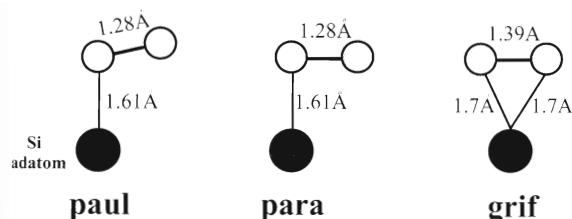


Fig. 2. The paul, para, and grif configurations for the major molecular state.

for room-temperature exposure [26], but it is the dominant species for exposure at low temperatures (30–60 K) [27]. It is not clear what the atomic configuration is for this second molecular state.

In the present work, we study the dynamic behavior of single adsorbed O₂ molecules on Si(111)-7×7 using a STM at temperatures ranging from room temperature up to 370°C. We observe

the site hopping of a major molecular species, two short-lived intermediate states mediating the site hopping, the reaction process for two adsorbed O₂ molecules, and so forth. We have also measured the energy barrier heights for several molecular events. Our observations suggest that the intermediate states in the site hopping process may be the second molecular state reported by Comtet et al.

2. Experimental procedures

Our experiments were performed using a JOEL STM (JSTM-4500VT) in an ultra-high vacuum chamber with a base pressure of 5×10^{-11} Torr. P-doped Si(111) samples of 0.05 Ωcm were used. Clean Si(111)-7×7 surfaces were prepared by annealing the sample up to ~1250°C and then

cooling down slowly. At the STM stage, the sample temperature was varied by passing current through the sample. The temperature reading was obtained using an optical pyrometer, which was calibrated with a thermal couple. We estimated the accuracy and precision in our temperature measurement to be $\sim 10^\circ\text{C}$ and $\sim 2^\circ\text{C}$, respectively. We waited for 2 h or longer for the thermal drift to disappear. Then, we exposed clean Si(111) surfaces to 0.04–0.2 L ($1\text{ L} = 1 \times 10^{-6}\text{ Torr} \cdot \text{s}$) of O_2 , corresponding to 0.001–0.006 ML ($1\text{ ML} = 7.84 \times 10^{14}\text{ O}_2\text{ molecules cm}^{-2}$) of coverage. At such low coverages, the chance for two oxygen-induced species to interact was very small, so we basically observed each individual species. Below 370°C almost all reacted sites were bright directly after adsorption, as in the case for room-temperature exposure. We noted that B sites usually appeared significantly brighter than Si adatoms in filled-state images (taken at negative sample biases), but in empty-state images (taken at positive biases), they appeared only slightly brighter or as bright, depending on the tip condition. Thus, we often used negative biases to identify the positions of B sites. In this study, we imaged the surface before the oxygen exposure. After the exposure, we imaged the same area and looked for new defects. We continuously imaged the products that we were interested in for tens of minutes or hours. In this paper, the STM images shown are usually selected from a sequence of successive images with a time interval of 2.4–9.2 s.

3. Results

3.1. Site hopping of the B site

As in the case of room-temperature exposure, B sites are very stable at temperature below 370°C . Interestingly, we find that B sites start to hop between neighboring 7×7 adatom sites above $\sim 250^\circ\text{C}$, and the hopping rate increases with the temperature. Fig. 3 shows six STM images for a B site hopping between different adatom sites in a faulted half of a 7×7 unit cell at 350°C . We find that almost all the hoppings are to a neighboring adatom site and are confined within its own 7×7

half. Very few jumps to an adjacent half are observed at temperatures below 370°C . The most frequent jumps are between neighboring edge sites. Also, we find that B sites have a higher probability of appearing in the faulted half than in the unfaulted half. Since there are four unequal adatom sites on Si(111)- 7×7 , there are six major hopping paths: FE \rightarrow FE, FE \rightarrow FO, FO \rightarrow FE, UE \rightarrow UE, UE \rightarrow UO, and UO \rightarrow UE. The corresponding average hopping rates are R_{fee} , R_{feo} , R_{foe} , R_{uee} , R_{ueo} , and R_{uo}_e , respectively. From thousands of successive STM images taken at various temperatures, we obtain the average hopping rate for each hopping path at each temperature, which is equal to the ratio of the total number of jumps to the total residence time at the initial adatom site. For example, R_{feo} is calculated by dividing the total number of FE \rightarrow FO hops by the total residence time at FE sites. We find that the hopping rates basically follow the Arrhenius relation:

$$R = R_0 \exp(E_D/k_B T),$$

where R is the transition rate, R_0 is the prefactor, E_D is the energy barrier height, k_B is the Boltzmann constant, and T is the temperature. Using the Arrhenius plots (Fig. 4), we deduce the activation energies and frequency factors for the six hopping paths. The effect of the STM tip is checked by measuring the residence time at FE for three different scan speeds (Table 1). The effect is nearly undetectable at 350°C and $\sim 20\%$ at 330°C . This produces only a small effect in the accuracy of the activation energies determined by the Arrhenius plots since they are semi-logarithmic plots.

The frequency factors obtained in Fig. 4 are very high (one to three orders of magnitude larger than 10^{13} s^{-1} , which is the value reported in most cases of single atom diffusion on surfaces). A molecule has a larger entropy than a single atom. Thus, it is possible that the contribution of the entropy term to the frequency factors is quite significant in this system. Also, the parameters obtained in Fig. 4 exhibit an interesting correlation: a large activation energy is accompanied by a large frequency factor. This may be related to the so-called “compensation effect” [32]. We hope

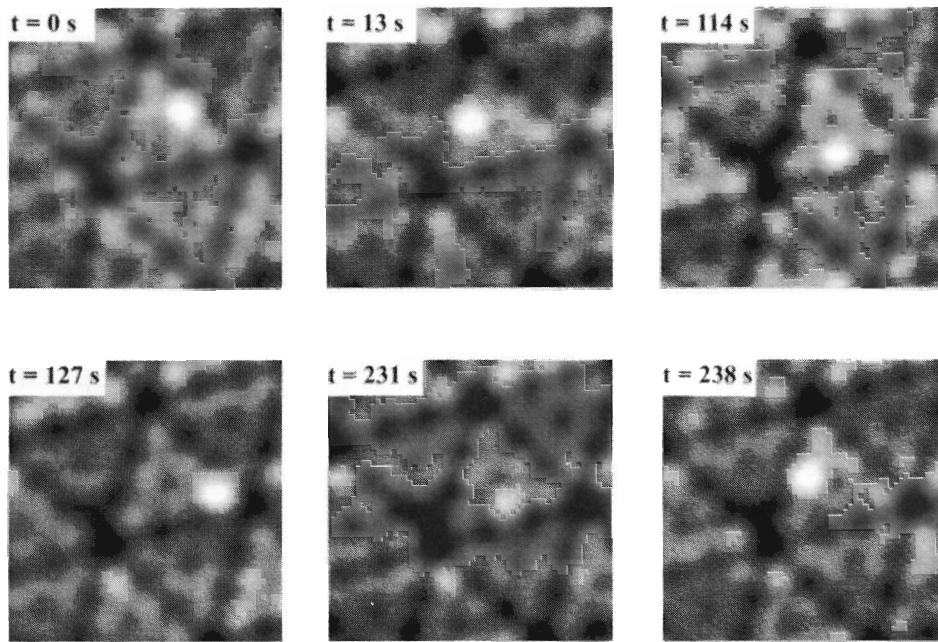


Fig. 3. Six $50 \text{ \AA} \times 50 \text{ \AA}$ STM images showing site hoppings at $350 \text{ }^\circ\text{C}$. The sample bias is -2 V .

that theoretical studies can shed some light on this experimental finding.

3.2. Intermediate-state mediated hopping

At a substrate temperature below 300°C , B sites are not very mobile (an average hopping time of more than 5 min). Continuous scanning using the STM reveals the detailed mechanism for the site hopping. Fig. 5 shows the STM images of a hopping from an edge site to a neighboring edge site. At $t=0$, a B site (the “ B_i ” state) can be seen at an edge site of the 7×7 unit cell outlined. The B site remains until $t=683 \text{ s}$, when it is displaced slightly to the right upper side, and the brightness is reduced somewhat. This is an intermediate state, and we denote it as the “ I_i^* ” state. It stays until $t=730 \text{ s}$, and the structure changes again to another similar intermediate state, the “ I_f^* ” state. At $t=742 \text{ s}$, the B site reappears at an adjacent edge site (the “ B_f ” state) and completes the site hopping. A careful examination of the STM topographs reveals that the image spots associated with

the intermediate species are located between an adatom and a neighboring rest atom, which both originally have a dangling bond (see also Fig. 1). The empty-state images for the I_i^* and I_f^* states (taken simultaneously with the filled-state image) are shown below (Fig. 5). The intermediate species appear somewhat darker than Si adatoms, and their image spots are also located between an adatom and a neighboring rest atom. We note that the site hopping is successful in only a small fraction of attempts. The pathway is usually “ $B_i \rightarrow I_i^* \rightarrow B_i$ ”, only a small fraction of the events follow the “ $B_i \rightarrow I_i^* \rightarrow I_f^* \rightarrow B_f$ ” pathway.

The atomic geometry for the B_i (B_f) state is shown in Fig. 6a, which is basically the paul configuration proposed by Schubert et al. [20]. One possible geometry for the intermediate states is the bridge configuration [20], i.e. an O_2 molecule is bonded with one end to an adatom and the other end to an adjacent rest atom. This may explain why the image spots are located between an adatom and a neighboring rest atom. The scenario for the site hopping is described as follows. At high temperatures, the O_2 molecule of the B_i state

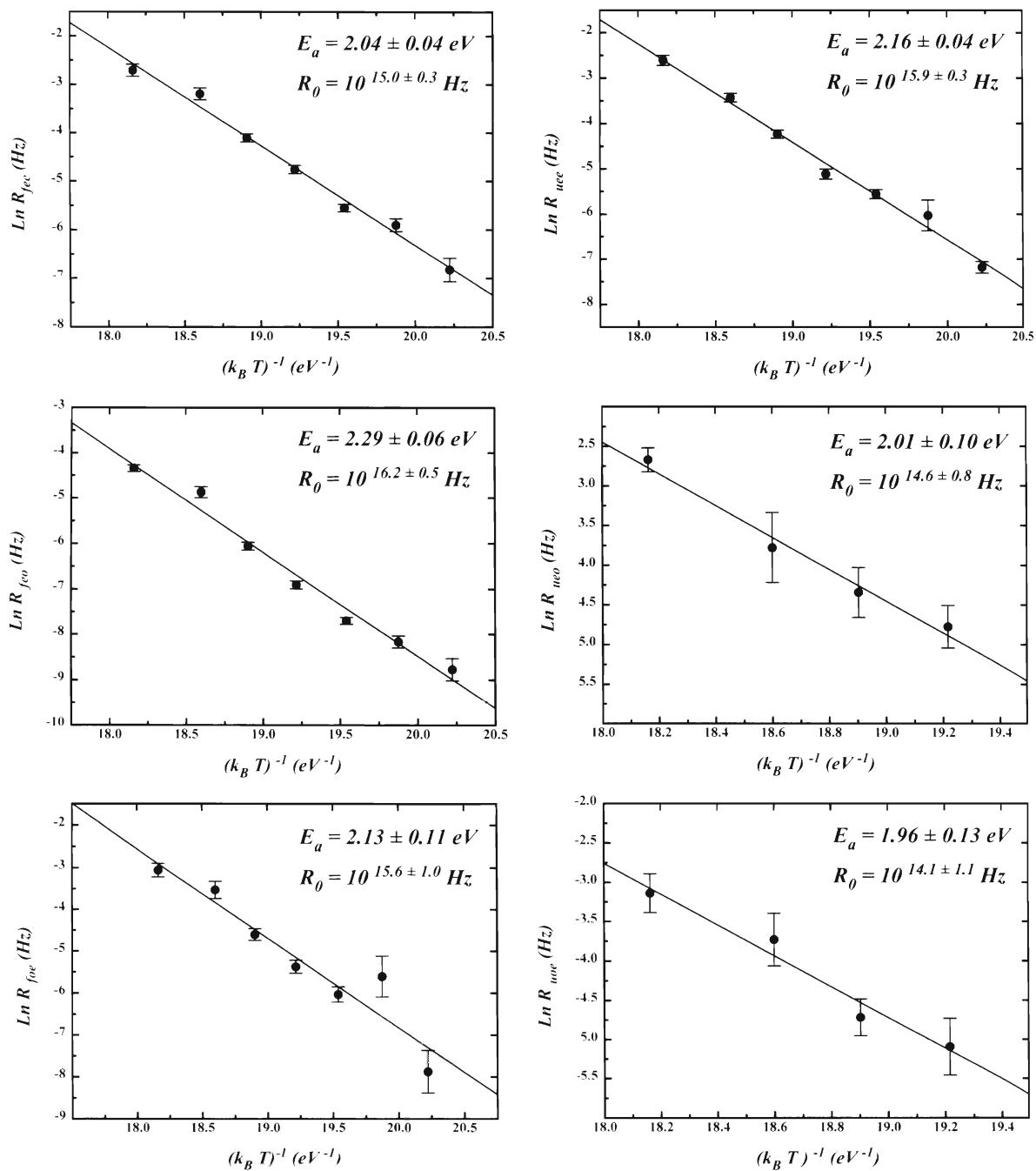


Fig. 4. Arrhenius plots for different site hopping paths.

Table I
Tip effect on the average residence time for B sites occupying the FE

Scan speed	350 °C	330 °C
9.2 s	22.9 ± 3.6 s	111.3 ± 6.1 s
4.6 s	20.7 ± 1.7 s	99.2 ± 11.7 s
2.4 s	20.0 ± 2.7 s	85.0 ± 10.3 s

would have a high vibrational amplitude, considering the single Si–O bond in the paul configuration, and thus has a probability to interact with the dangling bond of a neighboring rest atom. Sometimes, the O₂ molecule bonds with the other end to the rest atom and forms the bridge geometry (the “I_i*” state) temporarily. It may return back to the stable B_i state again by breaking the bond with the rest atom. However, it also has less of a chance of flipping over to bond with a neighboring Si adatom, which is also a bridge configuration (the “I_f*” state). Soon after, this bridge configuration will probably change to the more stable B_f state and complete the site hopping (Fig. 6a).

We think that what is imaged for the intermediate species in the STM topographs is an O₂ molecule. This molecule gives rise to a bright filled-state image but a rather dim empty-state image. The Si adatom bonded to the molecule is not visible due to saturation of its dangling bond. Very interestingly, on a Si(111)-7×7 surface that has been exposed to ~0.2 L of O₂ at room temperature, in addition to B and D sites, we also observe a very small concentration (~1%) of a new species that appears very similar to the intermediate species discussed above. Fig. 7 shows both filled-state and empty-state STM images of this species. The intermediate species found here may be the second molecular state reported recently by Comtet et al. using UPS measurements [26,27]. This state is predominant at low exposures (~0.03 L) at low temperatures (30–60 K) [27]. For room-temperature exposure, its characteristic peak (5.1 eV below the Fermi level) is very small but can be still detected with a small concentration [26]. In addition, the bridge configuration proposed here is consistent with the UPS results measured at 30 K

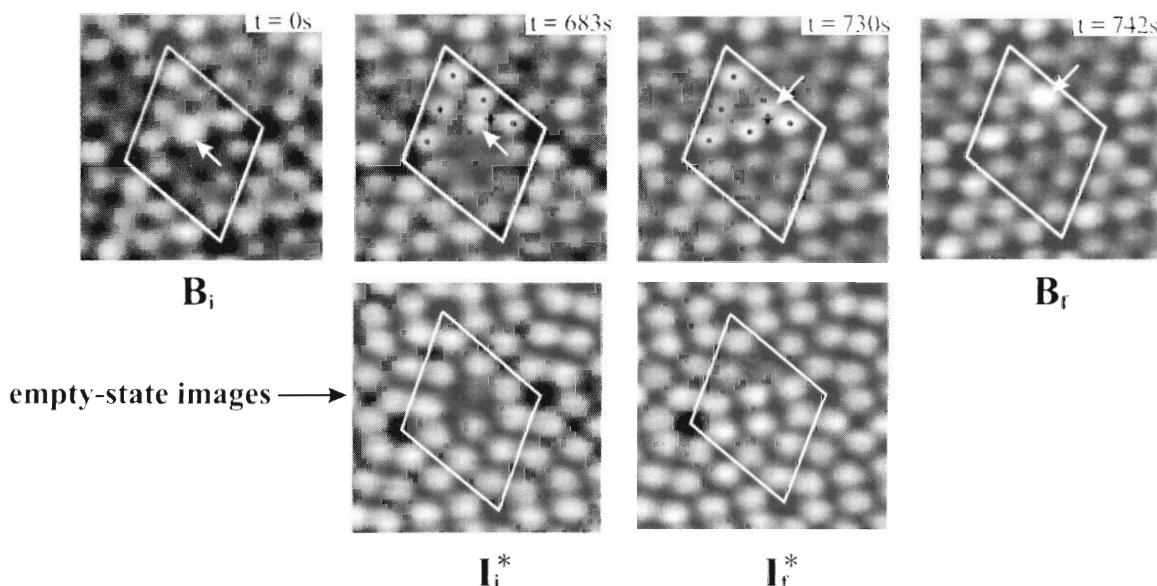


Fig. 5. 50 Å × 55 Å STM topographs showing the mechanism of a hopping from an edge site to a neighboring edge site, taken at 290 °C. The upper four filled state-images are obtained using a sample bias of -2 V, and the corresponding empty-state images (taken at the sample bias of +1 V) for the intermediate states are shown below. In the filled-state images for the intermediate states, dots mark the adatom sites of the faulted half of 7×7, and a “+” marks a rest atom site. It is clear to see that the intermediate species are located between an adatom and the rest atom site.

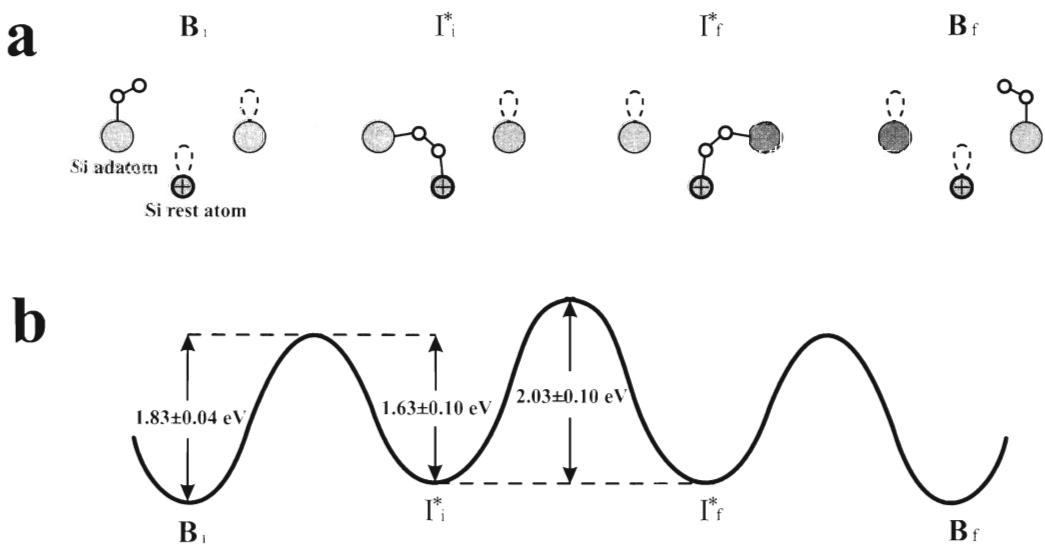


Fig. 6. (a) Schematic for detailed mechanism of the site hopping (side view). Note that thermal vibration and rotation of the O₂ molecule at high temperatures are not drawn. (b) Potential diagram for the site hopping process from an edge site to a neighboring edge site in the faulted half.

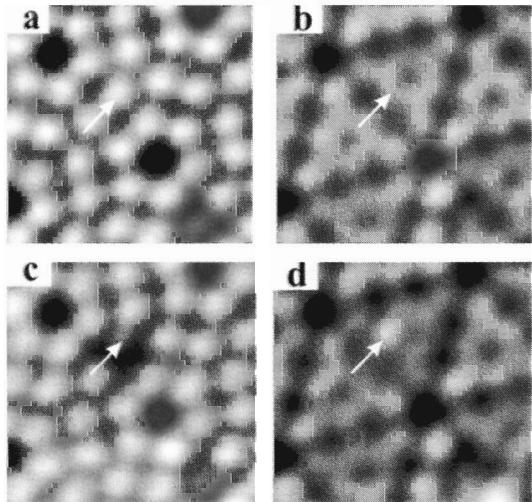


Fig. 7. 44 Å × 42 Å STM topographs showing a bridge species (indicated by an arrow) that appears after oxygen adsorption at room temperature. (a) Empty-state image taken before exposure (sample bias +2 V). (b) Filled-state images taken before exposure (sample bias -2 V). (c) Empty-state image taken after exposure (sample bias +2 V). (d) Filled-state image taken after exposure (sample bias -2 V).

[27], which show the reduction of both the S₁ (associated with adatom dangling bonds) and S₂ states (associated with rest atom dangling bonds) after exposure.

To determine the energy barrier for each state-transition in the hopping process, we acquired thousands of consecutive STM images at temperatures ranging from 290 to 340°C. Fig. 8 shows the Arrhenius plots for the state transitions in the site hopping from an edge site to a neighboring edge site in the faulted half. From these activation energies, a potential diagram shown in Fig. 6b is obtained. The I_i^{*} and I_f^{*} (B_i and B_f) states are at the same level because they are equivalent states. Note that the energy barrier height for I_i^{*} → I_f^{*} is higher than that for I_i^{*} → B_f, which is consistent with the observation that the site hopping is successful for only a small fraction of attempts.

We have also observed intermediate-state mediated site hopping for the cases of edge–corner and corner–edge hoppings. Fig. 9 shows an example of a site hopping from an edge site to a neighboring corner site in a faulted half. These are consecutive filled-state STM topographs taken at the substrate temperature of 300°C. Again, the image spots associated with the intermediate states are located between an adatom site and a rest atom site. We have not made any quantitative measurements for these two cases because of the much lower number of events observed, but we believe that the potentials for the I_i^{*} and I_f^{*} (B_i and B_f) states are slightly different because they are not equivalent states.

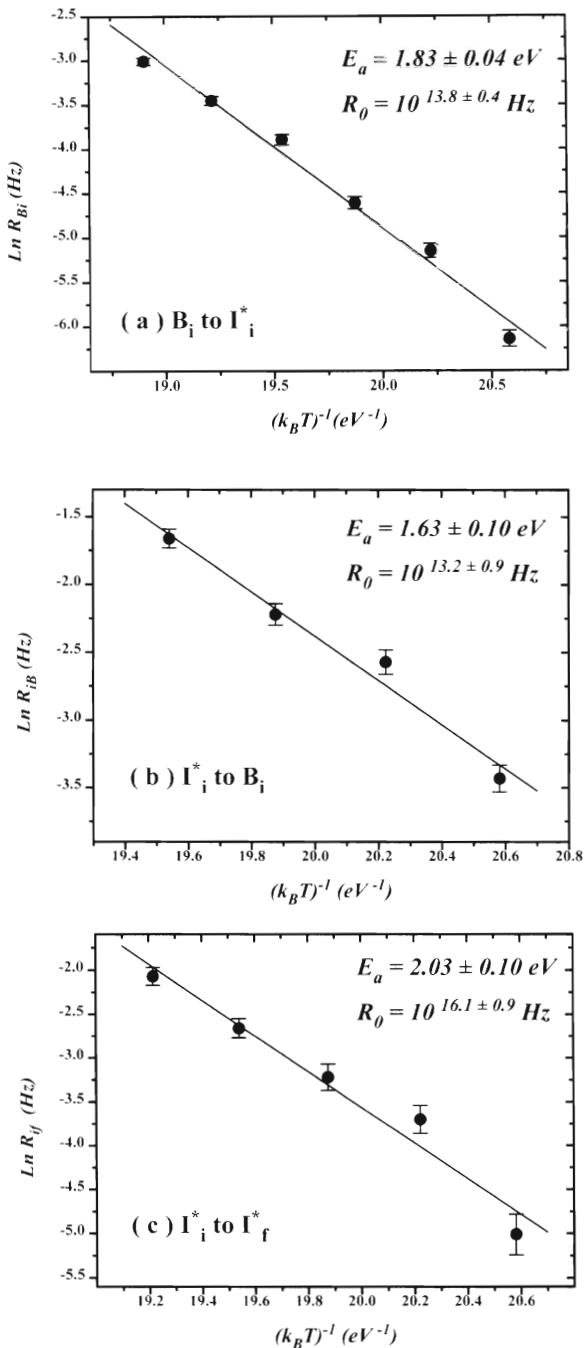


Fig. 8. Arrhenius plots for three state-transitions associated with the site hopping FE \rightarrow FE. (a) $B_i \rightarrow I_i^*$, (b) $I_i^* \rightarrow B_i$ and (c) $I_i^* \rightarrow I_f^*$.

3.3. Reaction of two B sites

We have found that a B site is very reactive to another B site nearby above ~ 300 C. The probability of observing this type of reaction increases with O₂ exposure. Fig. 10 shows a sequence of STM images taken at ~ 300 C that are selected from a number of consecutive images. Most of the images are taken at a sample bias of -2 V, and only the images at $t=336$ s, 535 s, 634 s, 706 s, and 2156 s are taken at a sample bias of +2 V. After exposure ($t=0$ s), two B sites (indicated with arrows) appear at corner adatom sites in a faulted half of 7×7 . At $t=11$ s, the B site on the right transforms into an intermediate state, and hops to an edge site later at $t=71$ s. At $t=188$ s, the B site on the left also hops upwards to another edge site. At $t=207$ s, the B site on the left transforms into an intermediate state. At $t=210$ s, two bright spots reappear, similar to the image at $t=188$ s. However, these two bright spots may not be the B sites. It seems that a series of chemical reactions is taking place, as seen in the images taken at $t=213$ s or later. Sometimes, we see only one bright spot, and sometimes two. These bright spots are probably not the B sites discussed before because we no longer see their site hopping and the characteristic intermediate states. Occasionally, we observe species with image spots displaced away from 7×7 adatom sites (e.g. images at $t=282$ s, 595 s, and 606 s). Some species have short lifetimes, and they may transform into a different species during the data acquisition, resulting in a partial image spot or a fuzzy image spot (see images at $t=236$ s, 282 s, 307 s). The reaction continues for over 2000 s, and finally a stable defect is formed, as seen in the images taken at $t=2150$ s (filled-state image) and $t=2156$ s (empty-state image). This dark species is very stable at 300 C, and we define it as a D₁ state. We have observed the reaction process of two B sites in the same 7×7 half several times. The detailed process is not the same each time, but it always results in a D₁ state. Note that the STM image of the D₁ species is not symmetrical along a [1̄1]2 direction. It has a small protrusion near two Si adatoms on one side (the left-hand side in Fig. 10), and filled-state images of these two Si adatoms are slightly brighter than

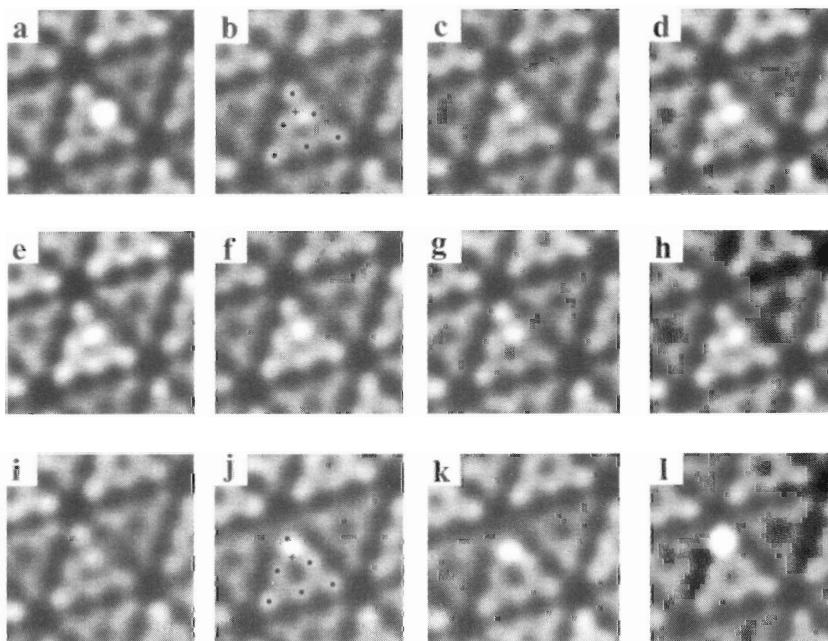


Fig. 9. Consecutive STM topographs showing hoppings of a B site from an edge site to a corner site, taken at the sample bias of -2 V and 300 C . The time interval between two images is 2.4 s . In (b) and (j), dots indicate the adatom sites of the faulted half of 7×7 , and a “+” indicates a rest atom site.

the two on the other side (right-hand side in Fig. 10).

We think that the two adsorbed oxygen molecules in Fig. 10 start to react with each other at $t \geq 207\text{ s}$ and are dissociated into atomic oxygen. The oxygen atoms can move around between the first two or three layers of Si atoms and form many possible short-lived metastable species during the reaction course until a stable configuration is reached. At this point, it is not easy for us to determine the atomic structures of these metastable states and the final D_1 species. We believe that no oxygen atom or molecule escapes during the reaction, and there are probably four oxygen atoms in these atomic species.

Very interestingly, two B sites in neighboring 7×7 halves can also react and form the D_1 species. Fig. 11 shows a sequence of STM images taken at 330°C . Again, most of them are filled-state images taken at the sample bias of -2 V , and only the images at $t=656\text{ s}$ and 688 s are taken at a sample bias of $+2\text{ V}$. At $t=0$, two B sites (indicated by arrows) are seen in two neighboring halves.

Originally, these B sites hop between neighboring adatom sites in their halves. At $t=179\text{ s}$, they hop to two adjacent edge sites, which are separated by only a dimer row (6.7 \AA). A reaction between these two B sites occurs around this time, and the two bright products in the image at $t=185\text{ s}$ are probably not B sites any more as their dynamic behavior has changed. The bright product in the unfaulted half (the lower half) hops downwards to an edge site at $t=185\text{ s}$ and soon becomes almost as bright as Si adatoms for quite a while. This species seems to be undergoing transformations. It appears very similar to Si adatoms most of time, but it occasionally reappears as a bright spot at this edge site (see images from $t=190$ – 626 s). At $t=631\text{ s}$ and 669 s , it appears slightly darker than Si adatoms, and the corresponding empty-state image taken at $t=656\text{ s}$ shows a dark spot at this edge site. Interestingly, in the filled-state image at $t=673\text{ s}$ and the empty-state image at $t=688\text{ s}$, it appears almost identical to Si adatoms. This species does not escape because later, it appears again and finally hops upwards.

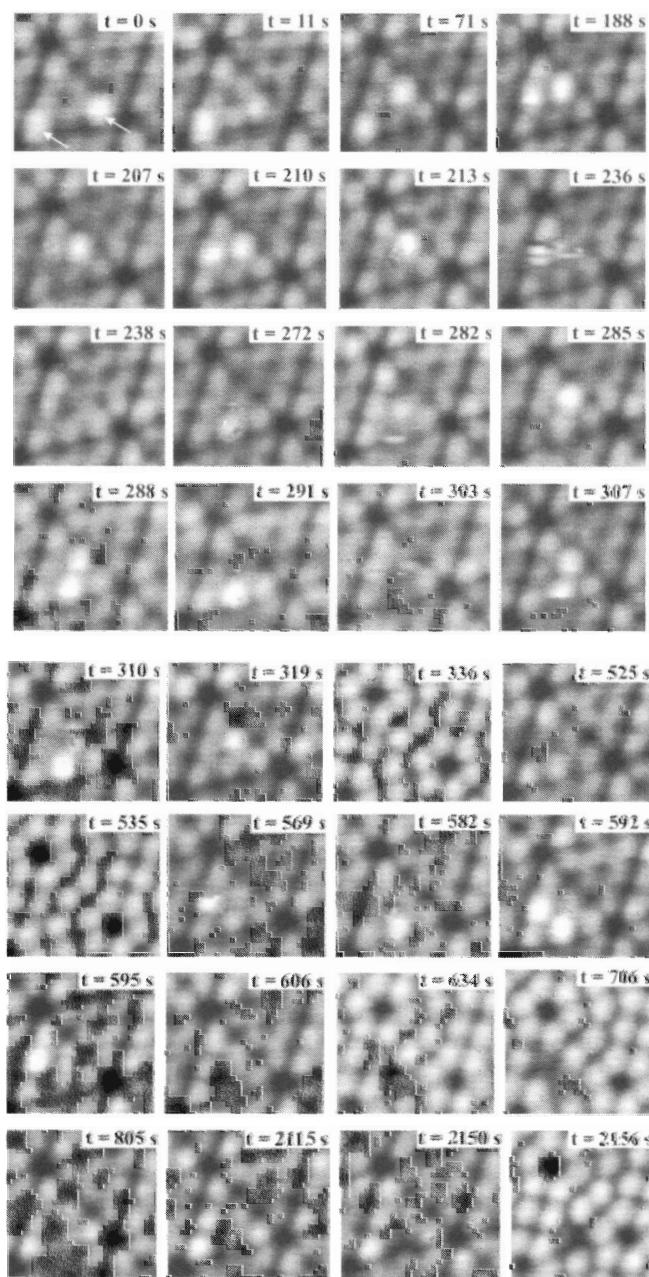


Fig. 10. Thirty-two $35 \text{ \AA} \times 35 \text{ \AA}$ STM images showing the reaction process of two B sites occurring at 300°C .

reappearing as a bright product. For the bright spot in the faulted half (the upper half) in the image at $t=185 \text{ s}$, it always appears bright and can hop between adatom sites. However, the hopping rate is several times higher than that for B

sites at this temperature, and we do not see the intermediate states in the hopping process. Therefore, we are very sure that it is not a B site. These two bright products hop to neighboring edge sites again at $t=910 \text{ s}$, which is almost iden-

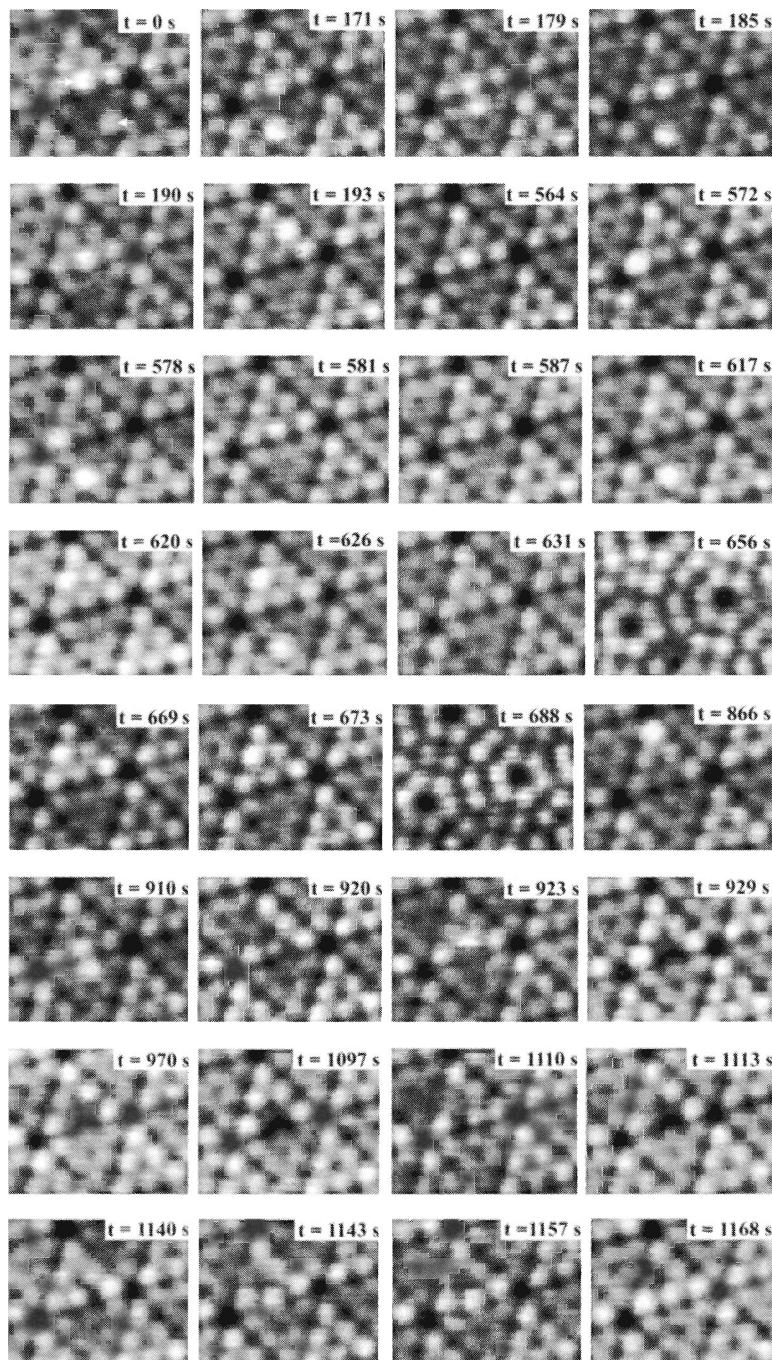


Fig. 11. Thirty-two $55\text{ \AA} \times 40\text{ \AA}$ STM images showing the reaction process of two B sites that are originally located in two neighboring half-cells. The images are taken at 330°C .

tical to the image at $t=179$ s. These two products react again, and we no longer observe any species present in the unfaulted half, suggesting that the species originally in the lower half has moved upwards. Some structure changes can be seen at $t=920$ s and 923 s. At $t=929$ s, a D_1 state is observed. At this temperature, the asymmetry in the image spots associated with the D_1 state can swap. For $t=929$ s, the two adatoms on the left-hand side are brighter than the two on the right. For $t=970$ s, the two adatoms on the right become brighter. The asymmetry changes again at $t=1097$ s. Not only is there a change in asymmetry in the image spots, but the D_1 state changes position to another edge site, as seen in the image at $t=1168$ s. There are several metastable structures present during this site change (see images taken at $t=1140$ s, 1143 s, and 1157 s). These dynamic behaviors are very interesting. Unfortunately, we do not know the exact atomic configurations of these species.

In Fig. 11, the two B sites react at around $t=179$ s and then are transformed into two different species. We guess that there is an oxygen atom transfer between these two B sites, resulting in a species (probably the upper one) containing three atomic oxygen and the other one containing one atomic oxygen. We find that two B sites in two halves do not always react with each other when they hop to neighboring adatom sites. Sometimes, the two B sites hop away, and we can see their site hopping and the intermediate states as in Figs. 5 and 9. There are also cases where the two B sites react immediately with all oxygen atoms going to one half, rather than the two-step reaction process as shown in Fig. 11. In this situation, we observe the formation of a D_1 site in a half and no oxygen-induced species in the other half.

4. Discussion

4.1. The B site: a molecular state or an atomic species?

There has been controversy about the atomic configuration for the B site. Previous studies using

UPS, ESD, XPS, second-harmonic generation, etc. [9,14,15,17,19–28] have shown that the major molecular state dominates for low-temperature (including room temperature) exposure in the low-coverage regime. In previous room-temperature STM studies, it was also found that B sites dominate for oxygen exposures <0.2 L [28,29]. Thus, B sites are very likely to be the major molecular species. However, the molecular state was reported to have a lifetime of ~ 15 min in an early experiment using XPS by Höfer et al. [9]. Since B sites seen in STM images are stable for hours, Avouris et al. [16] argued that B sites should be related to atomic oxygen, and proposed a model with an oxygen atom inserted in a backbond of the Si adatom. In recent years, much longer lifetimes (ranging from 50 to 1500 min) were measured for the molecular state by different groups [22–28], which again suggests that B sites may well be a molecular species.

The para–paul–grif model proposed by Schubert et al. [20], based on extended Hückel tight-binding calculations, agrees well with many experimental results. The predicted peaks of electronic density with states near 4 and 7 eV agree well with UPS measurements [9,14,17,19,20,25–28]. The adsorbed O_2 molecules have been found to lead to the disappearance of the S_1 state (associated with Si adatom dangling bonds) in UPS [17,19,20,25–27], and they are also determined to occupy the on-top site using electron-stimulated desorption ion angular distribution [22]. Besides, near-edge X-ray absorption fine structure (NEXAFS) measurements have shown that the O–O axis is approximately parallel to the surface [14]. Hence, the para–paul–grif model has been generally accepted as the atomic configuration for the molecular state. However, the calculations indicated that the paul, para, and grif configurations had no electronic density of state within 3 eV above or below the Fermi level. Thus, Schubert et al. claimed that the major molecular state should appear dark in the STM images. To explain the bright spots observed in STM images, Schubert et al. proposed that they are composed of several different reaction products. So far, this picture for the bright image spots has not been confirmed by any other experiment.

Recently, Dujardin et al. [28] proved that the B site is the major molecular state by combining STM and UPS measurements. At very low oxygen exposures, almost all new image features that appear after the exposure are B sites. UPS measurement shows the reduction of the S_1 state as well as the appearance of the peak associated with the molecular state (3.8 eV below the Fermi level). This strongly indicates that the B site is the major molecular state. Thus, the density-of-state calculation for paul–para–grif configurations by Schubert et al. [20] needs to be further evaluated. An early UPS measurements made by Höfer et al. [9] using He I ($h\nu=21.2$ eV, s-polarized) showed a peak at ~ 2.1 eV below the Fermi level (in addition to the two peaks around 3.8 and 7 eV) for the major molecular state. This extra peak is not predicted in the electronic density-of state calculation by Schubert et al. [20]. Furthermore, Bratu et al. [24] indicated that the O_2 $2\pi^*$ -derived levels of the adsorbed oxygen molecules are only partially filled, based on an earlier NEXAFS measurement [14]. Thus, unfilled O_2 $2\pi^*$ -derived levels should give rise to a high density of empty states near the Fermi level and appear bright in empty-state STM topographs.

Our earlier study of point defects on Si(111)-7 \times 7 [33] showed that the variable-temperature STM study of dynamic behavior is a very efficient way of distinguishing between different surface defects. Different species usually exhibit different levels of brightness in STM images at various biases. However, there are species that cannot be distinguished easily by their brightness alone, but they exhibit a very different dynamic behavior, such as different desorption temperatures, different hopping rates, different hopping processes, or different reaction paths. Hence, it is not difficult to distinguish different species from their dynamic behavior at several temperatures. In this work, we find that all bright image spots that appear immediately after oxygen exposure exhibit the same dynamic behavior. They have a similar residence time at the adatom sites, the site hoppings are mediated by two intermediate states as shown in Section 3.2, and so on. Thus, we can conclude that these bright spots are of the same species, rather than several different species pro-

posed by Schubert et al. [20]. In addition, the para–paul–grif model explains very well our observation of the site hopping mechanism. Even though we cannot rule out the possibility of a very intriguing model, so far, we do not know any other model that can explain satisfactorily the dynamic behavior that we have shown here.

4.2. The bridge configuration

We propose the bridge configuration for the intermediate states seen in the hopping process of the B site because it explains the mechanism very well. In the theoretical calculations by Schubert et al. [20], the bridge configuration has a total energy lower than a clean Si(111) plus one O_2 molecule without any interaction with the surface. However, their calculations also showed that the long O–O bond (1.5 Å) in the bridge configuration is very weak and would dissociate instantly. We cannot rule out a different configuration for the intermediate states observed in the hopping process of B sites. At this point, we do not have any better choice than the bridge configuration. In addition, the second molecular state reported recently by Comtet et al. [26,27] seems to indicate the existence of the bridge configuration because of the quenching of both S_1 and S_2 surface states in UPS measurements. Comtet et al. have pointed out that the second molecular state dominates for low oxygen exposures at 30 to 60 K and that it also exists at low concentrations when exposed at room temperature. Our STM observation of Si(111) surfaces exposed to oxygen at room temperature does show the existence of a species appearing like the intermediate states seen in the hopping processes of B sites. Therefore, we think that the molecular species with the bridge configuration exists, and it can explain the hopping process of B sites well. Also, it may be helpful to use a low-temperature STM to study the dominant species present on Si(111)-7 \times 7 which has been exposed to a small amount of O_2 at 30–60 K.

4.3. Atomic oxygen species

Low oxygen exposure at low temperatures (including room temperature) produces mainly

molecular products on Si(111)-7×7 [9,14,15,17,19–28]. It was reported that further exposure to oxygen molecules or annealing would lead to the dissociation of oxygen molecules into more stable species containing atomic oxygen [9,10,14,15,17,19–24,28]. EELS measurements for atomic species by Edamoto et al. [10] showed that there are Si–O species with atomic oxygen adsorbed on top of surface Si atoms and Si–O–Si species with atomic oxygen inserted between two Si atoms. Based on theoretical calculations, Schubert et al. [20] proposed several configurations containing two to five atomic oxygens to explain the oxidation sequence. These configurations are basically consistent with EELS measurements. However, it is not clear how these species would appear in STM topographs.

In room-temperature STM studies [18,28,29], it has been found that an incoming O₂ molecule (gas phase) can easily react with a B site and result in a dark site (a D site). Thus, the ratio of D sites to B sites increases with oxygen exposure [18,28,29]. It is believed that the D site is an atomic species, but it is not clear how many oxygen atoms each contains. In our STM topographs, D sites appear different from D₁ species. D sites do not exhibit the asymmetry in the image spots as seen for the D₁ state in Figs. 10 and 11. The D₁ state results from the so-called Langmuir–Hinshelwood (L–H) mechanism [34], which means that the reaction takes place between chemisorbed reagents. However, the D site results from the so-called Eley–Rideal (E–R) mechanism [34], which means that the reaction takes place via a gas phase molecule with a chemisorbed species. For low-temperature (including room temperature) exposure, we guess that the L–H mechanism is not efficient because of the low hopping rate of O₂ molecules, and the E–R mechanism is the major process for the formation of atomic species. A room-temperature STM study by Martel et al. [29] showed a large reaction cross-section ($\sim 73 \text{ \AA}^2$) for a B site to react with an incoming O₂ molecule. This indicates that an incoming O₂ molecule would feel a strong attractive interaction from an adsorbed O₂ molecule at a distance of about 5 Å. In our STM study, two neighboring B sites are rarely seen for room-temperature exposure. Very

interestingly, for exposure at the sample temperature above 250°C we do not see the formation of D sites even when we increase the oxygen exposure up to $\sim 1 \text{ L}$ (about 0.03 ML of coverage). Instead, we often see the appearance of a new B site next to a pre-existing B site, indicating that the E–R mechanism is not efficient at high temperatures. This suggests that the reaction cross-section for a gas phase O₂ molecule to react with a B site and form a D site may decrease with increasing temperature. At low temperatures, we think that when an incoming O₂ molecule approaches an adsorbed O₂ molecule within a distance about 5 Å, they would interact strongly with each other and probably go through some concerted motion to form a D site. At high temperatures, the large thermal vibrations and rotations of the adsorbed molecules would prevent the concerted motion from happening. The incoming O₂ molecule would rather adsorb on another Si adatom and form a B site. Via the site hopping, a reaction between two adsorbed B sites (the L–H mechanism) becomes possible.

Since we do not obtain D sites at high temperatures, and thus cannot observe their dynamic behavior, we do not know which model proposed by Schubert et al. [20] best describes the D site. However, the configurations proposed by Schubert et al. do not seem to explain the images and the dynamic behavior that we have observed for the D₁ species. Besides, we have observed many metastable atomic species present during the reaction process of two B sites. Therefore, there are atomic species that are not predicted in theoretical calculations. At temperatures above 370°C, we also find that single adsorbed O₂ molecules can eventually transform into several atomic species. Details about atomic species will be reported later in another paper [35].

These atomic species are very complicated to analyze; it may be helpful to expose Si(111)-7×7 to a small amount of oxygen atoms, rather than oxygen molecules, and study the reacted species. Studies like this will hopefully provide important clues for analyzing the complicated dynamic behavior exhibited for O₂/Si(111)-7×7 and lead to a better understanding of the reaction pathways.

during the initial stage of oxidation on Si(111) surfaces.

4.4. Lifetime of B sites

In an early XPS measurement, Höfer et al. found that the molecular state had a lifetime of ~ 15 min before being dissociated into atomic species [9]. Much longer lifetimes were reported in later measurements by several groups [22–28], but they vary a lot, ranging from 50 to 1500 min. Recently, Dujardin et al. [28] showed that the time decay of the molecular state is due to the reaction of adsorbed O_2 with H_2O molecules from the residual gases in the UHV chamber. They found that many B sites are transformed into dark species after leaving in the vacuum for 6 h or when exposed to a small amount of H_2O . This finding explains the large variation in previous lifetime measurements of the molecular state. This dark species, which results from the reaction of a B site with an H_2O molecule in gas phase, appears very similar to the D site in STM topographs. However, our recent results show that this dark species is neither the D nor the D_1 state [35].

In addition to H_2O , H atoms from the vacuum chamber can also affect the lifetime of B sites. H atoms are found to migrate between rest atom sites that originally have a dangling bond at temperatures from 300 to 400°C, and the hops are often found to cross the dimer row to a neighboring half. This species migrates on the surface and can react with a B site to form a dark species. However, adsorbed H atoms can be removed easily by annealing the sample above 800°C. They do not show up on surfaces within 6 h after annealing, and thus do not affect our measurements much.

As we have shown in Section 3.3, B sites are very reactive to another B site nearby at $\sim 300^\circ C$ or above. Thus, the lifetime of B sites is also affected by the oxygen coverage. Our study shows that as long as the substrate is clean, the vacuum is good, and the oxygen exposure is small enough, B sites can stay for over an hour below 370°C [36]. In previous experiments [7,9,10,14,15, 17,19,24], the molecular state was found to be dissociated into atomic states upon gentle annealing. However, those experiments were operated

for relatively high oxygen exposures and thus reactions between adsorbed oxygen molecules (as shown in Figs. 10 and 11) can occur easily. A recent UPS experiment on Si(111)- 7×7 surfaces exposed to a small amount of oxygen shows that the 3.8 eV peak (associated with the major molecular species) persists after over 10 min of annealing at $\sim 350^\circ C$ [36].

5. Conclusion

In the past three decades, there have been extensive studies of the initial stage of oxidation on Si(111)- 7×7 . It was believed that the adsorption is basically dissociative, preceded by a molecular precursor. In previous room temperature STM studies, there are also two species reported: one appears brighter than Si adatoms and the other appears darker. Our variable-temperature STM study shows that there is actually more than one molecular species and many atomic species. Some appear as bright products, others as dark products. Therefore, brightness alone cannot be used to identify these species. However, at very low oxygen exposures, the bright products that appear are of the same species because they exhibit the same dynamic behavior at elevated temperatures, and therefore, we can define them as B sites. B sites are found to hop between neighboring adatom sites with two intermediate states mediating the hopping process. A model is proposed to explained the detailed mechanism of the site hopping. We also quantitatively determine the activation energies for the site hopping and the state-transition in the hopping process, from which the energetic of the site hopping is clarified. We also found that a B site can react with another B site nearby at temperatures above $\sim 290^\circ C$. The reaction is directly imaged, and there are many atomic species present during the entire process.

Our variable-temperature STM study provides an atomic view of molecular dynamic processes at a surface, which is lacking in the traditional methods. As demonstrated in this work, variable-temperature STM can basically trace in time and in space the detailed changes of each individual species and intermediate states. By selecting the

appropriate temperature range, we can observe different dynamic processes, such as site hopping, the mechanism involving intermediate states, reactions, and so forth. In particular, the intermediate states have been known to play a crucial role in many dynamic processes, but it is very difficult to isolate them by traditional methods due to their short lifetime and very low concentration. We hope that this study will stimulate further experimental studies and theoretical calculations, which will lead to a better understanding of the entire oxidation process of silicon surfaces. We also believe that a further improvement in the time resolution of scanning tunneling microscopy will help us identify many more intermediate states with much ease.

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