Site Hopping of Single Chemisorbed Oxygen Molecules on Si(111)-(7 × 7) Surfaces

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We observe directly the site hopping motion of a molecular O_2 species on Si(111)-(7 × 7) surfaces using a variable-temperature scanning tunneling microscopy. At the temperature range of our observation, the hopping is mainly confined to one-half of the 7 × 7 unit cell between adjacent 7 × 7 adatom sites. Through Arrhenius plots, the activation energies for the hopping between different atomic sites are derived. We also resolve two short-lived intermediate states which mediate the site hopping. An atomic mechanism is proposed to explain the molecular hopping process. [S0031-9007(97)03375-9]

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Adsorption of molecules on surfaces has been an important subject in surface science [1–3]. The initial stage of chemisorption of oxygen molecules on Si(111)-(7 × 7) surfaces has been one of the most studied systems in gas-solid systems. For the past three decades, despite the use of many experimental techniques and theoretical calculations [4–27], many issues remain unresolved.

At room temperature the chemisorption of O_2 on Si(111)-(7 × 7) was considered to be essentially dissociative. It was discovered by Ibach *et al.* [4,5] and Höfer *et al.* [7] that in the low coverage regime a molecular precursor preceded the dissociated stable adsorption state, which was confirmed later by many groups [8,11,12,19–25]. The molecular state was found to be responsible for the disappearance of the S_1 state (associated with adatom dangling bonds) in ultraviolet photoelectron spectroscopy (UPS) [15,17,18,21–23], and it was also determined to adsorb at the on-top site using electron-stimulated desorption ion angular distribution [19,25]. In addition, the O-O axis was determined to be approximately parallel to the surface [11]. The para, paul, or grif model proposed by Schubert *et al.* [18] agrees well with the above experimental results. The predicted peaks of electronic density of states near 4 eV and 7 eV also agree well with UPS measurements [7,11,15,17,18,21–24]. Thus, the above model has been accepted by many researchers as the atomic configuration for the chemisorbed molecular state. Previous scanning tunneling microscope (STM) studies of the initial stage of O_2 adsorption on Si(111)-(7 × 7) were operated at room temperature [9,13–16,24,26]. Their results indicate that adsorption of oxygen molecules produces two stable sites at the adatom position of Si(111)-(7 × 7), "bright" and "dark" sites, depending on whether they appear, respectively, brighter or darker than the Si adatoms. Recent STM studies by Martel *et al.* [26] and Dujardin *et al.* [24] show that most of the reaction products are bright sites at very low exposure. Combining STM and UPS results, Dujardin *et al.* [24] have proved that bright sites seen in STM topographs are caused by the adsorption of single O_2 molecules on Si(111)-(7 × 7). In this work, with a high-temperature STM, we observe the site hopping of the molecular species (the bright sites) and measure the activation energies and frequency factors for hopping between different adatom sites of the substrate. In addition, we have observed short-lived intermediate states which mediate the site hopping. A detailed model for the site hopping process is then proposed.

Our experiments are performed using a JOEL STM (JSTM-4500VT) in an ultrahigh vacuum chamber with a base pressure of 5×10^{-11} torr. Clean Si(111)-(7 × 7) surfaces are prepared by annealing the sample up to ~1250 °C and then cooling down slowly. At the STM stage, the sample temperature is varied by passing current through the sample. The temperature reading is obtained by an optical pyrometer with accuracy ~10 °C and precision ~2 °C. We wait for 2 hours or longer for the thermal drift to disappear. Then, we expose clean Si(111) surfaces to 0.04–0.1 L ($1\ \mathrm{L} = 1 \times 10^{-6}$ torr s) of O_2 [28], which corresponds to 0.001–0.003 ML ($1\ \mathrm{ML} = 7.84 \times 10^{14}\ O_2\,\mathrm{mol/cm^2}$) of coverage at ~370 °C. At such low coverages, the interaction between two oxygen-induced species is negligible. At temperatures below 370 °C, almost all reacted sites are bright right after adsorption. We note that bright sites usually appear significantly brighter than Si adatoms at negative sample biases, but at positive biases they appear only slightly brighter or as bright, depending on the tip condition. Thus, we often use negative biases to identify the positions of bright sites. In this study, we consider only those bright species that appear after the exposure, for there are a few other kinds of surface defects which also appear bright. To study the dynamic behavior of bright sites, a large number of successive STM images are acquired. The time intervals between two successive STM images are chosen to be short enough to observe these dynamic processes clearly. Our room temperature results agree with previous STM works, so we present only the high-temperature results.

Figure 1 shows four STM images of the site hopping for a bright site at 350 °C, taken at a sample bias of −2 V and a tunneling current of 0.1 nA. These images are chosen from a sequence of successive STM images with a time interval of 2.4 s. In a faulted half of 7 × 7 [the

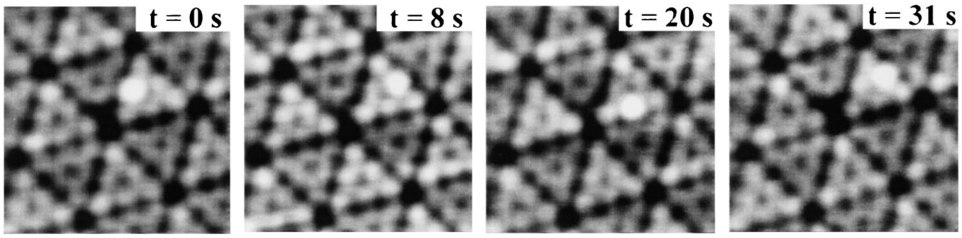

FIG. 1. Four 65 Å × 65 Å STM images showing site hoppings at 350 °C.

schematic for a Si(111)-(7 × 7) unit cell is shown in Fig. 2, which is the dimer-adatom-stacking fault (DAS) model proposed by Takayanagi *et al.* [29]], a bright site can be seen and it hops from a center site to an adjacent center site in these images. We trace the motion of bright sites for tens of minutes or hours and measure the hopping rate from 300 to 365 °C. In this temperature range, almost all the hops are to a neighboring adatom site and are confined within one-half of 7 × 7. Only a few jumps extending to an adjacent half of 7 × 7 are observed at temperatures below 365 °C. We find that bright sites have a higher probability of occupying the center site than the corner site, and most of the jumps are between two neighboring center sites. An Arrhenius plot for the hopping between two adjacent center sites in the faulted half of 7 × 7 is shown in Fig. 3. From the plot, the activation energy is found to be 2.04 ± 0.04 eV and the frequency factor is 10^{15} s^{-1}. In Table I, we list the activation energies and frequency factors obtained for different site hopping paths. The effect of the tip is checked by measuring the hopping rate at three different scan speeds: 2.4, and 4.6, and 9.2 s. The effect is nearly undetectable at 350 °C and less than 10% at 330 °C; or negligible to the determination of activation energies.

To observe how bright sites hop between adjacent adatom sites, we lower the substrate temperature to 300 °C or lower, when bright sites are less mobile (usually stay for over 5 minutes without hopping). Fast scanning of the surface reveals the existence of intermediate states during the hopping. Figure 4 shows four STM images of a hopping from a center site to its neighboring corner site at 300 °C, taken at a sample bias of -1 V. These four images are also chosen from a sequence of consecutive STM images taken at a time interval of 2.4 s. In Fig. 4(a) a bright site can be seen in the 7 × 7 unit cell outlined. Later, the bright site is displaced to the upper left side slightly and the brightness is also reduced somewhat [Fig. 4(b)]. This state remains until $t = 29$ s, when the structure changes again to that shown in Fig. 4(c). In Fig. 4(d), the bright site appears at a corner site, which completes a site hopping. From a careful observation of the intermediate states in Figs. 4(b) and 4(c), we find that the intermediate species are centered around an H_3 site (threefold hollow site), which is located between an adatom and an adjacent rest atom site which both originally have a dangling bond before adsorption (see Fig. 2).

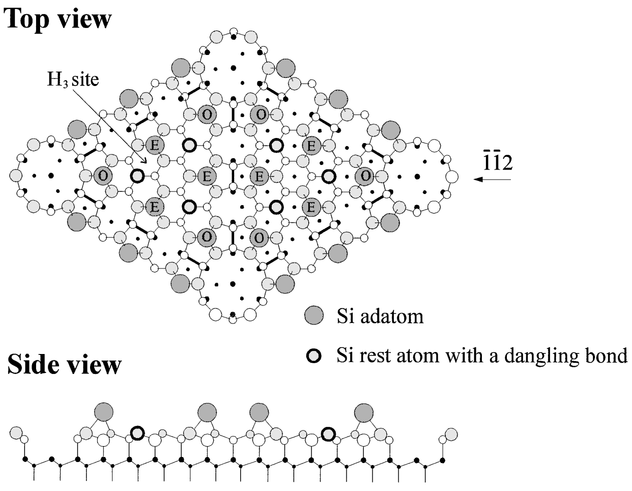

FIG. 2. The DAS lattice for Si(111)-(7 × 7). It consists of a faulted and an unfaulted half-cell. Each half has six adatoms. Three of them occupy the corner sites (indicated by an "O" in the figure), and the other three occupy the center sites (indicated by an "E"). Four inequivalent adatom sites are referred to as faulted corner (FO), faulted center (FE), unfaulted corner (UO), and unfaulted center (UE) sites, respectively. There are 19 dangling bonds in total for each 7 × 7 unit cell: 12 for adatoms, 6 for rest atoms, and 1 inside the corner hole. An H_3 site is also indicated, which is located between an adatom and an adjacent rest atom with a dangling bond.

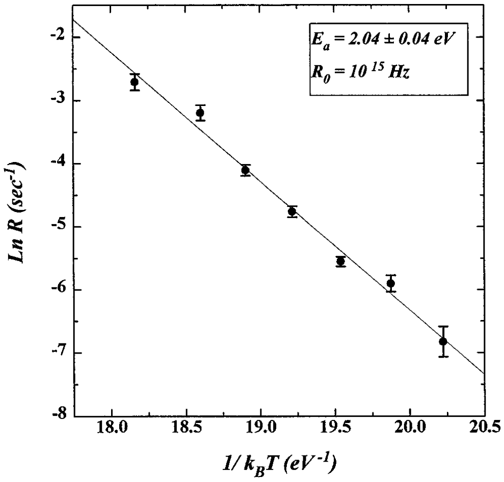

FIG. 3. Arrhenius plot for the site hopping from a center site to an adjacent center site in the faulted half.

TABLE I. Parameters for site hopping of O_2 on Si(111)-(7 × 7).

Hopping	Activation energy	Frequency factors
FE to FE	2.04 ± 0.04 eV	$10^{15.0}$ s^{-1}
FE to FO	2.29 ± 0.06 eV	$10^{16.2}$ s^{-1}
FO to FE	2.13 ± 0.11 eV	$10^{15.6}$ s^{-1}
UE to UE	2.16 ± 0.04 eV	$10^{15.9}$ s^{-1}
UE to UO	2.01 ± 0.10 eV	$10^{14.6}$ s^{-1}
UO to UE	1.96 ± 0.13 eV	$10^{14.1}$ s^{-1}

In order to explain how a bright site hops between two neighboring adatom sites in Fig. 4, we propose the pathway "$B_i \longrightarrow I_i^* \longrightarrow I_f^* \longrightarrow B_f$," as depicted in Fig. 5. The configurations B_i, I_i^*, I_f^*, and B_f correspond to Figs. 4(a), 4(b), 4(c), and 4(d), respectively. The atomic geometry for the B_i state is basically the para-paul hybrid proposed by Schubert *et al.* [18]. (Note, the para, paul, and grif configurations are basically the same if thermal vibration is taken into account, i.e., the bond angle and bond length are less defined at high temperatures.) For the intermediate states, one possible geometry is the bridge configuration [18], 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 the image spot centered around an H_3 site. At high temperatures, the O_2 molecule of the B_i state should have a high vibrational amplitude, considering the single Si-O bond in the para-paul configuration, and thus has a probability to interact with the dangling bond of a neighboring rest atom. After the O_2 molecule bonds with the other end to the rest atom and forms the bridge geometry (I_i^*) temporarily, it may return back to the stable B_i state again by breaking the bond with the rest atom. However, it also has a smaller chance to flip over to bond with a neighboring Si adatom, which also forms a bridge configuration (I_f^*). Sooner or later, this bridge configuration will probably change to the more stable B_f state and complete the site hopping.

In the STM images, the intermediate (I^*) states always appear to be centered around an H_3 site at tunneling biases of ±2 V and ±1 V. We think what is observed for the intermediate species is an O_2 molecule in the bridge configuration. The Si adatom bonded to the molecule is not visible due to saturation of its dangling bond. For negative sample biases, the I^* states are slightly brighter or as bright as Si adatoms, depending on the tip, but not as bright as bright sites. At positive biases, the I^* states appear somewhat darker than Si adatoms. We have observed the I^*-mediated site hopping for the cases of center-center, center-corner, and corner-center hoppings. We note that, most of the time, the site hopping is not successful and the pathway is usually "$B_i \longrightarrow I_i^* \longrightarrow B_i$." This suggests that the barrier height for "$I_i^* \longrightarrow I_f^*$" transition is higher than that for "$I_i^* \longrightarrow B_i$." This is consistent with our quantitative measurements, which show that the barrier height for the transition from an I_i^* state associated with a faulted center adatom to an I_f^* state associated with a neighboring center adatom is ~2.03 eV and that for the transition back to its B_i state is ~1.63 eV. Detailed statistics pertaining to the activation energies will be presented elsewhere.

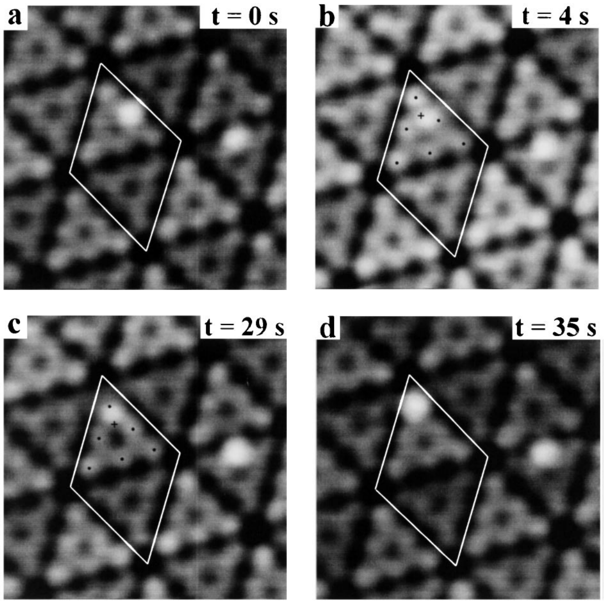

FIG. 4. Four 80 Å × 80 Å STM images showing the detailed mechanism of a site hopping from a center site to a corner site, taken at 300 °C and a sample bias of −1 V. In (b) and (c), each adatom position in the faulted half of the 7 × 7 unit cell outlined is marked with a "·" and a rest atom position is marked with a "+." It is clear to see that the intermediate species are located between an adatom and the rest atom sites. [(a)–(d) For complete details, see text].

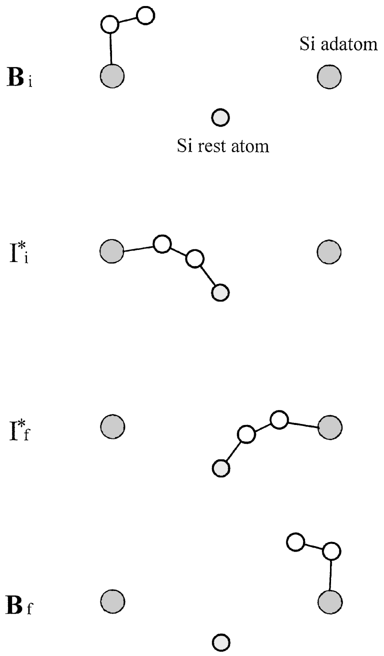

FIG. 5. The model for the site hopping.

The intermediate species we have found here may be the second molecular state reported recently by Comtet *et al.* using UPS measurements [22,23]. This state dominates for low exposure ($\sim$0.03 L) at low temperatures (30–60 K) [23]. For room temperature exposure, its characteristic peak (5.1 eV) reduces significantly, but it can still be detected from 0.1 L to 10 L [22]. After exposuring Si(111)-(7×7) to $\sim$0.2 L of O_2 at room temperature, we do observe a very small concentration of new species which appear very similar to the intermediate species we have discussed above. In addition, the bridge configuration proposed here is consistent with a UPS results measured at 30 K, which show the reduction of both the S_1 (related to adatom dangling bonds) and S_2 states (related to rest atom dangling bonds) simultaneously after exposure [23].

Previous experimental measurements of surface migration are for metal atoms on metallic surfaces, metal atoms on semiconductor surfaces, or semiconductor atoms on semiconductor surfaces [30]. No quantitative study of diffusion of single molecules on solid surfaces has been reported. O_2/Si(111)-(7×7) definitely provides a very interesting system for the study of chemisorbed molecules on semiconductor surfaces. It is clear that the pathway of site hopping in this kind of system strongly depends on the configuration of dangling bonds at the surface as well as the chemical bonding of the molecule.

We would like to point out three things here. First, the model proposed in Fig. 5 explains well the STM observations, but it may not be unique. Second, the frequency factors listed in Table I are very high (1 to 3 orders of magnitude larger than 10^{13} s^{-1}, the value reported for 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. Third, the parameters listed in Table I exhibit an interesting correlation: a large activation energy accompanied by a large frequency factor. This may be related to the so-called "compensation effect" [31]. To conclude, this work demonstrates the ability of variable-temperature STM in the study of surface chemistry.

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