

Observation of single oxygen atoms decomposed from water molecules on a Si(111)- 7×7 surfaceRong-Li Lo,¹ Chun-Ming Chang,² Ing-Shouh Hwang,^{1,3} and Tien T. Tsong³¹*Department of Physics, National Tsing-Hua University, Hsinchu 300, Taiwan, Republic of China*²*Department of Physics, National Dong Hwa University, Hualien, 974, Taiwan, Republic of China*³*Institute of Physics, Academia Sinica, Nankang 115, Taipei, Taiwan, Republic of China*

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Understanding the behavior and energetics of oxygen atoms on the silicon surface is important, and therefore water molecules dissociatively adsorbed on the Si(111)- 7×7 surface were studied. At elevated temperatures, complete decomposition of a water molecule into two hydrogen atoms and one oxygen atom was directly observed by scanning tunneling microscopy. The methodology employed in this study provided an opportunity to examine the dynamic behavior of single oxygen atoms. We found that an oxygen atom has at least four bonding states between 290 and 340 °C. The majority state appeared as an intensely bright spot located at an adatom site. At room temperature, this state can also be formed by stimulation of tunneling electrons at a water-reacted site. The hopping barriers between equivalent surface sites were determined from Arrhenius plots to be in the range of 1.8–2.0 eV, indicating that the diffusion barrier for oxygen atoms into the bulk of Si(111) was higher than 2.0 eV.

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I. INTRODUCTION

Oxidation of silicon is one of the most important processes in the modern microelectronic industry. Under the continuous demand of large-capacity integrated circuits, the thickness of the insulating silicon oxide layer is reduced to nearly 2 nm today.¹ The thickness of the silicon oxide layer is predicted to reach its limit of five-silicon-atom thickness by 2012.² The silicon oxide layer will lose its insulating property due to quantum tunneling when its thickness reaches the limitation. Presently, silicon oxide layers suffer from imperfect structure that degrades their quality. In order to promote the quality, improvement of the fabrication technologies of silicon oxide is needed.

Although silicon oxidation is a well-known reaction process, the earliest stages of oxidation are not well understood. These stages are vital for the formation of silicon oxide that follows. The generation and inward diffusion of surface oxygen atoms are necessary for the initial stage of oxide layer formation. On the Si(111)- 7×7 surface (thereafter 7×7 surface), the adsorption of O₂ molecules, which precedes the further reactions to form an oxide, remains controversial in both theory and experiment.³ The question of whether O₂ is dissociative or molecularly adsorbed on the 7×7 surface may be resolved by understanding the behavior and energetics of oxygen atoms on this surface. For the purpose of this study, single oxygen atoms were produced on the 7×7 surface by the full decomposition of water molecules above 290 °C. Using a variable-temperature scanning tunneling microscope (STM), we have succeeded in observing single O atoms hopping on the surface. Not only the image contrast, but also the dynamic behavior of adsorption states of an O atom was studied and presented in detail for the first time.

II. EXPERIMENT

Most of the experimental procedures and the commercial variable-temperature STM employed in this study have al-

ready been described in our previous publications.^{4–6} Water vapor was introduced into the STM chamber via a leak valve to a pressure in the range of 10⁻¹⁰ mbar. During an exposure of water, the ion gauge was turned off to prevent a possible decomposition of water molecules by the hot filament. Before being used in an STM experiment, the electrochemically etched tungsten tip was heat treated in an ultrahigh vacuum such that the oxide layer on tip surface could be removed effectively. The STM image resolution primarily depends on the structure of the tip apex. Negative sample voltage pulses, 4–6 V and hundreds of ms, were applied to carry out changes of tip apex on a clean surface to obtain a high-resolution tip.

III. 7×7 SURFACE AND PREVIOUS RESULTS

Figure 1(a) shows the widely accepted dimer-adatom-stacking (DAS) fault model of the Si(111)- 7×7 unit cell.⁷ In a 7×7 unit cell, there are 19 unsaturated Si bonds, 12 associated with the topmost adatoms, 6 with the rest atoms, and 1 with the corner hole. These unsaturated bonds are the most active sites for further chemical reaction and bond formation with foreign atoms or molecules. Depending on the tunneling direction of electrons, two types of STM images may be acquired. Figures 1(b) and 1(c) are the unoccupied state image (USI) and the occupied state image (OSI) for the 7×7 surface, respectively. Adatoms can be separately resolved in the USI's. In contrast, adatoms usually cannot be completely separated in the OSI's due to the emergence of a rest atom in the middle of three neighboring adatoms. The visibility of the rest atoms is tip dependent. Thus, this can be used as a criterion for a “good” STM tip on 7×7 surfaces, especially when an observation of reaction at a rest atom is needed.

We have studied the dynamic behavior of the H atom in detail earlier.⁵ An H atom is found to adsorb preferentially at the rest atom site, and the adsorption results in a dark rest atom surrounded by three neighboring unreacted and protruded adatoms, as shown in Fig. 2. These subtle changes

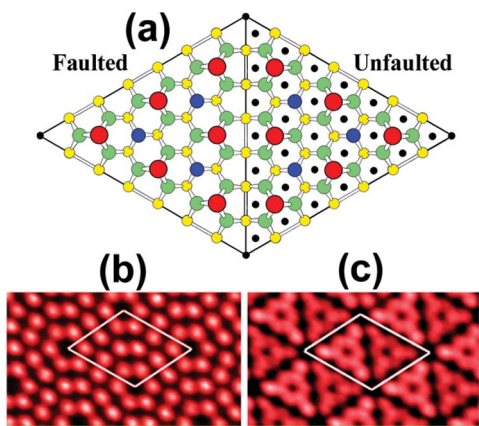


FIG. 1. (Color online) (a) is the DAS model of the Si(111)- 7×7 surface. Two triangular subcells, faulted and unfaulted halves, comprise the unit cell. The topmost 12 Si atoms (red) are adatoms. Those adatoms next to the corners of half-cell are corner adatoms. The others are center adatoms. Each adatom has two types of back bond. In the middle of three adatoms is a rest atom (blue). (b) and (c) are STM unoccupied (electrons tunnel into sample) and occupied (electrons tunnel out of sample) state STM images, respectively. A 7×7 unit cell is sketched.

due to H adsorption are revealed in the OSI's by a "good" tip. When an adsorbed H atom hopped among rest atom sites or across the cell boundary (not shown in the figure), it was like the jumps of a Si cluster of three neighboring adatoms.

IV. RESULTS

In this section, we first present the complete dissociation of water molecules, followed by the hopping of single O atoms on 7×7 surfaces. Then, we show that single O atoms can also be produced at room temperature (RT) by means of bombardment of STM tunneling electrons at water-reacted sites.

A. Complete dissociative adsorption of the water molecule at high temperatures

Typical adsorption and dissociation of the water molecule are shown in Figs. 3 and 4. Initially, we exposed the hot 7×7 surface to a very small amount of water vapor so that only a few new defects were found in an area of tens of 7

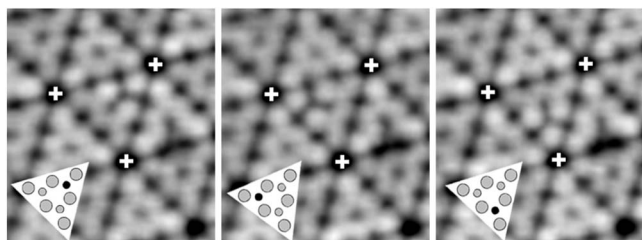


FIG. 2. Adsorption and hopping of H atom at 330°C . The half where the H atom stays is surrounded by three "+" symbols and a schematic diagram at the lower-left corner indicates the adsorption site.

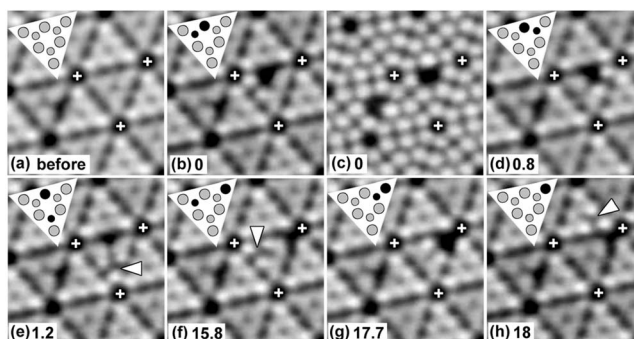


FIG. 3. Adsorption of water molecule on the 7×7 surface at 340°C . The reacted half is enclosed by three "+" symbols and drawn schematically at the upper-left hand corner. Gray (black) circles represent the nonreacted (reacted) atoms. The time unit in the image is min. (a) A clean 7×7 surface with an immobile dark adatom as landmark. (b) and (c) are the OSI and the USI, respectively, taken right after the water dose. The reaction involves a center adatom site and an H-adsorbed rest atom site. The species adsorbed at adatom changes its position to corner adatom in (f). The H atom hops among rest atom sites [(b)-(g)] and eventually jumps out of the reacted half in (h). The H atom not next to a dark adatom site is indicated by a white arrow.

$\times 7$ unit cells. Figure 3(a) shows an area before exposure with a fixed dark defect serving as a landmark. After exposure to one dose, a new defect appeared in the unfaulted half enclosed by three "+," as shown in Fig. 3(b). The reaction involved two sites: a dark adatom site and a dark rest atom site. However, in the simultaneously acquired USI [Fig. 3(c)], the water-reacted site appeared only as a dark adatom site. The dark rest atom site is the result of the adsorption of an H atom, because its STM images and dynamic behavior are identical to that previously observed for H atom adsorption.⁵ The H atom hopped around inside the unfaulted

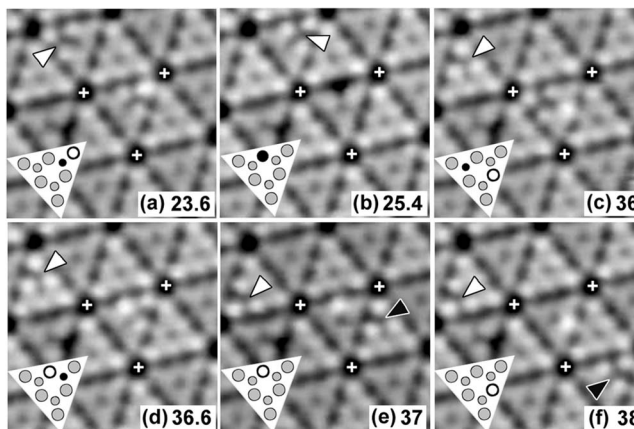


FIG. 4. (Fig. 3 continued) The O-adsorbed adatom site is depicted by a white circle in the schematic diagram. (a) The dark reacted corner adatom site turns into a bright O-adsorbed adatom site and an adjacent H-adsorbed rest atom. Later, they change back into a dark reacted center adatom site in (b). The process repeats, until the H atom jumps out of the reacted half (e). The second liberated H atom is indicated by a black arrow in (e) and (f). Image conditions: tunneling current 0.1 nA and bias voltage 1.8 V.

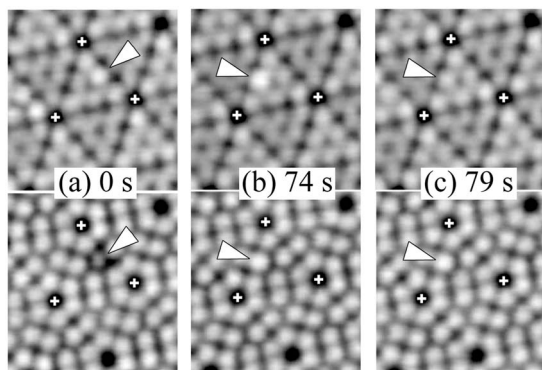


FIG. 5. Adsorption states of single O atom at 340 °C. The upper and lower figures are the OSI (voltage: 2.0 V) and the USI (voltage: 1.7 V) taken at the same time with tunneling current 0.1 nA, respectively. The adsorbed sites are indicated with arrows. These images are taken under the same tip conditions.

half and later jumped across the cell boundary upward to an adjacent faulted half as shown in Figs. 3(d)–3(h).

In addition to the hopping H atom, the dark reacted adatom site was also observed to change position at a slower rate, as shown in Figs. 3(e) and 3(f). Furthermore, it switched into an intensely bright adatom and a neighboring dark rest atom site [Fig. 4(a)] and recovered at another site [Fig. 4(b)]. We noted that the dark reacted adatom site has a longer mean residence time at the corner adatom site than at the center adatom site. The dark rest atom produced in the switching was identified to be the result of the adsorption of the H atom. During the observation period, the intensely bright adatom site did not turn into two or more reacted sites, and it might combine with a wandering H atom to form a dark adatom site. Obviously, the intensely bright adatom site was due to the adsorption of an O atom, and the dark reacted adatom site in Fig. 3 was due to the adsorption of an O atom and an H atom. Figures 3(h)–4(b) show the motion of the dark reacted adatom site. At the beginning, it separated into an H and an O atom, both mobile on the surface, and these two atoms then hopped to a new position simultaneously to form a dark adatom site. The process stopped once the H atom hopped across the cell boundary, leaving the O atom behind. Thus, the dynamic behavior of a single O atom on a clean surface can be studied in detail, as shown in the subsequent section.

B. Mobility and adsorption states of single O atoms

During most of the observation period, an O-adsorbed site simply appeared as an intensely bright spot in the OSI's, as shown in Figs. 4(e) and 4(f). However, when the USI's were carefully inspected, the adsorption seemed complex. At least four adsorption states were observed between 290 and 340 °C. Figure 5(b) displays the majority state that appeared with the highest probability.⁸ It was defined in this study as a bright state (B state) because it appeared as a bright adatom in both types of STM images. The B state stayed preferentially at a center adatom site as opposed to a corner adatom site, with a probability ratio of 3.2 ± 0.4 . Figure 5(a) shows another state that appeared as a bright adatom in the OSI's

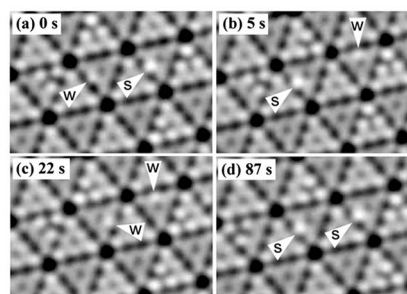


FIG. 6. Brightness alternation of substates B_s and B_w at 340 °C. B_s and B_w are both located at the center adatom site and are indicated by white and black arrows, respectively. Image conditions: tunneling current 0.1 nA and bias voltage 1.9 V.

and as a weak and tiny spot at the adatom site in the USI's. This spot was found to become completely dark for some tips. The third state [Fig. 5(c)] appeared similar to the B state in the USI's; however, in the OSI's, its appearance was indistinguishable from the normal Si adatoms. This state had unique properties. It did not combine with a nearby H atom to form a dark adatom site, and its typical residence time was 3 times longer than the B state. The probability ratio of the B state to the state of Figs. 5(a) and 5(c) was approximately 20 and 6 at 330 °C, respectively. The fourth state, believed to be a subsurface state, was not observed in both types of images. Such a subsurface state might last for tens of minutes and reappear as a B state usually in the same half. In addition, the subsurface state appeared more frequently at higher temperatures.

With a careful inspection of the B state, its brightness was found to change from a strong bright spot (B_s state) to a weak bright spot (B_w state) and vice versa at the same site. Figure 6 demonstrates such spontaneous brightness switches of these two states located at an unfaulted center adatom site. At the unfaulted center adatom site, the B_s state showed up with a slightly higher probability, a ratio 1.2, greater than the B_w state at 290 °C. These two substates characterized the predominant state (B state) of single-O-atom adsorption.

O-adsorbed species usually hopped within a half cell, as shown in Figs. 4(e), 4(f), 5, and 6. Using the same procedure from our previous works,^{4,5} average dwelling times of hopping species over a site were obtained at several temperatures. With Arrhenius plots, the hopping parameters for the B state between center adatom sites can be determined, as shown in Fig. 7. The activation energy and preexponential factor for hopping in the faulted half were 1.8 ± 0.1 eV and $10^{13.9 \pm 0.5}$ Hz, respectively, and 2.0 ± 0.1 eV and $10^{15.3 \pm 1.0}$ Hz in the unfaulted half, respectively.⁶

C. Tunneling electron stimulation at water-reacted sites

The B state can also be formed at RT by using STM tunneling electrons to stimulate the water-reacted site, as shown in Fig. 8. After scanning a water-dosed area [Fig. 8(b)] with a sample bias of 3.5 V, a contrast inversion was observed at the dark adatom sites formed by water exposure [Fig. 8(c)]. In the OSI's the brightness of a contrast-reversed adatom site was intense, but showed the same contrast as or

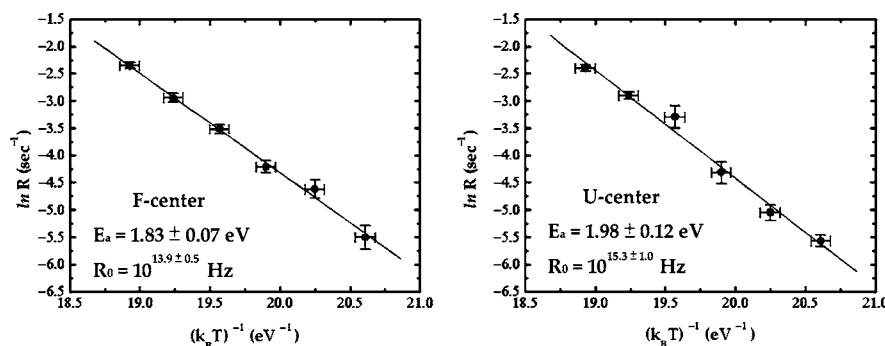


FIG. 7. Arrhenius plots of O atom hopping between center adatom sites at temperatures ranging from 290 to 340 °C.

slightly brighter than an unreacted Si adatom in the USI's. Based on a comparison to Fig. 4(a), the high-bias induced bright spots were determined to be the bonding state of single O atoms. However, the dark-to-bright inversion did not occur on every water-reacted adatom site. In our observation, among the 395 dark reacted sites, 238 sites (60.3%) transformed into bright sites. The unchanged dark reacted sites were probably due to adsorption of a different species because they did not change even after many times of scanning with a sample bias of 3.5 V.

Moreover, the high-bias scanning might result in a new dark adatom or rest atom site that appeared nearby the contrast-reversed site. The newly formed dark adatom site, indicated by an arrow in Fig. 8(c), was due to the adsorption of an ejected H atom and thus appeared as a dark adatom site in both types of STM images.⁵

V. DISCUSSION

Because it is difficult to distinguish between different species of adsorbed particles from STM image contrast, a method to distinguish adsorbed particles from their dynamic behavior was proposed.^{4,5,9,10} On the 7×7 surface, the dynamic behavior of O₂ molecules and H atoms was well characterized in our previous studies.^{4,5} The objectives of this study were to investigate the adsorptions of water molecule, single O atoms, and their adsorption configurations.

A. Structure of the dark site induced by reaction with water

The initial reaction between water and Si(100)- 2×1 and Si(111)- 7×7 surfaces has been investigated by many

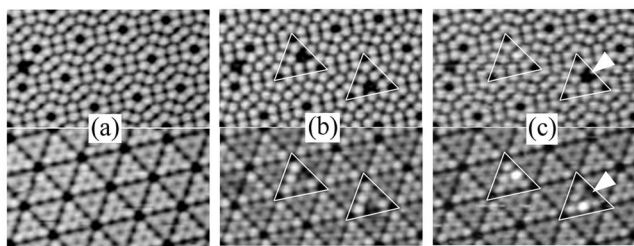


FIG. 8. STM electron-stimulated reaction at RT. The upper and lower figures are the USI (voltage: 1.5 V, 0.2 nA) and the OSI (voltage: 1.0 V, 0.2 nA), respectively. (a) is the area before dosing with water. Two reacted halves are enclosed by triangles in (b). After scanning the area of (b) with sample bias 3.5 V, contrast inversion occurs at the dark adatom sites shown in (c). One of the ejected H atoms readsorbs at an adatom site (pointed at by an arrow in the right half).

researchers.^{11–17} A water molecule is dissociatively adsorbed on the surface to form Si-OH and Si-H species at and below RT.^{11–17} Further decomposition of Si-OH to form Si-O-Si and Si-H was reported to occur at RT^{14,15} and progressively above 500 K.^{6,11,16} These results suggest that the structure of Si-O-Si together with Si-H is more stable than Si-OH, though the latter species dominates at and below RT probably due to an activation barrier for a transition into the former. Our *ab initio* calculation using a model of Si(111)- 7×7 also confirmed that the structure of H-Si_{ad}-O-Si_{back} had an energy level lower than H-O-Si_{ad} by 0.89 eV, where Si_{ad} and Si_{back} represent the Si adatom and back bond atom, respectively. Nevertheless, for the transition to H-Si_{ad}-O-Si_{back}, H-O-Si_{ad} had to surmount an energy barrier of 1.5 eV.

According to the results of contrast inversion, at least two species were adsorbed at the water-reacted adatom site at RT because they responded differently to the high-bias scanning of 3.5 V. Different responses to a high-bias scanning between water-reacted dark adatom sites at RT have also been reported previously.¹⁸ As shown in Fig. 8, the dark adatom sites should be at a higher energy level because they switched contrast when excited by 3.5-eV electrons. Based on previous conclusions and our calculation, this state was proposed to be H-O-Si_{ad}, which became a stable O adsorption state after the H-O bond was broken. The dark adatom site that remained unchanged under 3.5 V scanning was likely to be an H-adsorbed site or a configuration H-Si_{ad}-O-Si_{back}, because the H-adsorbed adatom [Fig. 8(c)] indeed remained unchanged after 3.5 V scanning. The results implied that when a H₂O molecule approaches the 7×7 surface and undergoes a dissociation process, the scission probability of the O-H bond near the rest atom side (which formed H-O-Si_{ad} and H-Si_{ad}-O-Si_{back}) was larger than 60%. This inference was consistent with the calculation that rest atoms are more active than adatoms in the dissociation of a lone-pair electron donor molecule.¹⁹ Although the H-O-Si_{ad} is dominant at RT adsorption, the lower-energy state H-Si_{ad}-O-Si_{back} prevails at high temperatures.⁶ Thus, the water-reacted dark adatom site observed in Figs. 3(b)–3(h) and 4(b) was the structure H-Si_{ad}-O-Si_{back}, and its position-change was ascribed to the encounter of an H atom with an O atom at a same adatom site.

B. Adsorption states of single O atoms at high temperatures

When an O atom bonds with Si atoms on the 7×7 surface, insertion of O atom into a Si adatom back bond—i.e., a

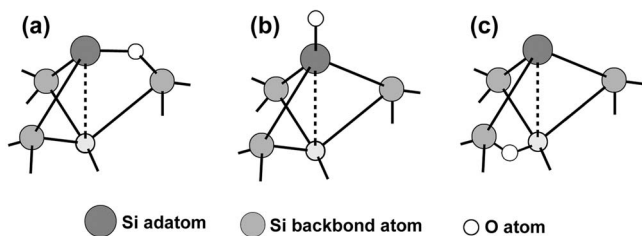


FIG. 9. Atomic models of O states. The B states (a) and (c) possess an insertion configuration, and (b) is the “ad” state.

structure of $\text{Si}_{\text{back}}\text{-O-Si}_{\text{ad}}$ (“ins” state hereafter)—is concluded to be the most stable state in both experimental and theoretical studies.^{11,12,14,20–23} Reference 18 also showed that electronic states populate in the neighborhood of Fermi level of the “ins” state, which would lead to a bright spot in both types of STM images. Among the adsorption states of single O atoms described in Fig. 5, the B state was the best candidate for the “ins” state due to its high appearing probability and its bright appearance. On the other hand, the O-reacted dark adatom site in the USI’s is proposed to be an O atom adsorbed on top of a Si adatom (“ad” state hereafter) no matter whether there are O-inserted adatom back bonds or not.^{21,24} Among the O states, only Fig. 5(a) possessed the dark feature in the USI’s. Because of its lower appearance probability and short dwelling time, the state of Fig. 5(a) should situate at a higher-energy level and have a lower-energy barrier for an O atom to escape than the “ins” state did. From the calculation of density functional theory with a cluster model, Ref. 22 showed an energy barrier 0.05 eV for the “ad” state to transfer to the “ins” state and about 0.7 eV for the opposite transferring direction. Also, the adsorption energy of the “ad” state was calculated to be higher than that of the “ins” state by 1.32 eV.²³ Our observation of the state of Fig. 5(a) was qualitatively consistent with the theoretical results of the “ad” state.

The state of Fig. 5(c) might keep the Si-O-Si structure, but located at the next deeper layer such that it did not affect the surface adsorption of H atoms. The subsurface state was thought to be situated deeper than the state of Fig. 5(c), so that it had no observable features. The state of Fig. 5(c) and the subsurface state showed that single O atoms could diffuse inward to the region beneath the surface. However, the disappearance of O-induced species was rarely observed. This suggests that the O atoms generated on the surface favored the sites at or near the surface rather than the sites in the bulk in the studied temperatures. Hoshino and Nishioka²² estimate the energy barrier for inward diffusion of O atoms to be 1.6 eV. Nevertheless, our results indicated that O atoms should have an inward diffusion barrier higher than the surface hopping barrier 2.0 eV. Thus, we proposed the atomic models for the B state (the “ins” state) in Fig. 9(a), the state of Fig. 5(a) (the “ad” state) in Fig. 9(b), and a possible configuration of the state of Fig. 5(c) in Fig. 9(c).

The origin of substates B_w and B_s of the “ins” state is demonstrated in Fig. 1(a), as each adatom has two types of back bonds according to their bonding environment. Among the three back bonds of center adatom, one is toward the inner and two are toward the outer unit cell (bonding with a

Si dimer). The B_w and B_s states shown in Fig. 6 are expected to be formed by O insertion into different kinds of back bonds. Combining the statistical results from the STM observation with the calculation, the assignment of these two substates to different back bonds was determined as follows. The energy difference between B_w and B_s states at the center adatom site $E_w - E_s$ was obtained from the Boltzmann factor: $P_s/P_w = f \exp[(E_w - E_s)/k_B T]$, where P is the appearing probability, f the statistical factor, and k_B and T Boltzmann’s constant and temperature, respectively. The statistical factor f designates the locations of B_w and B_s . We obtained $E_w - E_s = -0.02$ and 0.04 eV when f was 2 (B_s locates at the outer back bond) and 1/2 (B_s locates at the inner back bond) at 290 °C, respectively. These results were compared with our density functional calculations by using the VASP code²⁵ within local-density approximation.²⁶ The oxygen adatom is added on the surface of the 7×7 DAS supercell. Our calculation yielded $E_{\text{outer}} - E_{\text{inner}} = -0.014$ eV, where E_{outer} and E_{inner} are the adsorption energies when single O atom inserts into outer and inner center adatom back bond, respectively. Thus, B_s was a consequence of O insertion into the outer back bond and B_w into the inner back bond.

VI. CONCLUSION

When water molecules were entirely dissociated on a Si(111)- 7×7 surface above 290 °C, surface H and O atoms were produced. Their appearances, adsorption sites, hopping rates, and diffusion characteristics were clearly identified. H atoms preferred to adsorb at rest atom sites as reported before. Single O atoms possessed at least four adsorption states. We proposed two bonding structures, the O- Si_{ad} (“ad” state) and the insertion configuration Si-O-Si, for the states. The brightness in STM images and appearing probability of an insertion configuration were inversely proportional to its depth. The topmost insertion configuration $\text{Si}_{\text{ad}}\text{-O-Si}_{\text{back}}$ (“ins” state) was the predominant adsorption state. The “ad” state had a shorter site-resided time compared to the insertion structures at the near surface. From Arrhenius plots, the surface hopping barriers of O atoms were determined to be close to 2.0 eV, indicating that an O atom had an inward diffusion barrier higher than that value. We also showed that the “ins” state was possible to be created at RT via the scission of an O-H bond by the stimulation of STM tunneling electrons.

Studies of the dynamic behavior of single atoms, such as H and O atoms, are fundamental and important because not only the dominant states can be observed, but some intermediate states can also be revealed. These states may play key roles in complicated chemical reactions and may help scientists to identify the reaction pathway of other reactants. For example, like water molecules, the adsorption of ammonia molecules on the 7×7 surface is believed to be dissociative. However, the dissociation process and the bonding configurations of the decomposed products are not yet consistent.²⁷ These questions could be clarified if the dynamic behavior of NH_x (x from 0 to 2) species is carefully studied as we have done here for H_2O .

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