

Symmetry breaking and Si-based molecular flip-flop motion

Jinwoo Lee, Jinhee Park, Woojin Jung, and In-Whan Lyo*

Department of Physics, Yonsei University, Seoul, Republic of Korea

(Received 9 June 2011; published 13 September 2011)

We report on molecular binary switching by oxidation products on Si(111)-(7×7) surfaces. By using scanning tunneling microscopy, we show that the oscillator consists of a triad of center adatoms in the half-unit cell of a Si(111)-(7×7) surface. With two adatoms oxidated, each adatom of the triad plays a unique role. Two adatoms construct two mutually exclusive, flip-flopping bistable structures and the other a stationary structure that stabilizes the triad. Time series data of the flip-flop motion exhibits the Arrhenius behavior with the barrier height of about 0.7 eV. Decomposed triads show that a thermally activated mobile species, attributed to a molecular precursor, drives the flip-flop motion. The triad provides a novel example in which a symmetry breaking charge transfer provides the collective stability to the structure, and at the same time sheds new light on oxidation processes on silicon surfaces.

DOI: [10.1103/PhysRevB.84.115305](https://doi.org/10.1103/PhysRevB.84.115305)

PACS number(s): 68.37.Ef, 81.65.Mq, 68.43.Bc, 68.43.Fg

I. INTRODUCTION

The existence of easily produced, atomically uniform and stable oxide of silicon had been one of the key ingredients in the phenomenal success of Si-based devices. Motivated by the technological importance of a few nanometer-thick dielectric layers in semiconductor devices, an atomistic understanding of silicon oxidation has been a topic of experimental and theoretical investigations over the last three decades. In particular, the Si(111)-(7×7) surface has long served as a prototypical system to gain understanding on the initial stage of Si oxidation, partly because of the limited number of oxidation pathways on the surface.^{1–16}

Upon adsorption on a Si(111)-(7×7) surface, oxygen may bond in a molecular form, or dissociate and bond to a Si adatom in a few different configurations as shown in Fig. 1. Here we use the notation *paul* to denote any configurations in which oxygen chemisorbs to a Si adatom in the form of a molecular precursor. When an oxygen molecule dissociates and reacts with silicon, there exist three different kinds of bonding positions available to an oxygen atom. An oxygen atom may bond to a Si adatom in the on-top position, or may insert itself in one of the three back-bonds of the adatom. Or it may be in the subsurface position in which an oxygen atom bonds to the first- and second-layer Si atoms.^{1,9} We will refer to these three atomic oxygen bonding positions as *ad*, *ins*, and *tri* states, respectively as shown in Fig. 1.

While it has been generally accepted that the initial oxidation of Si(111)-7×7 follows a second-order reaction kinetics, the detail of oxidation processes are still a subject of many debates. One of the controversies is the existence of molecular precursors at the secondary reaction process in which an oxygen molecule chemisorbs on preoxidated Si adatoms in the form shown in Figs. 1(b) and 1(c). The possibility of molecular precursors was ruled out theoretically by density functional theory (DFT) calculations⁵ and experimentally by Cs⁺ reactive scattering measurements¹⁷ as well as electron energy loss spectroscopy (EELS),¹⁸ which found no evidence of O₂ molecules on this surface. On the other hand, the existence of a molecular form of oxygen had been also advanced by scanning tunneling microscopy (STM)^{8,16} and x-ray photoelectron spectroscopy (XPS),^{6,10,19} based on the

evidence of the weakly binding species that desorbs under high bias stress or O 1s core levels that exhibits a finite lifetime.

Lacking in these studies is the consideration of the intermolecular interactions among oxidation products as well as the substrate. As oxygen is the most electronegative element but fluorine, strong charge redistribution is expected among silicon and the oxidation products, which may then drastically modify their physical properties. In fact, a large charge transfer had been theoretically predicted between the rest atoms of the Si(111)-(7×7) surface and the oxidation products.^{1,9} However, no systematic study to investigate the effect has been presented so far.

In this work we report on an oxidation-induced molecular oscillator sustained by the strong intermolecular interactions on the Si surface, and the accompanied collective switching phenomena. By analyzing the dynamics as well as the associated behaviors of the oscillator during the operation and after the collective breakdown, we propose the structure of the oscillator including that of the mobile species. Our work shows that symmetry-breaking charge transfer in the molecular oscillator is the key factor to the surprising thermal stability of the complex that consists of metastable species.

II. EXPERIMENTS

The experiments were performed in a ultra high vacuum (UHV) chamber (3×10^{-11} mb) by using an Omicron variable temperature scanning tunneling microscope (VT-STM) equipped with home-built software and electronics. Clean Si(111)-(7×7) surfaces were prepared from *n*-type P-doped silicon wafers with a resistivity of 0.7 to 1.3 Ω cm. In the UHV chamber, the Si wafers were annealed at 950 K for 24 h for outgassing and flashed to ~1500 K to remove oxide. Electrochemically etched and Ar-sputtered tungsten tips were used. The STM was modified to have a tungsten wire heater mounted onto the STM head for the enhanced thermal stability and uniformity up to 500 K. This was done in order to avoid the thermal instability caused by the negative thermal coefficient of resistivity in this temperature range, as well as the large thermal gradient across the Si sample. Desired temperatures were obtained either by applying a stable constant power source overnight, or by using a programmable temperature

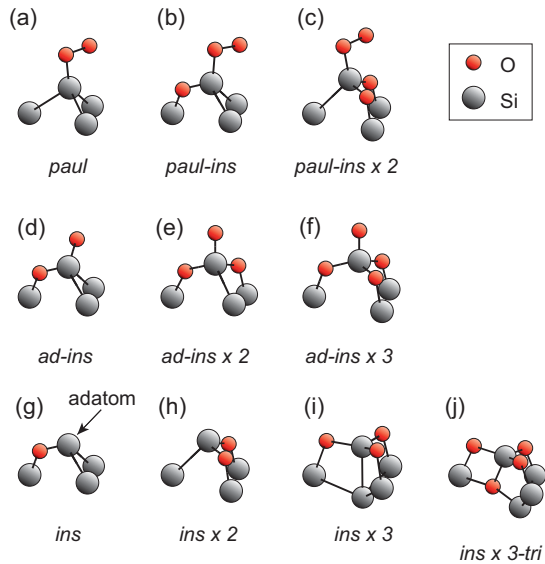


FIG. 1. (Color online) Schematic diagrams of possible bonding configurations of atomic oxygen to the Si adatom structures of Si(111)-(7 × 7) surface. (a)–(c) The *paul* configurations that have an oxygen molecule bonding to the adatom in the on-top position, (d)–(f) the *ad* configurations that have an oxygen atom in the on-top position, (g)–(i) the *ins* configurations that have oxygen atoms inserted in the back-bonds of the Si adatom, and (j) the *tri* configuration that has an oxygen atom bonding to the first- and the second-layer Si atoms as well as the adatom. Small circles (red) represent oxygen atoms, while larger circles (gray) represent Si atoms.

controller. Temperature readings were made by using a Si diode mounted on the STM head during the experiment runs, and they were later calibrated by using a thermocouple pair attached directly to the Si wafer. To produce the switching triads, the Si sample was exposed to typically about 1 L of oxygen, which was filtered via a low-temperature trap to remove possible contaminants.

The time series data of the tunneling current were obtained by positioning the STM tip over a selected site, while keeping the feedback loop turned off to maintain the vertical position of the tip, and recording the tunneling current at typically 5 ms intervals for up to 10 s through 16-bit digitizers. To compile the statistics, this process was repeated from 30 to 180 times. It was essential to maintain thermal-drift-free conditions in both surface parallel and normal directions.

III. RESULTS

Figure 2 shows the formation of the multicentered oxidation-induced structure on a Si(111)-(7 × 7) surface. A comparison of the same area of a Si(111)-(7 × 7) surface before and after the oxygen gas dose presents two different types of oxidation products: Bright sites and two neighboring dark sites. Two *bright* sites in Figs. 2(b) and 2(c) are typical oxidation products, attributed to a Si adatom that has one or more oxygen atoms inserted in the back-bonds of the adatom.^{5–7,13,14,18} On the other hand, two neighboring dark sites are not ordinary ones. Strikingly, they are not static. The structure alternates in time between two configurations, as demonstrated in Figs. 2(b) and 2(c). The unusual dynamic structure consists of three center adatoms within the half-unit

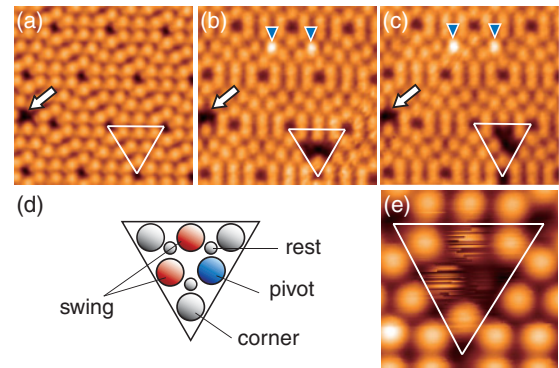


FIG. 2. (Color online) (a) A pristine Si(111)-7 × 7 surface prior to oxygen dosing. The arrow and the large inverted white triangle mark a pre-existing vacancy defect and the HUC of 7 × 7 surface, respectively. (b) and (c) Successive images of the same area taken immediately after 0.1 L oxygen dose. Small blue triangles point to oxygen-induced *bright* sites, and large empty triangles denote the HUCs with two different flip-flop configurations, where two of the three center adatoms are *dark*. Imaging conditions are 1.2 V, 10 pA, and 300 K. (d) A schematic diagram of the HUC that matches the orientations of the triad in (b), (c), and (e). The three large circles near the vertices of the triangle represent the corner adatoms, while the large three inner adatoms, labeled as swing and pivot, and three small circles represent the center adatoms and the rest atoms of the HUC, respectively. The pivot (blue) and the swing (red) sites, denoting the immobile and the mobile sites, respectively, compose the triad. (e) An image of the HUC at an elevated temperature (356 K).

cell (HUC) of a Si(111)-(7 × 7) surface, which will be from here on referred to as a *triad*. Of the two *dark* features, only one feature is mobile and hops back and forth, exclusively between the two center adatom sites within the HUC, while the other *dark* feature remains immobile.

As illustrated in Fig. 2(d), we would call the stationary dark site as the *pivot* site, and the bistable flip-flopping sites as the *swing* sites, in a structural analogy to a mechanical pendulum, although the analogy should be taken with the caveat that the flip-flop motion between the swing sites are aperiodic, as will be shown. Consistent with earlier works, we would call an adatom site *bright*, *normal*, or *dark* based on the contrast of the unoccupied state image.

Peculiarly enough, only the center adatoms within a single HUC qualify as the triad of two swing sites and one pivot site, as shown in Fig. 2. No other types of active triads have been found such as involving inter-HUC ones or corner adatoms. Furthermore, not all of two *dark* center adatoms in a HUC exhibited the flip-flop motion either. Nonequivalence between a pivot and a swing sites, and a low rate of occurrence of the triad on the surface, indicate that the triad is not a mere collection of two ordinary *dark* sites that happen to form next to each other. Furthermore, the triad was apparently formed in a single step, as shown in Figs. 2(a)–2(c), as opposed to sequential formations of pivot and swing sites or vice versa.

The rate of the flip-flop motion is very low at room temperature, about 0.04 Hz on average as will be shown in detail later. This as well as the low population density of the triads makes it difficult to find them, as they were found in

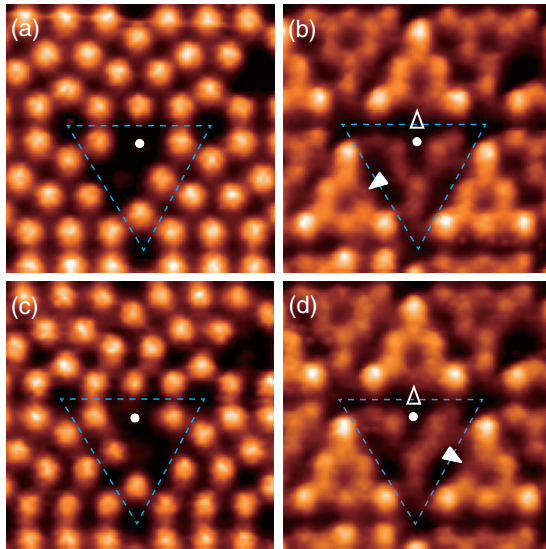


FIG. 3. (Color online) Dual-bias scan images of two flip-flop configurations, (a) and (b) vs. (c) and (d) (imaging conditions: ± 1.5 V, 100 pA, and 300 K). Large dashed triangles indicate an identical HUC area. White dots denote the pivot sites, and small filled and empty triangles point to the center adatom sites, that are located in the neighboring HUC and exhibit no adatoms.

less than 0.1% of HUCs at 1 L oxygen dose. Thus the typical procedure to locate the triad involved the repetitive scan over the same large area and search for a change in comparison with the earlier images. As the substrate temperature was raised, however, the flip-flop motion over the swing sites increased in frequency. Figure 2(e), imaged at an elevated temperature, exhibits irregular normal and dark topographic streaks only over both swing sites, which signify the rapid flip-flop motion and consequently the reduced residence times in both *normal* and *dark* configurations.

Dual bias images shown in Fig. 3 reveal that the formation of a triad induced a number of changes in a HUC. In the occupied state image, all corner adatoms appear very dim, whereas the rest atoms appear intact, indicating that the rest atoms do not contribute to the triad. Figure 3 further shows that two configurations are the mirror image of each other. While the pivot site displays no change between the two configurations, the swing sites switch every feature associated with the alternation, making the transition from one configuration to the other, fully symmetric. Comparison of the filled state images shows that the pivot site and the *dark* swing site are not identical. The pivot site appear consistently *dark* in both occupied and unoccupied states, while the *dark* swing site exhibits contrasting behavior between occupied and unoccupied states. In the occupied state it appears dimly in an ill-defined shape, while disappearing in the unoccupied state. The difference in contrasting behavior between the pivot and the *dark* swing sites suggests that while the pivot site has strong bonding with oxygen, the *dark* swing site has weakly bonding oxygen because the density of states near the Fermi level is not fully removed.

Interestingly, the center adatom of the neighboring HUC (CANH) nearest to the pivot site looks pristine in the unoccupied state but it completely disappears in the occupied

state, as indicated by empty arrows in Figs. 3(b) and 3(d). Such contrasting behavior between occupied and unoccupied states are also found in two additional sites in Fig. 3. One is the *normal* swing site that looks pristine in the unoccupied state. The other is the CANH nearest to the *dark* swing site, as indicated by filled arrows in Figs. 3(b) and 3(d). When the *dark* swing site becomes *normal* in a flip-flop motion, the CANH site reverts back to the ordinary adatom. In short, all center adatoms directly facing *dark* triad sites appear pristine in the unoccupied state but gone in the occupied state.

Triads were found active at 360 K even 48 h after the oxygen dose, which vouches for the stability of the structure. Not just the stability of the triad as a whole, but also the stability of the pivot site *within* the triad was remarkable. Deliberate attempts were made to modify the swing direction so that one of the swing sites exchange the role with the pivot site. This was performed by scanning the triad at high current to increase the interaction in 60° intervals with respect to the swing direction of the triad. That none of these attempts were successful suggests that the pivot site is not only the chemically most stable site in the triad, but also a site chemically distinct from the *dark* swing site. In comparison, in the case of vacancy defects, the migration of an adjacent adatom into the vacant site could be induced by using atomic force microscopy.²⁰

As shown in the schematic diagram of Fig. 4(a), during the measurement period, the triad switches between the mirror configurations α and β with each characteristic residence time τ_α and τ_β . Here it is assumed that an adsorbed mobile species makes a *dark* state. In configuration α , the tunneling current would be high as the adatom is in the *normal* state. In configuration β , the tunneling current would be low as the adatom is in the *dark* state. A typical time series data is shown in Fig. 4(b). Consistent with Figs. 2 and 3, only two configurations exist, with the configurations α and β commanding high and low tunneling currents, respectively. Figure 4(c) shows the frequency distribution of the residence time τ_α and τ_β for configuration α and β . The residence times were extracted from the time series data by using the averaging method.²¹ As the linear fit to the log data indicates, the frequency of the residence time for each configuration decayed exponentially. Switching between two configurations may be thus described as a random event with the exponentially decreasing probability in time. Also clear from the linear fits to the data is that the residence times for α and β configurations are identical within the error bars, as the fits to the data are hardly distinguishable. This means the equal probability of being in either state, confirming that two configurations are the mirror image of each other. Below the low tunneling current range (~ 1 nA) tested, no dependence of the residence time on tunneling current was found.

Figure 4(d) shows an Arrhenius plot of the transition rates in the flip-flop motion from 300 to 370 K. Also shown are the data on two different types of HUCs, faulted and unfaulted halves. The linear fit to the data represents the Arrhenius equation

$$\frac{1}{\tau} = \nu_0 \exp(-E_b/k_B T), \quad (1)$$

where ν_0 , E_b , k_B , and T denote the pre-exponential factor (PEF), the activation energy barrier, the Boltzmann constant, and temperature, respectively. As shown in Fig. 4(d), the

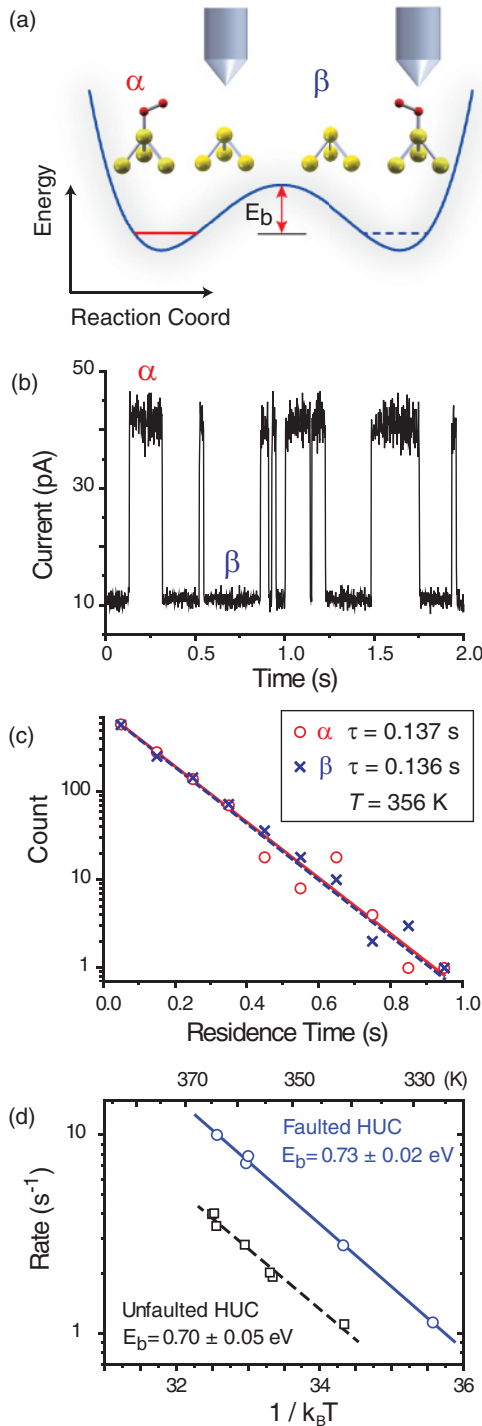


FIG. 4. (Color online) Dynamics in a triad. (a) A schematic view of potential energy diagrams for the two configurations α and β , which correspond to *normal* and *dark* states, respectively. (b) Typical time series data of tunneling current on a swing site with the STM feedback loop off (1.2 V, 10 pA, and $T = 356$ K). (c) A semilog plot of the frequency of the residence time for high and low current states. Solid and dashed lines represent exponential fits to high (\circ) and low (\times) current states, respectively. (d) An Arrhenius plot of the transition rates in the faulted (blue circle) and unfaulted (black square) HUCs. Lines are fits to the data.

equation gave excellent fits to the data, indicating that the process is thermally activated. The fitting yielded the activation

energies and PEFs for the flip-flop motions, 0.73 ± 0.02 eV and $10^{11.3 \pm 0.3}$ Hz in the faulted HUC and 0.70 ± 0.05 eV and $10^{10.5 \pm 0.6}$ Hz in the unfaulted HUC, respectively. Thus the activation energy barriers of both HUCs are identical within the error bars, whereas the PEF of the faulted HUC is about 6 times as large as that of the unfaulted HUC.

The size of the barrier height for the flip-flop motion in the triad is intermediate for the species adsorbed on Si surfaces. Weakly binding species such as metals have barrier heights typically less than 0.3 eV,^{22,23} while covalently chemisorbed oxygen² and hydrogen²⁴ species have the diffusion barriers greater than 1.7 eV. The adatom vacancy has a theoretically estimated barrier of about 0.8 eV, close to that of the triad.²⁰ However, vacancy defects are ruled out as a possible candidate for the *dark* state. As will be shown, after the breakdown, the triad does not show any vacancy-like states. Furthermore, their images display qualitatively dissimilar bias dependencies. Compared to the vacancies, the triad has significant bias dependency and shows internal structures.

PEFs of both faulted and unfaulted HUCs are significantly lower than usual 10^{13} to 10^{14} Hz. This usually indicates that substantial difference exists between the entropies possessed by the mobile species in the ground state and the transition state involved in the flip-flop motion. Furthermore, the large difference in PEFs between faulted and unfaulted HUCs suggests that the flip-flop motion is sensitive to the local environmental difference between two HUCs, of which the dominant factor is the local charge density.

Although the triad possesses excellent stability even at elevated temperature, it occasionally underwent the structural breakdown, an event attributed to the interaction with the STM tip. One may draw several conclusions from Fig. 5 that shows two possible outcomes of the breakdowns. First, there are no missing adatoms after all, indicating that the flip-flop motion is not driven by vacancies. Second, the breakdown results are different from the pivot and the swing sites. The breakdown of a triad always produced a *bright* state in place of the pivot site, whereas it produced in place of the *dark* swing site, occasionally a *normal* state, or more often a *bright* state. It thus

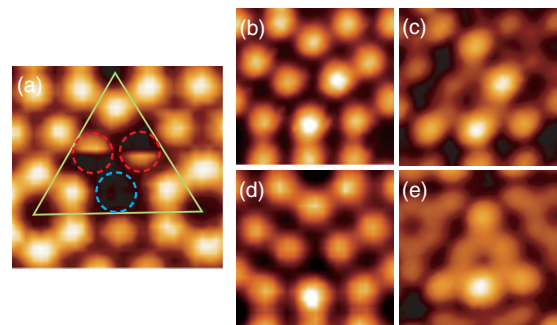


FIG. 5. (Color online) Breakdown of triads. STM images of (a) a typical working triad, (b) and (c) filled and empty states of a typical triad breakdown case, and (d) and (e) filled and empty states of a rare triad breakdown case. The case (b) and (c) is more frequently found compared to the case (d) and (e). Green triangle denotes the faulted HUC. Two red and a blue circles mark the swing sites and the pivot site, respectively. Images were obtained at +1.5 V [(a), (b), and (d)] and -1.2 V [(c) and (e)] with 10 pA and 300 K.

appears that in the breakdown, the mobile species of the swing site reacted with the Si adatom [Figs. 5(b) and 5(c)], or simply desorbed [Figs. 5(d) and 5(e)]. Lastly but most significantly, Fig. 5 shows that the breakdown leaves no *dark* states behind, indicating that both *dark* adatoms of the triad are metastable species. Thus it follows that the *dark* swing site is the one that hosts a mobile species responsible for the flip-flop motion, not the *normal* state.

IV. DISCUSSION

Let us consider possible structural models of the triad and the mechanism that sustains the flip-flop motion. Clearly the models have to satisfy several important criteria. The mobile species of the *dark* swing site must have a bond weak enough to hop in the flip-flop motion, while the pivot site should be stable enough to withstand any thermal perturbation and stabilize the whole structure. Lastly, when the triad ever decomposes, there should be no *dark* sites standing.

A Si adatom appears *dark* if its dangling bond is eliminated via bonding with an on-top oxygen atom⁵ or a molecular precursor.¹¹ Therefore adatom states with either a paul or an ad bond would make prime candidates for *dark* pivot and swing sites.

According to Lo *et al.*,² site-to-site hopping of an ins-only state has activation barriers greater than 1.8 eV, much larger than that of the flip-flop motion. In view of possible hopping paths, an ad state cannot have the site-to-site hopping barrier any lower than an ins state. Thus the ad state is ruled out as the mobile species, whereas it is the only viable candidate for the pivot. The pivot site should be in ad-ins $\times n$ configurations, where n is the number of oxygen atoms in the ins position. At room temperature, $n = 1$ configurations are unstable,^{1,5,18} whereas $n = 2$ and $n = 3$ configurations are long lived.⁶ As the pivot site turns into a *bright* state in the event of an occasional breakdown, the ad-ins $\times 2$ state is favored over the ad-ins $\times 3$ state. This is because the ad-ins $\times 2$ state may transform into ins $\times 3$ state and appear *bright*, while the ad-ins $\times 3$ state is not expected to produce such an outcome.⁹

By the same reasoning, the mobile species should be a molecular precursor. However, a molecular precursor had not been detected in the primary oxidation process nor is it expected to be long lived at room temperature. On the other hand, the presence of a molecular oxygen in the triad does not contradict either case. First, the triad is a minor species, as mentioned earlier. At such a low population density, detecting a molecular oxygen in the triad would be a challenge by any surface-sensitive techniques. Second, the chemical environment of the triad that has two reacted sites within a single HUC is by no means similar to that of a Si adatom in a pristine environment. In particular, chemical bonding between Si and oxygen involves a large charge transfer from Si to oxygen because of the large difference in electronegativity. Lee and Kang^{1,9} reported by using DFT calculations that the formation of an ad state requires a charge transfer of nearly two electrons from nearby rest-atom sites, while the formation of ins state require little from the rest-atom sites.

Such a charge transfer process can explain what happens in Fig. 3. Disappearance and reappearance of unreacted CANH's facing *dark* sites of the triad in the occupied state at every

flip-flop motion indicate that the mobile species of the *dark* swing site is a negative charge acceptor that drains CANHs. On the other hand, rest atoms appear hardly affected, while all corner adatoms within the same HUC appear depleted of charge. This is contrary to the DFT calculations that predicted a charge transfer of nearly two electrons from nearby rest atoms to an ad state, which would have driven rest atoms to appear completely *dark*. The discrepancy is attributed to the lack of adatoms in the small unit cell used to model a Si(111)-(7 \times 7) surface in the calculations.²⁵

In addition, the low PEF of the flip-flop motion may be understood if the mobile species is indeed a molecular precursor. A molecular precursor bonding in the on-top position would enjoy additional degrees of freedom such as rotation, compared to an oxygen atom in an ad state. Thus the molecular precursor would possess large excess entropy relative to transition states that is restricted to the vibrational degree of freedom. The difference would produce a lower PEF.²⁶⁻²⁸

Another interesting issue to be addressed is how the structure was formed in the first place. The clue to the question lies in the outcome of the triad breakdown again. As Fig. 5 shows, not only did *dark* sites not survive the breakdown, but also they decayed at once, not separately. Such a *collective decay* implies the existence of a strong intermolecular interaction in the triad.

We propose the mechanism for the collective decay as shown in Fig. 6. Figure 6(a) shows an initial step to a triad, where two incident oxygen molecules adsorb to form a paul-ins $\times n$ and a paul states concomitantly on two of center adatoms. Adsorption of a molecular oxygen would be initiated by a charge transfer of a single electron from the substrate. If the paul-ins $\times n$ happens to decay first to an ad-ins $\times n$ state, as depicted in Fig. 6(b), then a triad is formed with a long-lived O₂ precursor. This happens because the formation

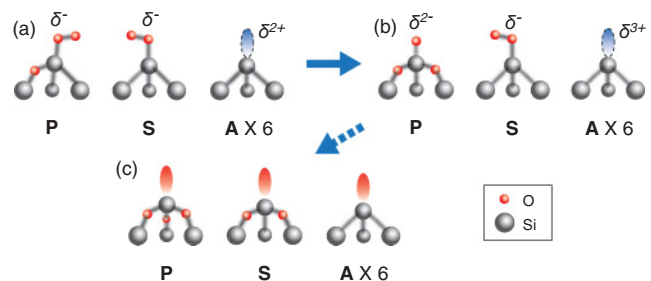


FIG. 6. (Color online) Schematic diagrams on the formation and the breakdown of a triad. For simplicity, among six adatoms of a HUC and two CANHs participating in the interaction at any given moment, drawn is one from each category of a pivot (P), a swing (S), and the rest of adatom (A) sites. Lobes pointing up represent dangling bonds. (a) Initial concomitant adsorption of two oxygen molecules on two ins and *normal* center adatom sites. The charge transferred from unreacted adatoms amounts to the total sum from the surrounding area. (b) The formation of a triad by the decay of the initial ins-paul state into the ad-ins $\times 2$ state accompanied by a further charge transfer from surrounding adatoms to the O(ad) bond. (c) The configuration after the breakdown. The charge is now returned to the adatoms. Small red and large blue circles denote oxygen and silicon atoms, respectively.

of two O(ad) bonds by the simultaneous decays of two O₂ precursors would have required additional charge transfer of two more electrons, stripping the adatoms of all available charge within the HUC. Clearly this would be energetically prohibitive because of the large Coulomb energy buildup. Thus the pivot site formed by the symmetry-breaking charge transfer prevents the O₂ precursor on the swing site from dissociating, thereby providing the triad with the stability and the flip-flop motion. This state may persist until the collective decay of the triad, in which ad-ins \times *n* decays, releasing the locked charge, and allows the decay of the molecular precursor to the final breakdown state of Fig. 6(c). In this mechanism, therefore, the lifetime of a triad would primarily depend on that of the pivot state, a long-lived ad-ins \times *n* states with *n* = 2 or 3.⁶ This model naturally favors a center adatom as a pivot site in accordance with the experiment, because a corner adatom as a pivot site would have only swing sites in its immediate neighborhood within the same HUC, thus too isolated from the ready electrons of unreacted adatoms. Nevertheless, still unanswered questions remain such as the nature of an attractive force that exists between the pivot and the mobile species to keep them together. Detailed theoretical investigations may shed further light on these issues.

V. CONCLUSIONS

In summary, we report on the investigation of a Si-based molecular flip-flop motion manifested by a triad of center

adatoms on Si(111)-(7 \times 7) surfaces. The active triad, produced by oxygen adsorption, exhibits a thermally activated, flip-flop motion. The frequency of the flip-flop motion was measured by the tunneling current change, and shows that the flip-flop motion is symmetric and bistable. The temperature-dependent flip-flop rate shows a typical Arrhenius behavior. Faulted and unfaulted halves of the surface have identical reaction barrier heights and dissimilar attempt frequencies. Based on the analysis of STM data, the triad structure is proposed. The pivot site was assigned to an ad-ins \times *n* state, and the *dark* swing site to a paul state, namely an adatom bonded to a molecular precursor that caused the flip-flop motion by hopping between two identical center adatoms. The low PEF and the dependence of PEF on the faulted and unfaulted HUCs support the molecular precursor assignment. It is suggested that the symmetry breaking charge transfer driven by the intermolecular interaction between oxidation products is the origin of the collective stability for the triad and consequently of the flip-flop motion. Our findings shed a new light not only on the initial oxidation process, but also on the pivotal role of intermolecular interactions in modifying the reaction kinetics.

ACKNOWLEDGMENTS

I.-W. Lyo would like to thank Professor M.-H. Kang for useful discussions. J. Lee, J. Park, and W. Jung acknowledge the financial support by MOEST through the BK21 fellowships.

*lyo@yonsei.ac.kr

¹S.-H. Lee and M.-H. Kang, *Phys. Rev. B* **61**, 8250 (2000).

²R.-L. Lo, C.-M. Chang, I.-S. Hwang, and T. T. Tsong, *Phys. Rev. B* **73**, 075427 (2006).

³I.-S. Hwang, R.-L. Lo, and T. T. Tsong, *Phys. Rev. Lett.* **78**, 4797 (1997).

⁴G. Dujardin, A. Mayne, G. Comtet, L. Hellner, M. Jamet, E. Le Goff, and P. Millet, *Phys. Rev. Lett.* **76**, 3782 (1996).

⁵S.-H. Lee and M.-H. Kang, *Phys. Rev. Lett.* **82**, 968 (1999).

⁶K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, *Phys. Rev. B* **68**, 075302 (2003).

⁷H. Okuyama, Y. Ohtsuka, and T. Aruga, *J. Chem. Phys.* **122**, 234709 (2005).

⁸K. Sakamoto, S. T. Jemander, G. V. Hansson, and R. I. G. Uhrberg, *Phys. Rev. B* **65**, 155305 (2002).

⁹S.-H. Lee and M.-H. Kang, *Phys. Rev. Lett.* **84**, 1724 (2000).

¹⁰K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, *Phys. Rev. B* **70**, 035301 (2004).

¹¹B. Schubert, P. Avouris, and R. Hoffmann, *J. Chem. Phys.* **98**, 7593 (1993).

¹²B. Schubert, P. Avouris, and R. Hoffmann, *J. Chem. Phys.* **98**, 7606 (1993).

¹³I.-W. Lyo, P. Avouris, B. Schubert, and R. Hoffmann, *J. Phys. Chem.* **94**, 4400 (1990).

¹⁴P. Avouris, I.-W. Lyo, and F. Bozso, *J. Vac. Sci. Technol. B* **9**, 424 (1991).

¹⁵P. Avouris and I.-W. Lyo, *Surf. Sci.* **242**, 1 (1991).

¹⁶R. Martel, P. Avouris, and I.-W. Lyo, *Science* **272**, 385 (1996).

¹⁷K.-Y. Kim, T.-H. Shin, S.-J. Han, and H. Kang, *Phys. Rev. Lett.* **82**, 1329 (1999).

¹⁸H. Okuyama, T. Aruga, and M. Nishijima, *Phys. Rev. Lett.* **91**, 256102 (2003).

¹⁹K. Sakamoto, H. M. Zhang, and R. I. G. Uhrberg, *Phys. Rev. B* **72**, 075346 (2005).

²⁰Y. Sugimoto, P. Jelinek, P. Pou, M. Abe, S. Morita, R. Perez, and O. Custance, *Phys. Rev. Lett.* **98**, 106104 (2007).

²¹J. Lee and I.-W. Lyo, *Rev. Sci. Instrum.* **81**, 063704 (2010).

²²K. Wang, G. Chen, C. Zhang, M. M. T. Loy, and X. Xiao, *Phys. Rev. Lett.* **101**, 266107 (2008).

²³O. Custance, S. Brochard, I. Brihuega, E. Artacho, J. M. Soler, A. M. Baró, and J. M. Gómez-Rodríguez, *Phys. Rev. B* **67**, 235410 (2003).

²⁴R.-L. Lo, I.-S. Hwang, M.-S. Ho, and T. T. Tsong, *Phys. Rev. Lett.* **80**, 5584 (1998).

²⁵The (4 \times 2) unit cell used in the DFT calculations contains two adatoms, reacted and unreacted, and a rest atom. Thus, compared to the (7 \times 7) HUC with a triad that has twice as many unreacted adatoms as reacted adatoms, the (4 \times 2) unit cell has only one free electron available for a charge transfer before resorting to the rest atom with a fully occupied dangling bond.

²⁶H. A. Kramer, *Physica (Amsterdam)* **7**, 284 (1940).

²⁷P. Hänggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.* **62**, 251 (1990).

²⁸C.-H. Chung, W.-J. Jung, and I.-W. Lyo, *Phys. Rev. Lett.* **97**, 116102 (2006).