

Identification of the Initial-Stage Oxidation Products on Si(111)-(7 × 7)

Sung-Hoon Lee and Myung-Ho Kang

Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea

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Density functional theory calculations are used to study the initial-stage adsorption of O₂ molecules on the Si(111)-(7 × 7) surface. Contrary to experimental suggestions, we find no evidence of metastable O₂ molecular states on this surface, i.e., O₂ molecules dissociate spontaneously without any barrier. Our electronic and vibrational analysis reveals that the resulting atomic-oxygen products can explain the “molecular” features reported in previous experiments. [S0031-9007(99)08404-5]

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Chemisorption of oxygen molecules on silicon surfaces has been a subject of both fundamental and technological importance as a model for the initial stage of silicon oxidation. In most cases, however, the adsorption-induced chemical and geometrical complexity has greatly hindered experimental or theoretical identifications of the atomic structure of the reaction products, and thus many structural and spectroscopic issues still remain unresolved.

Of particular interest among such examples is the so-called “molecular precursor” model for the initial-stage chemisorption of O₂ molecules on the Si(111)-(7 × 7) surface, which was proposed to explain the observed oxygen-induced metastable features: In their vibrational electron energy loss spectroscopy (EELS) studies, Ibach *et al.* [1] and Edamoto *et al.* [2] found a loss peak at 149–155 meV that was extinguished by 400 K annealing. Later Höfer *et al.* [3,4] reported in their ultraviolet photoelectron spectroscopy (UPS) studies two metastable spectra at 2.1 and 3.9 eV which were also quenched by ~400 K annealing. These metastable features have been ascribed to chemisorbed O₂ states (i.e., molecular precursors), and the reported lifetime at room temperature varies from ~10 min in early studies [3,4] to several hours in recent studies [5–7]. The concept of O₂ molecular precursors on Si(111)-(7 × 7) has been put forward in a more concrete but controversial way in recent scanning tunneling microscopy (STM) studies: Oxygen-induced bright sites in STM topographs are the most numerous product at low O₂ exposures and are known to be quite stable at room temperature and to survive heating up to 600 K [8–14]. These bright sites have usually been assigned to atomic-oxygen species [8–12]. Recently, however, Dujardin *et al.* [13] emphasized their molecular origin by identifying the bright sites with the metastable state that gives a 3.9 eV UPS peak. Furthermore, initiated by the Dujardin *et al.*'s molecular assignment, Hwang *et al.* [14] interpreted even the motion of the bright sites at 300–365 °C as hopping of single O₂ molecules. Despite these experimental proposals, however, the structural identification of the O₂ molecular precursors is yet to be done. Previous theoretical studies [15–18] were based either on the unreconstructed Si surface structure or on

a qualitative theoretical scheme, and so more elaborate theoretical studies are needed.

In this Letter, we report an atomistic identification of the initial-stage oxidation products on Si(111)-(7 × 7), based on density functional theory (DFT) calculations for O₂ chemisorption on the most reactive Si adatom site. Our investigation shows, contrary to the experimental suggestions, that (1) there are no (meta)stable molecular states, i.e., O₂ molecules dissociate spontaneously, and (2) the resulting atomic-oxygen products can explain quantitatively the “molecular” features reported experimentally. This result disproves the prevailing concept of chemisorbed molecular precursors for this system and instead provides energetically and spectroscopically sound, alternative structural models.

The Si(111) surface is modeled by a periodic slab geometry with a computationally feasible (4 × 2) surface unit cell. Each slab contains eight layers of Si atoms. On each side of the slab, two adatoms are added and one of the two restatom dangling bonds is saturated by a hydrogen atom, in order to maintain the same population ratio of adatoms and restatoms as the (7 × 7) surface. This surface was found to be a good approximation of the (7 × 7) surface in previous DFT calculations for the study of hydrogen diffusion [19]. A single O₂ molecule is added on this surface. Several adsorption sites are possible, but we focus presently on the Si adatom site as primary O₂ reaction sites at low coverages, based on experimental evidences [8–11] that the UPS peak corresponding to the adatom dangling-bond state is readily quenched after small oxygen exposure, and the oxygen-induced changes in STM topographs also occur primarily on the adatom sites.

In our DFT calculations, we use the generalized gradient approximation allowing spin polarization [20]. The electronic wave functions are expanded in a plane-wave basis of 20 Ry with the use of norm-conserving pseudopotentials for Si and H atoms [21] and ultrasoft pseudopotentials for O atoms [22]. Details and tests of our implementation can be found in Ref. [23]. The equilibrium bond length, vibration frequency, and binding energy of the O₂ molecule in the spin-triplet ground state

are 1.24 Å, 0.21 eV, and 6.3 eV, respectively. The experimental values are 1.21 Å, 0.20 eV, and 5.2 eV. We take two \mathbf{k} points in the (4×2) surface Brillouin zone for the \mathbf{k} -space integration. In the course of the structural optimization, we allow all the atoms to relax except for the innermost two Si layers. Convergence tests on the plane-wave basis size, the \mathbf{k} -point sampling, and the Si substrate thickness have shown that the error in the calculated adsorption energy is less than 0.1 eV/O₂ with negligible structural changes.

Our first concern was to identify any of the molecular precursor states, but we have only found that any molecularly adsorbed configuration is unstable with respect to further relaxation that eventually leads to its dissociation. In Fig. 1, three representative molecular configurations and their adsorption energies are displayed. While the paul configuration maintains a spin-polarized molecular state (O₂⁻) with an O-O bond length of 1.36 Å, the grif configuration has zero spin with a larger bond length of 1.58 Å. These two molecular configurations (paul and grif) were discussed as possible molecular precursor structures in previous studies [1,2,6,7,13–16,18]. However, as shown in Fig. 1, our energy diagram has no local minimum around these molecular configurations. There is a marginally stable molecular configuration (“stand” in Fig. 1), but it may also be regarded as unstable with too low a barrier of 0.02 eV toward eventual dissociation. It is also likely that adsorbing O₂ molecules dissociate directly from the grif or paul state, bypassing the stand configuration, driven by a large energy released from initial molecular adsorption. In

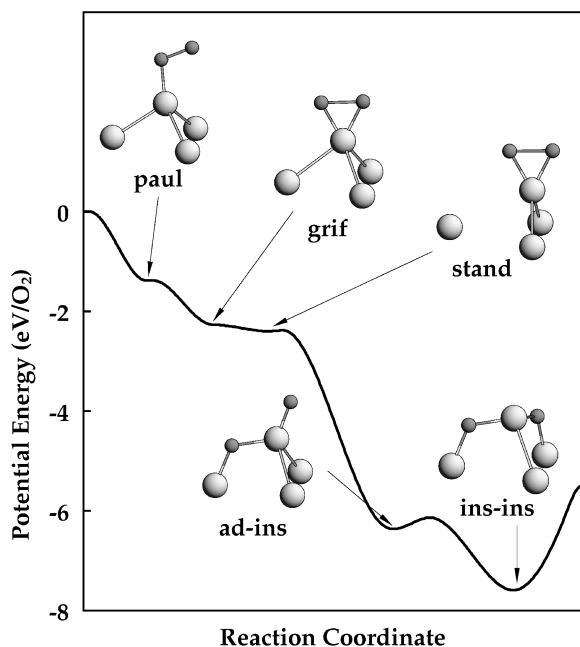


FIG. 1. Calculated energy diagram for O₂ adsorption on the adatom-covered Si(111) surface with the atomic geometries at representative points in the diagram. The large and small circles represent Si and O atoms, respectively.

any case, the present calculations do not support the possibility of molecular precursors on this system.

We next identify the resulting dissociation products. There are two possible configurations as shown in Fig. 1, ad-ins and ins-ins, where “ad” denotes an O atom bonding on top of the Si adatom and “ins” denotes an O atom inserted into a Si adatom back bond. Since ad O atoms make a weaker bonding than ins O atoms, the ad-ins state turns out to be less stable than the ins-ins state by 1.3 eV, and there exists a low-barrier (~ 0.15 eV) transformation pathway to the stable ins-ins configuration [24]; that is, the ad-ins configuration is *metastable*. Figure 2 shows the optimized ad-ins and ins-ins structures. An interesting feature in the ad-ins configuration is that the ad O atom is tightly bonded to the Si adatom: the resulting Si-O(ad) bond length, 1.56 Å, is almost identical to the value calculated for free SiO molecules (1.54 Å). We also find that the Si adatom in the ins-ins configuration is a little lifted up to the vacuum region by the formation of two strong Si-O-Si bridges.

The present *dissociative* chemisorption picture for the initial-stage oxidation process on Si(111)- (7×7) is not particularly surprising in view of the fact that the Si(100) surface with similar dangling-bond states also does not exhibit any chemisorbed O₂ molecular states [25], but our result of no molecular precursors on this surface raises an essential question on the chemical origin of the experimental molecular features. This compelling question demands careful spectroscopic examinations of the dissociation products. We find in our electronic and vibrational analysis, as will be shown below, that the ad-ins and ins-ins structures can reproduce quantitatively the available molecular features.

We begin with the metastable UPS peaks. In Fig. 3, we display the projected density of states (PDOS) of oxygen 2*p* orbitals for the ad-ins and ins-ins structures, in comparison with the oxygen-induced UPS peaks [3,4]. Of the five UPS peaks observed after small O₂ exposure at 150 K, two peaks at 2.1 and 3.9 eV were quenched by 400 K annealing and attributed to a molecular state, partly based on tight-binding calculations [16,17] predicting that dissociated oxygens produce no peaks in the energy region of 2.1 and 3.9 eV. In our DFT spectra in Fig. 3(b),

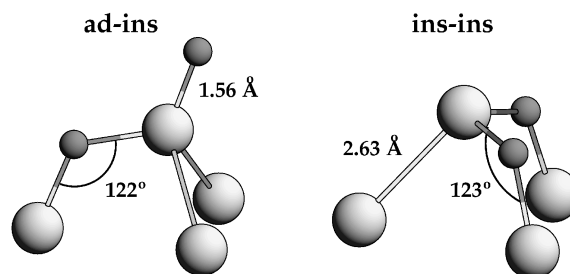


FIG. 2. Optimized atomic structures for the ad-ins and ins-ins configurations.

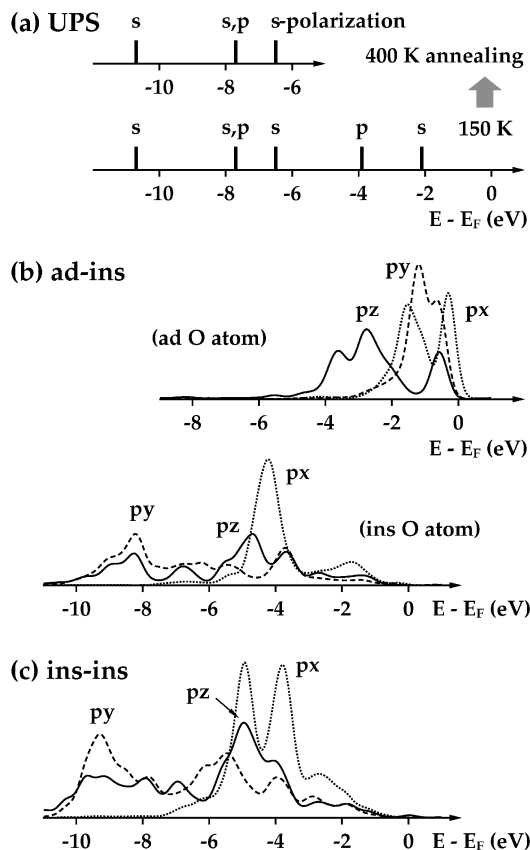


FIG. 3. (a) Oxygen-induced peaks in the polarization-dependent UPS spectra of Höfer *et al.* (Ref. [3]). The s (p) labeled peaks are more prominent by s -polarized (p -polarized) light. (b) and (c): Projected density of states of oxygen $2p$ orbitals for the ad-ins and ins-ins configurations, respectively. Here, the z axis is surface normal and the x axis is normal to the Si-O-Si plane.

however, we find that the metastable ad-ins configuration does produce the peaks: The prominent peaks in the PDOS of ad O atoms lie at ~ 1 eV for p_x and p_y orbitals and at ~ 3 eV for a p_z orbital. Provided that DFT calculations tend to underestimate binding energies for localized orbitals [26], these two peaks coincide with the 2.1 and 3.9 eV peaks when offset by 1 eV [27]. More convincing is that the oxygen orbital characters of the PDOS peaks accord with the polarization dependencies of the UPS peaks, since the p_x and p_y orbitals are more sensitive to the s -polarized light and so is the p_z orbital to the p -polarized light [4]. It is also noticeable in Fig. 3 that the PDOS of ins O atoms in the ad-ins or in the ins-ins configuration accounts well for the stable UPS peaks in the range of 6–11 eV.

The ad-ins configuration is also found to produce the metastable EELS peak at 149–155 meV [1,2]. In our vibrational analysis for the ad-ins structure, the highest frequency is found at 143 meV, corresponding to the Si-O(ad) stretching vibration mode. Since our calculation for a free SiO molecule (148 meV) slightly underestimates

its experimental value of 154 meV, the present Si-O(ad) stretching mode can be well identified as the origin of the metastable EELS peak. In fact, Schell-Sorokin and Demuth [28] attributed the metastable EELS peak to a diatomiclike SiO species, but Ibach *et al.* [1] and Edamoto *et al.* [2] disputed this SiO assignment by reasoning that a SiO species bonded to the surface would not give such a high frequency comparable to that of a free SiO molecule. However, the present Si-O(ad) unit in the ad-ins configuration appears quite similar to a free SiO molecule vibrationally as well as structurally (as evidenced by the nearly identical Si-O bond lengths). This interesting quasimolecular behavior of the Si-O(ad) unit calls for further studies on its chemical and dynamical nature in surface reactions.

Since the ad-ins configuration accounts well for the metastable UPS and EELS spectra, a brief comment on its structural metastability is in order: The calculated energy barrier of ~ 0.15 eV would be too low to explain its room-temperature stability, in a usual Arrhenius analysis. We expect, however, that the attempt frequency for the highly involved activation pathway [24] would be significantly lower than the usual value of 10^{13} s $^{-1}$, allowing the ad-ins configuration to survive at somewhat high temperatures. The possibility of an extremely low attempt frequency in this system was also discussed by Höfer *et al.* in their x-ray photoemission and optical analyses [3,5].

Finally, we wish to explore the underlying structure of the bright sites in STM topographs that were also attributed to a molecular state [13,14]. Since the bright sites are stable even at 300 °C [14], they should be distinguished from the metastable state that gives the UPS and EELS peaks disappearing at much lower temperatures. Naturally, the stable ins-ins structure could be a possible candidate for them. Figure 4 displays its simulated constant-current STM images with a 2 eV energy window for both filled and empty states. The ins-ins site appears clearly brighter than the unreacted site in both filled-state and empty-state images, in accordance with experiments [8–14]. Its brightness in both images reflects well the structural feature of the ins-ins state that the reacted Si adatom is more (by 0.67 Å) protruded to the vacuum region than the unreacted adatom. The height corrugation between the ins-ins and the unreacted sites is 1.2 Å in the filled-state image and 0.5 Å in the empty-state image. Based on this result and its structural stability, we convincingly propose the ins-ins structure as the origin of the bright sites in STM topographs. We expect that the metastable ad-ins configuration will appear dark in both filled- and empty-state images because the ad O $2p$ orbitals lie below -2 eV according to our analysis of the UPS spectra, and therefore it probably forms a part of the dark sites found in STM experiments [8–14].

In summary, the present DFT calculations have shown no evidence of O $_2$ molecular precursors on Si(111)-(7 × 7) and provided alternative dissociative structural models:

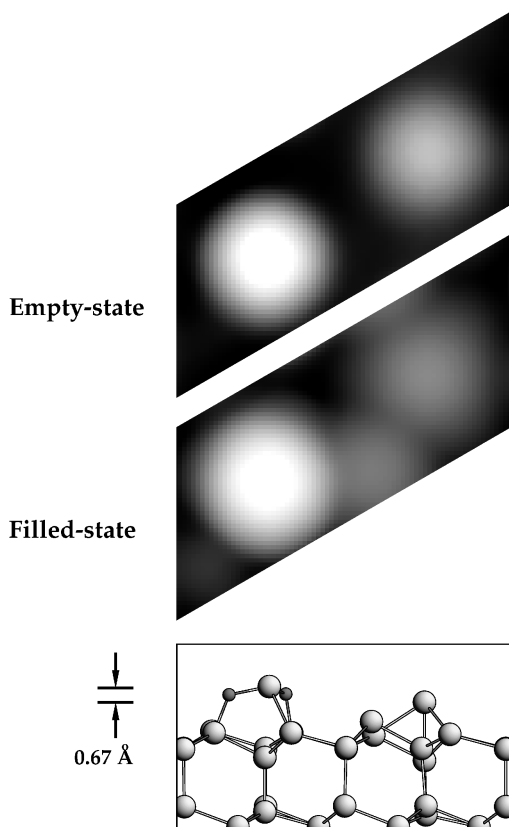


FIG. 4. Theoretical constant-current STM images of the ins-ins site and the unreacted adatom site for empty states (upper panel) and filled states (middle panel). The lower panel shows the side view of the underlying surface structure.

The ad-ins configuration has been identified as the metastable structure that gives the metastable UPS and EELS spectra, and the ins-ins configuration, characterized by a large protrusion of the reacted Si adatom, has been identified as the underlying structure of the highly stable bright sites in STM topographs. The present results offer new information on the initial stage of Si(111)-(7 × 7) oxidation that is essential in understanding more complex oxidation processes such as additional O₂ reactions at high coverages or subsurface diffusion of atomic oxygens at high temperatures.

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