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Temperature effect as an essential factor in scanning tunneling microscopy studies demonstrated by the analysis of an oxygen-adsorbed Si(111)-7×7 surface

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The very initial oxidation of a Si(111)-7×7 surface was studied by scanning tunneling microscopy (STM). The bias-dependent STM images of Si(111)-7×7 surfaces with oxygen adsorbed at RT, 80 and 5 K were compared by observing them at (RT and 80 K), (80 and 5 K) and 5 K, respectively. An essential influence of the measurement conditions on the STM images was clearly demonstrated. Through the experiment, the B-site state, which was defined as having a brighter site than that of normal adatoms, was found to have two different structures at each adsorption site. The recently identified precursor state was shown to change into the well-distinguished B sites, and its thermal activation was also confirmed.

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The adsorption and chemical reaction of molecules onto solid surfaces have been attracting considerable attention from both fundamental and practical points of view. In particular, the understanding and control of the oxidation processes of silicon surfaces are the main subjects in the development of future nanostructural devices in utilizing semiconductor techniques. Over the past decade, the interaction of oxygen molecules with silicon surfaces has been investigated by a large variety of experimental techniques and theoretical methods.[1–11] Of particular interest is the identity of the precursor of the stable oxidation products, i.e., the geometry and electronic structures of the initial state of the O_2 molecules adsorbed on the Si(111)-7×7 surface. However, despite extensive research efforts, many aspects of the molecular-level mechanism of Si(111)-7×7 oxidation remain controversial.

According to previous scanning tunneling microscopy (STM) studies at room temperature, the adsorption of oxygen molecules produces two stable species at the adatom positions of Si(111)-7×7. One appears brighter than normal Si adatoms (referred to hereafter as the B site) and is preferentially located on the corner adatoms in the faulted-half (FH) unit cells. The other appears darker, similar to missing adatoms (referred to hereafter as the D site), and exhibits less site selectivity. At very low O_2 exposure, most of the reaction products are B sites, and the ratio of the number of D sites to the total number of reacted sites increases with additional oxygen exposure. Therefore, a widely accepted model is that the B site is formed by the oxidation of a Si adatom with a single oxygen molecule, and the additional incoming oxygen molecules react with B sites, resulting in the formation of D sites. Existence of the precursor state of the B site was reported by analyzing the temperature dependence of the ultraviolet photoemission spectroscopy (UPS) spectra.[2]

Recently, using low-temperature STM and electron energy loss spectroscopy (EELS), a new adsorption species was found.[10] The new species is dark at bias voltages lower than ~1 V, and changes into a bright site after the STM scan at voltages higher than ~1 V. In comparison with the theoretical prediction that the metastable ad-ins and the stable ins-ins structures appear in dark and bright images in STM,[8] the new species were attributed to the precursor state of the B site. Here, ad and ins denote the O atom bonding on top of the Si adatom and that inserted into a backbond of the Si adatom, respectively. From the isotope-labeled vibrational analysis, the precursor product was concluded to be formed by dissociated oxygen atoms instead of molecular oxygen. All controversies seemed to have settled down.

However, in the EELS spectra as a function of exposure time to O_2, the second species appears after 0.03 L $(1\ \mathrm{L}=1\times10^{-6}$ Torr s$)$ exposure following the first species that is considered to be the precursor state, which was attributed to a different structure such as the ad-ins×3. Since the characteristic product appearing between the precursor state and the B site has not yet been observed by STM, there may be some other mechanisms for these phenomena.

In this paper, we present our results on the initial stage of oxygen adsorption onto the Si(111)-7×7 surface in consideration of the temperature effect in the STM images. In previous STM studies, oxygen adsorption species were studied at only either negative or positive bias images. We examined the oxygen adsorption species with both negative and positive bias voltages to understand their electronic structures in more detail, and the difference in the four adsorption structures of the B site were clearly distinguished. Namely, each of the adsorption species at corner (Co) and center (Ce) adatom sites both in faulted and unfaulted halves (FH and UH) of the Si(111)-7×7 unit cell was found to have two types with different temperature-bias voltage dependences.

The samples used were *P*-doped, *n*-type Si(111) surfaces, with a conductivity of 0.001–0.005 Ω cm. In order to reduce the effect of band bending in the study of bias dependence at low temperature, highly doped samples were used in this experiment. The base pressure was 4.0×10^{-9} Pa. Oxygen gas of ~99.97% purity was introduced through the variable leak valve (typically $\sim5\times10^{-8}$ Pa). After confirmation of the completed 7×7 structure, the STM tip was retracted from the sample during oxygen exposure, and observation was resumed over the same area with adsorbed oxygen. This process ensured that all the observed reacted sites were formed due to oxygen gas exposure. All STM images shown in this paper were taken in the constant-current mode by W

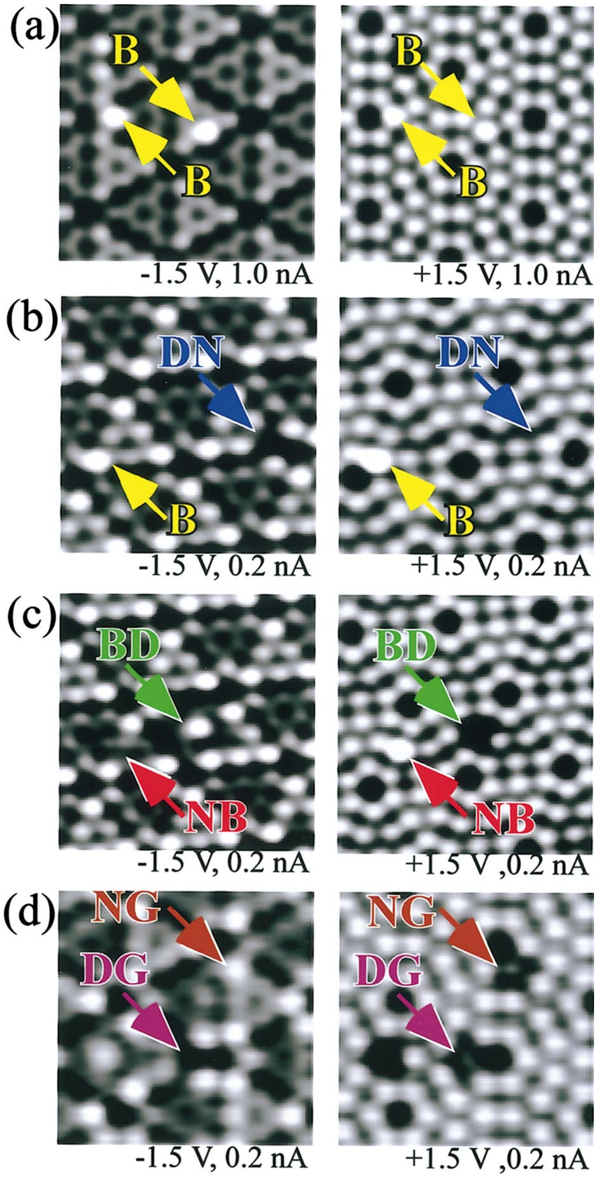

FIG. 1. (Color) STM images of the oxygen adsorption species on Si(111)-7×7 surface. (a) B site at 300 K ($V_s = \pm 1.5$ V; $I_t = 1.0$ nA). (b) B and DN sites at 80 K ($V_s = \pm 1.5$ V; $I_t = 0.2$ nA). (c) NB and BD sites at 80 K ($V_s = \pm 1.5$ V; $I_t = 0.2$ nA). (d) DG and NG sites at 5 K ($V_s = \pm 1.5$ V; $I_t = 0.2$ nA).

tip. Preparation of the STM tips was performed carefully, and reproducibility was well confirmed to avoid tip-dependent effect.

Figure 1 shows typical negative (−1.5 V) and positive (+1.5 V) sample bias voltage STM images of the B site obtained at RT. As has been observed in the previous STM studies, the B sites are imaged bright both at negative and positive bias voltages. The distribution of the B sites classified on the basis of four adsorption sites at RT is shown in Fig. 2(a); adsorption species at corner (Co) and center (Ce) adatom sites both in faulted and unfaulted halves (FH and UH) of the Si(111)-7×7 unit cell. Here, in order to analyze the B site, formation of the D site was excluded by allowing only very low oxygen coverage (<0.03 ML) of the surface.

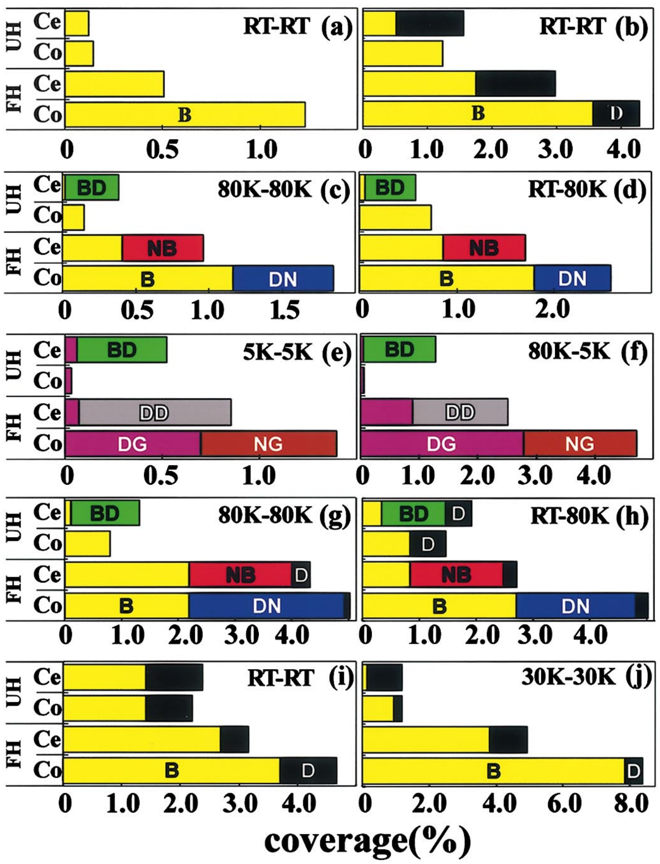

FIG. 2. (Color) The distribution of oxygen adsorbates on Si(111)-7×7 surface at adsorption and observation temperatures of (a), (b), and (i) (RT and RT), (c) and (g) (80 and 80 K), (d) and (h) (RT and 80 K). (e) (5 and 5 K), (f) (80 and 5 K), (j) (30, 30 K). Yellow, blue, red, dark blue, gray, black, brown, and purple bars indicate the B, DN, NB, BD, DD, D, NG, and DG sites, respectively. Data in (i) and (j) are from Ref. 11.

D sites appeared at higher coverages [Fig. 2(b)], which is similar to the result observed by Mayne *et al.* as shown in Fig. 2(i) (from Table I in Ref. 11).

On the other hand, when the oxygen adsorption and the observation of the adsorbed surface were performed at low temperatures, the adsorption sites were imaged in completely different forms. Namely, at 80 K, BD, NB, and DN sites were observed in addition to the B site, as shown in Fig. 2(c). And BD, DD, DG, and NG sites were observed at 5 K instead of the B sites [Fig. 2(e)]. Here, N, D, G, and B represent the brightnesses of the oxygen adsorbate STM images compared to the brightness of the unreacted adatoms as is shown in Figs. 1(b)–1(d), namely, N: normal (unchanged), D: dark, G: gray (less bright), and B: bright, as defined for the B and D sites. For example, since the brightness was compared for −1.5 and +1.5 V, DN site corresponds to site whose brightness is dark and normal at −1.5 and +1.5 V. With this definition, although the B site should be represented as the BB site, we use the original definition to avoid confusion. The DD site is different from the original D site.

As shown in Figs. 2(c) and 2(e), the observed species are different, however, their relative proportions are similar if we replace the B, NB, and DN sites at 80 K with the DG, DD,

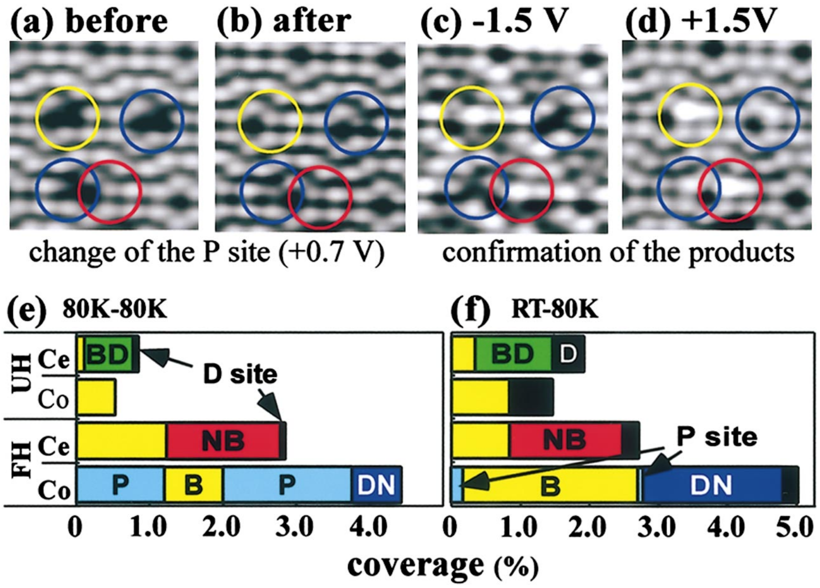

FIG. 3. (Color) STM images of the structural change of the precursors (P site) observed at ($V_s = +0.7$ V, $I_t = 0.2$ nA) before (a) and after (b) scanning at +1.5 V. The yellow, blue, and red circles indicate the change of P→B sites, P→DN sites and the B site thermally reacted from the beginning, respectively. STM images obtained at (c) ($V_s = -1.5$ V, $I_t = 0.2$ nA) and (d) ($V_s = +1.5$ V, $I_t = 0.2$ nA) are also shown to confirm the products. Distributions for the oxygen absorbates obtained for the adsorption and observation temperatures of (e) (80 and 80 K) and (f) (RT and 80 K).

and NG sites, respectively. Their site dependence on the four adatom sites (FH-Co, FH-Ce, UH-Co, UH-Ce) is close to that obtained at RT [Fig. 2(a)]. In addition, D site appeared at higher coverage as shown in Fig. 2(g), but the critical coverage seemed to be higher compared to the case at RT. This phenomenon is in good agreement with that observed by Mayne *et al.*, as shown in Figs. 2(i) and 2(j). Namely, appearance of D sites is suppressed at low temperature as was pointed out by them. Therefore, the most comprehensive explanation is to consider that the B sites originally have two different structural types at each adatom site, which are imaged similarly at RT.

In order to confirm this point, we examined the temperature effect on the STM images. Namely, samples prepared at higher temperatures (300 and 80 K) were observed at lower temperatures (80 and 5 K). For example, Fig. 2(d) shows the result obtained for the samples on which oxygen was adsorbed at RT and which were observed at 80 K after quenching from RT. The new species BD, NB, and DN sites were observed similarly despite the samples being exposed to oxygen at RT. The distributions of these species observed at 80 K [Fig. 2(d)] is almost the same as that obtained for the samples prepared at 80 K [Fig. 2(b)]. In addition, D sites appeared at higher coverage [Fig. 2(h)]. The result obtained by quenching from 80 to 5 K is shown in Fig. 2(f), which can be compared with that in Fig. 2(e).

According to our experimental result, the DN site was imaged brighter at +2 V, and a slight difference in the effective bias voltage due to band bending is expected to occur at low temperature depending on the difference in the dopant density (doping of our sample is higher and the effect is less). If the NB and DN sites and BD site in Fig. 2(h) are attributed to the B and D sites, respectively, the result in the case of Mayne *et al.* [Fig. 2(j)], can be explained in the same way systematically. The different appearance of the B site at 5 K may be caused by further charge transfer supposed to occur at lower temperature.

In order to confirm the existence of the two types for the B site further, we examined the change of the precursor state recently reported.[10] The precursor state changes into the B site by scanning at a voltage higher than ~1 V. Therefore, the surface was first observed at ~0.7 V to identify the precursor state sites [Figs. 3(a) and 3(b)]; the surface of what following the scan at +1.5 V to transform the precursors into B sites, was checked again at ±1.5 V to observe the distribution [Figs. 3(c) and 3(d)].

The precursor state was observed at the Co sites in the FH. When the oxygen adsorption and its observation were performed at 80 K [Fig. 3(e)], the amount of the precursor state was 20% of the total oxygen adsorption species. By comparing the positive and negative bias STM images of oxygen adsorption species after the tip-bias-induced reaction, the change of the precursor state into the B and DN sites was clearly confirmed.

These results clearly indicate the extreme importance of the temperature effect on the STM images. Namely, the observed change in the STM images of the oxygen adsorption species on the Si(111)-7×7 surface is due not to the adsorption temperature but to the observation temperature. Recently, the temperature effect was pointed out for the hydrogen-adsorbed Ge surface.[12] However, since structure is very simple in that case, the oxygen-adsorbed Si(111)-7×7 surface is an example of the detailed temperature effect on the STM imaging of the local variety of the electronic structures. In fact, in addition to the adsorption site dependence, the noteworthy point is that each adsorption site was found to show two different species at low temperature.

The adsorption structures have been analyzed with comparison of the electronic structures between experimental and theoretical results, assuming the oxygen atom forms bonds with an adatom and one of the three backbonds with a threefold symmetry. However, the observed temperature dependence is more complicated as shown in Fig. 2. When the complex underlayers of the 7×7 unit cell are taken into account, the atomic structure of the B site lacks the threefold symmetry due to the asymmetry of the backbonds of the adatoms in the inside and outside directions of the unit cell as shown in Fig. 4 for the case of the corner adatom. There-

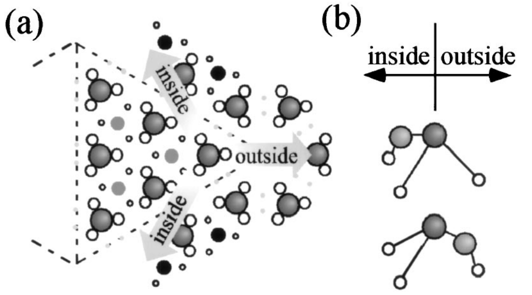

FIG. 4. Schematic to show the asymmetry of ins structure depending on the adsorption site of oxygen atom.

fore, the asymmetry may result in an observable difference between STM images and its temperature-dependent change if a detailed theoretical analysis were performed. Charge transfer at the adatom sites and its effect on the adsorption processes has been studied extensively.[13] However, in order to understand the details of local electronic structures related to chemical reactions, the temperature effect is very important, as has been observed, and must be included into the theoretical analysis in addition to the real complicated structures.

On the basis of the obtained results, thermal reaction process of the precursor state was investigated by performing a similar procedure for the analysis of the B site. Namely, oxygen was adsorbed at RT, and the sample was observed at 80 K after quick cooling to eliminate the thermal reaction at RT [Fig. 3(f)]. As shown in the histogram, the amount of precursors was 5% of the total oxygen adsorption species, which is much less than that in Fig. 3(e) which shows the results of adsorption and observation performed at 80 K. Although difficulty in the bias-dependent discrimination of the species at 5 K enables us to compare the results at only two different temperatures, which clearly shows that the precursors are thermally reacted. However, since the precursor states were stable under observation with the voltage of 0.7 V at 80 K, thermal energy of the adsorbed oxygen itself must have played a role at least for the initial change of them into the B and DN sites at the FH-Co site [Fig. 3(e)]. Since the B site appears in the same form at the UH-Co site, charge transfer may be less there, which may be related to the low activity of the site.

Oxygen atoms were mostly adsorbed at the FH-Co sites, indicating that this site has the highest reaction probability. Since the precursors remain only at the FH-Co adatom site, the activation energy for the thermal reaction is the highest there among all the adatom sites. Therefore, the reaction of oxygen may be strongest at this site. Further experiments are necessary to understand the site-dependent activation processes in more detail, which issues we leave for the future study, together with the detailed analysis of the tip-induced reaction.

In the EELS spectra, a new additional signal appeared upon oxygen exposure following the first signal, which was attributed to the structure between the precursor (ad-ins) and the B site (ins-ins) states.[10] However, since such a new structure was not observed in our STM study, and the B sites had already formed even at 80 K, the structure may be related to the newly identified different types of B sites. Since the probe electron energy was 7 V for the EELS study, the measurement procedure may have changed the precursors to the B sites, in consideration of the tip-induced change at 1.5 V. In such a case, the species analyzed by EELS would no longer be the precursor state, and the conclusion of the dissociative interaction for the precursor state may need to be reconsidered.

In conclusion, we have demonstrated the importance of the temperature effect in the STM study by the analysis of the very initial oxidation of the Si(111)-7×7 surface. The B site, which was originally defined at RT, was found to have two different species at each adsorption site. The precursor state, which was recently found, was confirmed to change into the newly identified B sites, as expected. Since the adsorption species that was predicted by the EELS study to appear between the precursor and B site was not observed by STM, and the B site was observed even at 80 K, reconsideration of the species attribution is necessary.

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