Vibrational Characterization of the Oxidation Products on Si(111)-(7 × 7)

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The oxidation products on Si(111)-(7 × 7) are investigated at 82 K by means of high-resolution electron energy loss spectroscopy. The isotope-labeled vibrational spectra with $^{16}O_2$, $^{18}O_2$, and $^{16}O\,^{18}O$ show that, in the initial stage of the oxidation, an O_2 molecule dissociates to form a metastable product with an O atom bonding on top of the Si adatom and the other inserted into the backbond. The metastable product is observed as a dark site in the topographic scanning tunneling microscopy (STM) image and can be transformed to a stable product by the STM manipulation. Our results are in good agreement with recent theoretical calculations.

The oxidation of silicon surfaces is an important subject for the fabrication of microelectronic materials. Over the last three decades, the reaction of O_2 gas with Si(111)-(7 × 7) attracted great attention from both experimental and theoretical points of view. Although a great deal of effort was devoted to the molecular-level understanding of the reaction, it is still under debate even whether the initial adsorbed state of O_2 is molecular or dissociative.

The presence of a molecular precursor state was proposed by early experimental works [1–7], which were subsequently supported by the theoretical calculations [8–10]. Vibrational electron energy loss spectroscopy (EELS) measurements showed a metastable feature at ~150 meV in the initial stage of the reaction at 100 K, which was assigned to the O-O stretch mode of the precursor [1]. On the other hand, Lee and Kang [11,12] concluded in their density functional calculations that the molecular state is unstable on Si(111)-(7 × 7): an O_2 molecule spontaneously dissociates without any barrier. They reassigned the metastable ~150 meV feature as the Si-O stretch mode of the atomic products [12].

Scanning tunneling microscopy (STM) studies of O_2 adsorption on Si(111)-(7 × 7) were conducted at 300 K [13–16], 600 K[17], and 30 K[16]. The consensus is that the initial reaction of O_2 occurs at the Si adatom site and the main products appear bright in the topographic images above room temperature. However, there remains controversy, in the interpretation of the bright site, whether it is ascribed to the atomic product [11,13,14,16] or molecular O_2 [9,10,15,17].

Recent electronic studies with ultraviolet photoelectron spectroscopy at 120 K [18] and 300 K [19] and with near-edge x-ray absorption fine structure at 135 K [20] suggested that the initial reaction is dissociative, and the molecular O_2 was observed as a secondary product on the oxidized Si(111) surface. The initial dissociation of O_2 on Si(111)-(7 × 7) was also supported by other experimental techniques [21,22].

Our aim in this study is to identify the oxidation products by using vibrational spectroscopy which di-rectly reflects the chemical configurations (atomic or molecular) of the adsorbates. We show that the initial reaction is dissociative with an O atom bonding on top of the Si adatom and the other inserted into the backbond. The on-top O atom migrates into other back-bond by thermal activation at 200 K. The metastable species is imaged and manipulated into the stable product with STM.

The experiments were carried out in an ultrahigh vacuum (UHV) chamber equipped with a high-resolution electron energy loss spectrometer (LK-5000, LK Technologies, Inc.) and a four-grid retarding-field analyzer for low-energy electron diffraction (LEED). The base pressure of the chamber is below 1×10^{-10} Torr. For the EELS measurements, the primary electron energy $E_p = 7$ eV, incidence angle $\theta_i = 60°$, reflection angle $\theta_r = 60°$, and typical energy resolution of 3.5 meV (the full width at half maximum of the elastic peak) were used. According to the angle-dependent measurements, all the observed loss peaks are dipole excited [23]. The scattering plane is aligned along the [01$\bar{1}$] direction. The sample was cooled at 82 K. STM was conducted in a separate UHV chamber with the base pressure below 5×10^{-11} Torr [24]. The STM head was cooled at 78 K with liquid nitrogen.

The Si(111) sample was cleaned by the overnight de-gassing at 900 K, followed by the flashing up to 1400 K. For a clean surface, a sharp (7 × 7) LEED pattern was observed and EELS showed no trace of impurities. We used isotope gases of $^{16}O_2$, $^{18}O_2$, and $^{16}O\,^{18}O$ for EELS with the purities of 99.9%, 99%, and 50%, respectively. The $^{16}O\,^{18}O$ gas bottle contains $^{16}O_2$ (25%) and $^{18}O_2$ (25%). The sample was exposed to O_2 gas via a tube doser which was positioned ~1 cm apart from the sample surface. The exposure is given by the background O_2 pressure multiplied by time in units of L (1 L = 1×10^{-6} Torr s).

A series of EELS spectra of $^{16}O_2$/Si(111)-(7 × 7) at 82 K as a function of the exposure is shown in Fig. 1. In the initial stage of oxidation, two peaks are observed at 80 and 146 meV [1(b) and 1(c)]. Spectrum 1(c′) is taken for
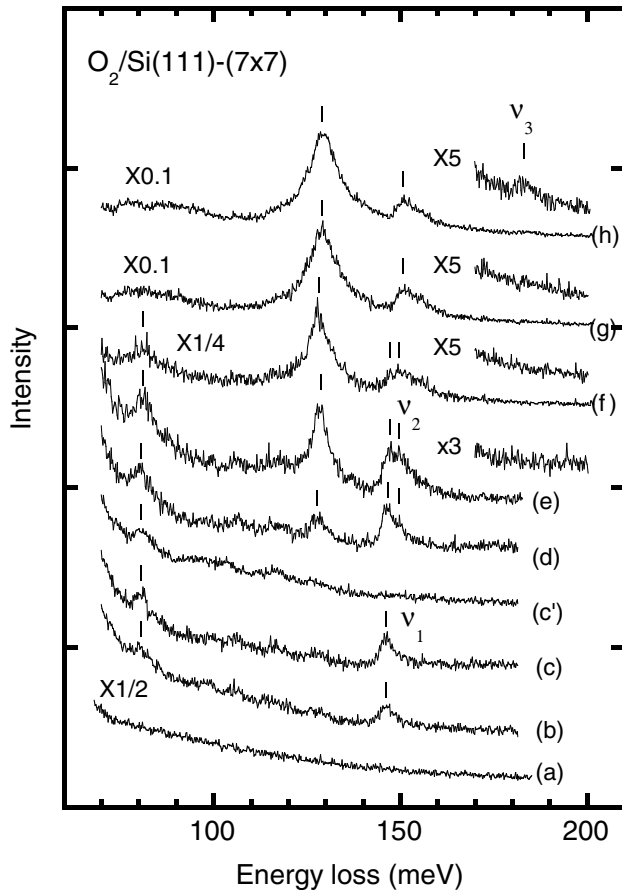
FIG. 1. EELS spectra of Si(111)-(7 × 7) at 82 K as a function of the exposure to $^{16}O_2$. The exposures are (a) 0, (b) 0.008, (c) 0.015, (d) 0.03, (e) 0.07, (f) 0.1, (g) 0.2, and (h) 0.3 L. The O-derived losses are marked, and the higher three losses are labeled by ν_1, ν_2, and ν_3. The spectrum (c') is for the 0.015 L exposure followed by annealing at 200 K. ν_1 disappears upon the annealing, indicating the metastability of the initial product. The loss intensities are normalized to the elastic peak intensities.

the sample exposed to 0.015 L $^{16}O_2$ and then annealed at 200 K. The 146 meV loss disappears upon the annealing, indicating that the initial product is thermally metastable. At an exposure of 0.03 L, two other peaks start to develop at 129 and 150 meV [1(d)]. These results are consistent with the previous EELS study at 100 K [1]. With further increasing exposure, the 146 meV peak is attenuated [1(g)]. All peaks are broadened and saturated in intensity, accompanied with the appearance of a new peak at 184 meV [1(h)]. We label the losses at 146, 150, and 184 meV as ν_1, ν_2, and ν_3, respectively.

The origin of the ~150 meV peak, which is resolved as ν_1 and ν_2 in this study, has been under debate: It was argued in the previous EELS study that the losses were most likely due to the superoxy O_2 species [1]. However, the SiO species was not completely ruled out since the gas-phase SiO molecule exhibits a vibrational energy at 153 meV [25]. A theory predicted the SiO vibrational energy on Si(111) to be 136–143 meV [12]. Thus, the

molecular or atomic nature of the oxidation products cannot be determined from the vibrational energies; we conduct the EELS measurement with the $^{16}O\,^{18}O$ isotope.

EELS spectra of Si(111)-(7 × 7) exposed to 0.02 L of (a) $^{16}O_2$, (b) $^{16}O\,^{18}O$, and (c) $^{18}O_2$ are shown in Fig. 2. Under this condition, ν_1 is mainly observed and ν_2 appears as a shoulder at the higher-energy side of ν_1 for $^{16}O_2$ or $^{18}O_2$. We can clearly detect the isotope shift between $^{16}O_2$ and $^{18}O_2$, where ν_1 is observed at 146 and 142 meV, respectively. The 80 meV loss shifts to 78 meV. The spectrum 2(b) taken with $^{16}O\,^{18}O$ shows two peaks at 142 and 146 meV, which indicates that ν_1 is attributed to the vibration of atomic oxygen. The 146 meV peak is more intense than the 142 meV peak in 2(b), which is due to the overlap of the higher-energy shoulder of the 142 meV loss (ν_2) with the 146 meV peak. These results conclude straightforwardly that the initial adsorption of O_2 on Si(111)-(7 × 7) is dissociative and that ν_1 is assigned as the Si-O stretch mode.

The isotope dependence of ν_2 and ν_3 is shown in the insets of Fig. 2. ν_2 and ν_3 are observed at 150 (146) and 183 (172) meV for $^{16}O_2$ ($^{18}O_2$), respectively. For ν_2, the spectrum of $^{16}O\,^{18}O$ shows two peaks at 146 and 150 meV, indicating that ν_2 is attributed to the vibration of another

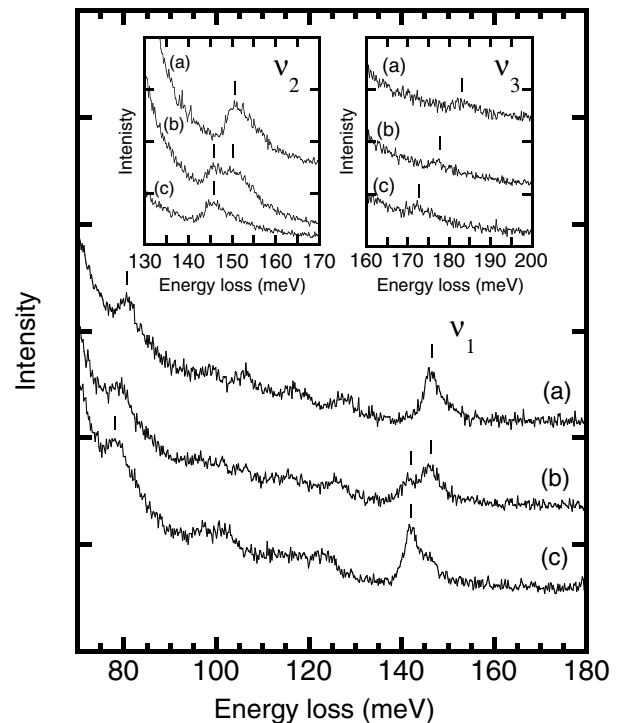FIG. 2. Isotope-labeled EELS spectra with (a) $^{16}O_2$, (b) $^{16}O\,^{18}O$, and (c) $^{18}O_2$ for ν_1, ν_2 (inset), and ν_3 (inset). The oxygen exposures for ν_1, ν_2, and ν_3 are 0.02, 0.2, and 0.3 L, respectively. For ν_1 and ν_2, the spectra of $^{16}O\,^{18}O$ show the doublet structures, which indicates that these modes are due to the Si-O stretch vibration. On the other hand, ν_3 of $^{16}O\,^{18}O$ shows a peak at the intermediate energy of $^{16}O_2$ and $^{18}O_2$, indicating that this mode is assigned to the molecular O-O stretch.

SiO species. On the other hand, ν_3 is observed at 177 meV in the spectrum of ^{16}O ^{18}O; ν_3 is assigned to the O-O stretch mode of molecular O_2 adsorbed on the surface. Thus, our vibrational spectra demonstrate that O_2 molecules adsorb dissociatively on Si(111)-(7 × 7) at 82 K, which gives rise to ν_1 and ν_2, and the molecularly adsorbed state (labeled as ν_3) exists only after the surface is thoroughly oxidized.

The chemical configurations of the reaction products are determined by comparing our vibrational spectra with those predicted by the recent theoretical calculations [12]. ν_1 is assigned to the stretch mode of the SiO with an O atom bonding on top of the Si adatom, and the initial product is identified as the ad-ins structure which is depicted in Fig. 3, where "ad" denotes an O atom bonding on top of the Si adatom and "ins" denotes an O atom inserted into a backbond of the Si adatom. The theory predicted the Si-O(ad) stretch mode at 143 meV and the Si-O(ins)-Si stretch mode at 79 and 103 meV. The Si-O(ins)-Si unit in the ad-ins structure can be represented by the C_s point group, and thus, there exist two symmetric modes with respect to the mirror plane. The 103 meV mode mainly involves the motion of O(ins) along the Si-O(ins)-Si bond direction, while the 79 meV mode mainly involves the motion perpendicular to the bond [12]. We assign the observed loss at 80 meV to the latter, whereas the former is not resolved in our spectra, which may be due to the relatively small dynamic dipole moment induced by the excitation.

After annealing the surface to 200 K, ν_1 disappears, indicating the reaction of the ad-ins product by thermal activation. The new product exhibits a loss at 80 meV [Fig. 1(c′)], and is identified as the ins-ins species (Fig. 3). The ins-ins structure is also represented by the C_s point group, and the two O(ins) atoms are coupled and give
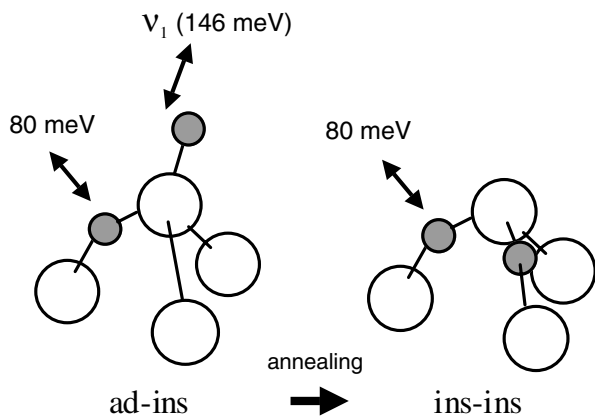

FIG. 3. Schematic models of the initial oxidation products on Si(111)-(7 × 7). The Si and O atoms are depicted by the open and closed circles, respectively. The O_2 molecules dissociate on the surface and forms the metastable ad-ins structure (left) at 82 K. Upon thermal activation at 200 K, the ad-ins species is transformed to the ins-ins structure (right). The observed vibrational energies are shown with the atomic motions depicted by the arrows.

three symmetric modes. Among these, the vibrational energy of the motion perpendicular to the Si-O(ins)-Si bond is predicted to be 78 meV [12], to which the observed loss (80 meV) is assigned. The peak shift upon the reaction is so small (1 meV by the theory) that it is not observed. Although there are now twice as many O(ins) atoms, the intensity of the 80 meV peak does not increase; the presence of an O(ad) atom may affect the dynamic dipole moment for the motion of O(ins) atom. The theory showed that the ad-ins structure is thermally metastable and is the sole candidate for the precursor to the stable ins-ins structure [11], which is in agreement with our results.

With increasing exposure, we observe the development of ν_2 accompanied with the 129 meV peak. We attribute ν_2 to a further oxidized product of the ad-ins species, most probably with the ad-ins × 3 structure [12]. The 129 meV peak is attributed to O(ins) of the further oxidized products. At 0.07 L [Fig. 1(e)], mainly two species (ad-ins and tentatively ad-ins × 3) coexist on the surface. Beyond 0.2 L [1(g) and 1(h)], the ν_1 peak is attenuated, indicating that the surface is fully oxidized (note: exposures correspond to the background pressure, not the local pressure at the Si surface). The peak broadenings indicate the inhomogeneity of the oxidized surface with various O(ins) configurations.

The molecular adsorbate is observed after prolonged oxidation of the surface. ν_3 is not correlated with the superoxy species observed, e.g., at 128 meV on Pd(111) [26], but with the condensed (physisorbed) O_2 at 195 meV [7]. Thus, the ν_3 is ascribed to the nearly neutral O_2 species weakly chemisorbed on Si(111). Chemisorbed O_2 on Si(111) has attracted considerable attention from many researchers [1–9,14,15,17–20], and it was recently shown that the molecular state is not a precursor in the oxidation process but a secondary product on the oxidized Si(111) [18–20], which is consistent with our results.

An STM image of Si(111)-(7 × 7) exposed to O_2 at 78 K is shown in Fig. 4(a). The image is taken at 0.7 V sample bias and 0.2 nA tunneling current. In the initial stage of the oxidation, the ad-ins product is mainly present on the surface. The STM image shows that the Si adatoms are reacted and observed as dark features compared to the unreacted Si adatoms. This is consistent with the theoretical prediction that the ad-ins species exhibits a dark image [11].

STM-induced reaction of the ad-ins species is demonstrated in Figs. 4(b)–4(d). The ad-ins products (dark features) on the corner adatom sites are shown in Fig. 4(b), imaged at the sample bias of 0.7 V. To induce the reaction, the area is scanned with the sample bias at 1.2 V. After the 1.2 V scanning, the area is imaged with the sample bias at 0.7 V, which is shown in Fig. 4(c). The dark features are found to disappear and look similar to the unreacted Si adatoms, indicating that the ad-ins species have reacted. The same area is imaged at the sample
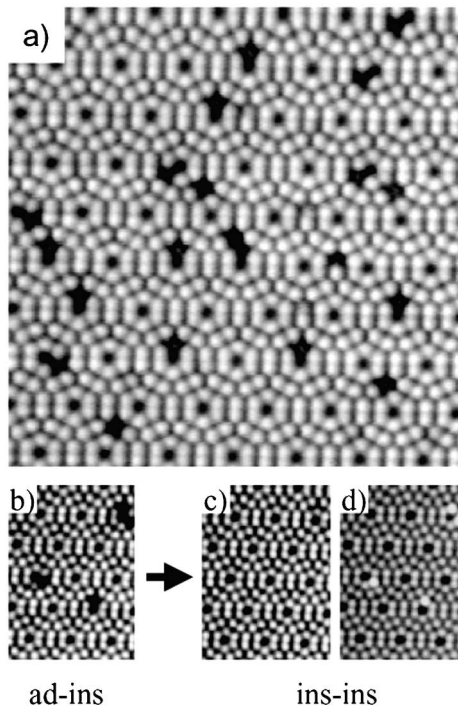
FIG. 4. (a) Topographic STM image of the initial oxidation products on Si(111)-(7 × 7) at 78 K. The image is taken at 0.7 V sample bias and 0.2 nA tunneling current. The reacted sites (ad-ins species) appear darker than the unreacted Si adatoms. (b)–(d) A series of STM images which demonstrate the conversion of the dark sites (ad-ins species) to the stable bright sites (ins-ins species). After imaging the dark sites at 0.7 V and 0.2 nA (b), the area is scanned at 1.2 V and 0.2 nA. Then the area is recorded at 0.7 V and 0.2 nA, which is shown in (c). The scanning at 1.2 V induces the reaction of the dark sites. The same area is recorded at 1.8 V and 0.2 nA (d), where it is found that the dark sites observed in (b) convert to the bright sites (ins-ins species) by the 1.2 V scan. The ins-ins products appear bright only when imaged at the sample bias higher than ~1.8 V.

bias of 1.8 V, which is shown in Fig. 4(d). The reacted sites appear bright when imaged at the sample bias higher than ~1.8 V, and are stable with further scanning. In the room-temperature measurements, we observe that the bright sites are present mainly on the surface, as reported by the previous experiments [13–16]. The EELS shows that the ad-ins species is thermally metastable and transforms into the ins-ins structure above 200 K. Thus, we assign the bright site to the ins-ins product. These results indicate that the high-bias STM induces the reaction of the ad-ins species to the ins-ins product.

In summary, we identify the initial oxidation products on Si(111)-(7 × 7) at 82 K as the ad-ins species and rule out the molecular adsorption by isotope-labeled vibrational spectroscopy with $^{16}O_2$, $^{18}O_2$, and $^{16}O\,^{18}O$. The ad-ins product is thermally metastable and reacted to form the ins-ins structure at 200 K. In the STM topo-

graphic images, the ad-ins products appear dark compared to the unreacted Si adatoms. We show that the reaction of the ad-ins product to the stable ins-ins structure can be readily induced by the STM.

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