Observation of two metastable oxygen species adsorbed on a Si(111)-(7×7) surface: Reinterpretation of the initial oxidation process

Kazuyuki Sakamoto,[1,2,*] H.M. Zhang,[2] and R.I.G. Uhrberg[2]

[1]*Department of Physics, Graduate School of Science, Tohoku University, Sendai, 980-8578, Japan*
[2]*Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden*

Using high-resolution core-level photoemission measurements, we show that two different metastable species exist on a Si(111)-(7×7) surface, instead of only one as suggested in the literature. One metastable species has a finite lifetime and is composed of both molecular and atomic oxygen. The other one, which is formed by atomic oxygen only, is stable in terms of time at 300 and 100 K but disappears after annealing at 600 K. The present study reconciles the inconsistent former results and provides a detailed atomic-level understanding of the complex initial oxidation process of this surface.

I. INTRODUCTION

The production of nanoscale devices is one of the most important subjects in the electronics industry. However, although some molecules—e.g., fullerenes and carbon nanotubes—have been suggested as good candidates for nanoscale metallic and semiconducting structures, nanoscale dielectric materials, which are essential for the production of such devices, have not been developed so far. One candidate for such a dielectric material is a silicon dioxide film whose surface area is nanoscale. In order to understand and control the formation of this nanoscale material, it is important to know how the silicon oxidation proceeds at *an atomic level*. The details of the oxidation process have been in the focus of experimental and theoretical investigations over the last two decades, motivated by the fundamental interest in the oxidation processes of materials. At present, a layer-by-layer oxidation process is known to take place through a barrierless dissociation of oxygen molecules without any metastable species on a Si(001)-(2×1) surface,[1,2] whereas the oxidation process of a Si(111)-(7×7) surface has not been determined so far. The difficulty to completely explore the oxidation process on a Si(111)-(7×7) surface is due to the fact that the oxidation progresses via metastable species.

A metastable species was suggested to form by adsorption of molecular oxygen on a Si(111) surface, on which oxygen atoms are already adsorbed.[3–7] These reports indicate that metastable oxygen is formed by a secondary reaction process and that the oxidation path should be different from the paths suggested based on the metastable species as a precursor with either molecular paul[8–22] or atomic ins-ad and ins×3-ad configurations[23–25] (Fig. 1) in the former studies. The "paul" configuration corresponds to an oxygen molecule adsorbed on top of an adatom of the dimer-adatom-stacking fault structure[26] of the Si(111)-(7×7) surface, and "ad" and "ins" denote an oxygen atom bonding on top of an adatom and an oxygen atom inserted into its back bond, respectively. However, quite recently, the presence of different metastable species at different temperatures was proposed.[27] The presence of more than one metastable species indicates the necessity to consider a more complicated oxidation path and,

therefore, calls for an urgent and careful investigation of the following two questions. (1) *How many metastable-oxygen-containing species* exist on the Si(111)-(7×7) surface? (2) What are their *bonding configurations*? The answers to these questions are indispensable in order to achieve a breakthrough in the atomic-level understanding of the initial oxidation process of Si(111)-(7×7) surface.

In this paper, we present time-resolved high-resolution O $1s$ core-level and valence-band measurements of oxygen adsorption and reaction on a Si(111)-(7×7) surface. High-resolution core-level spectroscopy provides stringent spectroscopic criteria for a correct structural model. Among the six O $1s$ components observed in the core-level spectra, three of them originate from an oxygen species that has finite lifetimes at 300 and 100 K. Further, one of the three O $1s$ components, which is stable in terms of time at 300 and 100 K, disappears after annealing the sample at 600 K. This indicates the presence of a second metastable species. Taking the O $1s$ relative binding energies of the metastable components and the valence-band results into account, we have determined the bonding configurations of the two metastable
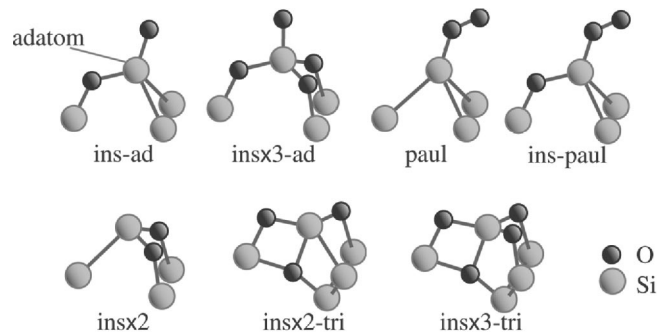

FIG. 1. Bonding configurations of the metastable and stable oxygen species discussed in the text. The large gray circles represent Si adatoms and first- and second-layer Si atoms situated below an adatom of a Si(111)-(7×7) surface, and the small black circles are oxygen atoms. "paul" indicates a molecular oxygen adsorbed on top of an adatom, and "ad" and "ins" correspond to an O atom bonding on top of a Si adatom and to an O atom inserted into its back bond, respectively. "tri" denotes an O atom bonding between the first- and second-layer Si atoms.

species. These results reconcile the former inconsistent results on the metastable oxygen species and provide a detailed atomic-level understanding of the complex oxidation process of a Si(111)-(7×7) surface.

II. EXPERIMENTAL DETAILS

The high-resolution core-level and valence-band photo-emission measurements were performed at beamline I311 at the MAX-II synchrotron radiation facility in Lund, Sweden. The photoemission spectra were obtained with an angle-integrated photoelectron spectrometer with an acceptance angle of 15°. The total energy resolution was ~230 meV at a photon energy ($h\nu$) of 665 eV and ~60 meV at $h\nu$ =40 eV. The base pressure was below 7×10^{-11} Torr during the room-temperature measurements and below 4×10^{-11} Torr when low-temperature measurements were done. The Si(111) sample, cut from an Sb-doped (n-type) Si wafer, was annealed at 1520 K for 3 sec in a vacuum chamber to obtain a clean surface. After the annealing, a sharp 7×7 low-energy electron diffraction pattern was observed, and neither the C 1s nor the O 1s peak was detected in the core-level spectra before oxygen exposure.

III. RESULTS AND DISCUSSION

In order to investigate the difference in adsorbed oxygen species at different temperatures and to investigate the possibility of the presence of other metastable species, we have measured (i) the O 1s core levels of Si(111)-(7×7) surfaces just after 10 Langmuir (1 L=1×10^6 Torr×s) O$_2$ exposures at 300 and 100 K [Fig. 2(a)], (ii) the O 1s core level and valence band of oxygen adsorbed Si(111)-(7×7) surfaces 2 h after a 20-L exposure at 300 K, and (iii) the same spectra after annealing the 20-L-exposed surface at 600 K [Fig. 2(b)]. The O 1s core-level spectra were recorded using $h\nu$ =665 eV, and the valence-band spectra were recorded using $h\nu$=40 eV. In order to identify the O 1s components that contribute to the spectral shapes and to relate them to the bonding configuration of adsorbed oxygen species, we have analyzed the spectra by a standard least-squares-fitting method using Voigt line shapes. The solid lines overlapping the data points (open circles) are the fitting results obtained using the binding energies and Gaussian and Lorentzian widths of the components as variable parameters. A 200-meV full width at half maximum (FWHM) was used for the Lorentzian contribution of all O 1s components that are shown below the spectra. This value agrees well with the Lorentzian broadening estimated by the lifetime of the O 1s core hole; i.e., a lifetime of 3 fs (Ref. 28) leads to a Lorentzian FWHM of approximately 200 meV based on the Heisenberg uncertainty principle. Regarding the Gaussian widths, 925 and 875 meV FWHM were used for the O 1s components at 300 K and 100 K, respectively. The origin of different Gaussian widths at 300 K and 100 K should be the temperature-dependent phonon broadening. From the results of the fitting procedure, we realize that each spectrum recorded just after the exposure [Fig. 2(a)] consists of six O 1s components, whose relative binding energies are −4.4,
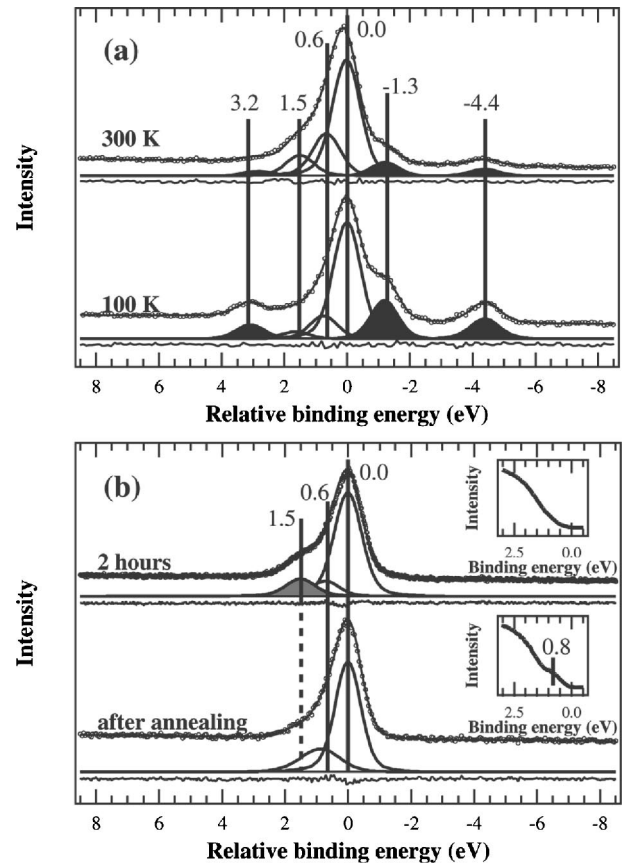

FIG. 2. (a) O 1s core-level spectra of Si(111)-(7×7) surfaces exposed to 10 L O$_2$ at 300 and 100 K. (b) O 1s core-level spectra recorded 2 h after a 20-L O$_2$ exposure on a Si(111)-(7×7) surface at 300 K and after annealing this surface at 600 K. The open circles are the experimental data, the solid lines overlapping the open circles are the fitting results that are obtained using the components shown below each spectrum, and the solid line at the bottom of each spectrum is the residue. The zero of the relative binding energy is taken at the position of the main peak in each O 1s core-level spectrum. The insets in (b) show the valence-band spectra recorded 2 h after exposing a Si(111)-(7×7) surface to 20 L of O$_2$ and after annealing the surface. O 1s core-level spectra and valence-band spectra were recorded using $h\nu$=665 eV and 40 eV, respectively.

−1.3, 0.0, 0.6, 1.5, and 3.2 eV. Since these components are present in both 300 and 100 K spectra, we conclude that the bonding configurations of the adsorbed oxygen species are identical in the two cases. The difference in the relative intensities indicates, however, that the relative abundance of the different oxygen species is different at the two temperatures.

Among the six O 1s components, the intensities of the −4.4, −1.3, and 3.2 eV components decrease after the exposure was stopped, whereas the intensities of the components at 0.0, 0.6, and 1.5 eV do not show any decrease at 300 and 100 K. These indicate that the −4.4, −1.3, and 3.2 eV components are metastable, and the other three components are stable with time at both temperatures. Regarding the three metastable components, their relative intensities are the same ($I_{-4.4\ eV}:I_{-1.3\ eV}:I_{3.2\ eV}=2:3:1$) at both temperatures. Further, these three components have the same lifetime and

their intensities saturate at the same dosage at a given temperature. The lifetime and saturation dosage at the two temperatures were 20 min and 2 L at 300 K and 300 min and 0.5 L at 100 K, respectively. This indicates that the -4.4, -1.3, and 3.2 eV components originate from one and the same metastable species. Thus one can conclude that the bonding configuration of this species should contain three oxygen atoms with rather different chemical environments. Since the ins$\times n$-paul oxygen species is the only bonding configuration that contains three oxygen atoms with different chemical environments among the proposed configurations, we conclude that ins$\times n$-paul is the only configuration, at both 100 and 300 K, of the metastable species. Here, we notice that $I_{-4.4\,eV}:I_{-1.3\,eV}:I_{3.2\,eV}$ shows a photon energy dependence and, thus, does not represent the relative number of the oxygen atoms due to the diffraction effect.[29] Moreover, the time-dependent increases in intensities of the 0.0, 0.6, and 1.5 eV O 1s components observed after stopping the exposure indicates that the reaction of the ins$\times n$-paul species produces the three other O 1s components.

As shown in Fig. 2(b), a structure is clearly observed at 1.5 eV together with the main peak at 0.0 eV, and none of the components originating from the ins$\times n$-paul oxygen is recognized in the O 1s core-level spectrum recorded 2 h after the exposure. The fact that the O 1s components at -4.4, -1.3, and 3.2 eV are invisible results from the finite lifetime of the ins$\times n$-paul species; i.e., only $100\times\exp(-2\times60/20)$ $=0.25\%$ of the ins$\times n$-paul oxygen exists 2 h after the exposure. By analyzing this spectrum, we realize the presence of the 0.6 eV component, and thus that the three components which are stable in terms of time at 300 and 100 K contribute to the shape of the spectrum.

After annealing the 20-L O$_2$-exposed surface at 600 K, the 1.5-eV structure disappears. The disappearance of this O 1s component indicates the existence of *a second oxygen species*. The presence of this second metastable species suggests that the origin of the inconsistency reported in the former study is the unfounded assumption used in the literature; i.e., only one species, which is metastable in terms of both time and temperature, exists on the Si(111)-(7$\times$7) surface. In the valence-band spectra shown in the inset of Fig. 2(b), a new peak appears at a binding energy of 0.8 eV after the 600 K annealing. The binding energy of the dangling bond state of an adatom with one or more atomic oxygen adsorbed into its back bond—i.e., the dangling bonds of the ins$\times n$ configuration—was reported to be between 0.5 and 0.8 eV.[4,7,21,22,30] Thus, the change observed after the 600 K annealing indicates that the origin of the 0.8-eV peak is the dangling bonds of the ins$\times n$ configurations and the 1.5 eV component observed in the core-level spectra before annealing originates from oxygen species adsorbed on top of adatoms. Taking into account that no molecular species exists in the spectrum recorded 2 h after exposure and that no oxygen atom can adsorb on the top site of an adatom if there is no oxygen atom in a back bond,[21,30] we conclude that the bonding configuration of the second metastable species is "ins$\times n$-ad."

A complete atomic-level understanding of the oxidation of a Si(111)-(7$\times$7) surface can only be obtained by deter-
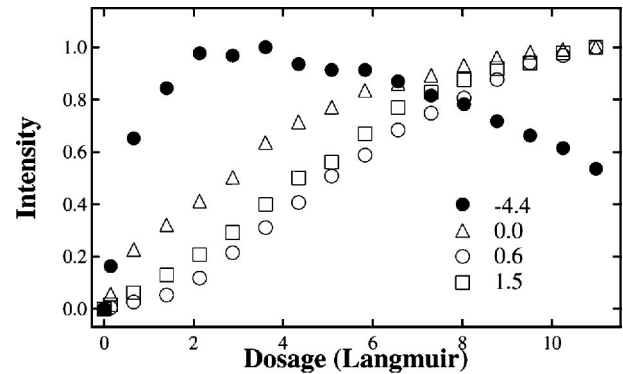

FIG. 3. Dosage-dependent intensities of the -4.4, 0.0, 0.6, and 1.5 eV O 1s components at 300 K. The intensity of each component is normalized to its maximum intensity.

mining the origins of the two other O 1s components at 0.0 and 0.6 eV. As stated above, the intensities of these two components increase after the exposure was finished, and one can therefore conclude that they are produced by the decay of the metastable ins$\times n$-paul species. Regarding the dosage-dependent intensities of these two components, the increase rates are different, especially at the initial oxidation stage as shown in Fig. 3, which is obtained by continuously measuring photoemission spectra of the Si(111) surface exposed to an ambient O$_2$ pressure of 5×10^{-9} Torr. That is, the intensity of the 0.0 eV component shows a steeper increase than the 0.6 eV component at dosages below 2 L. Here, we notice that the lengths of error bars of the 0.0 and 0.6 eV components are shorter than the size of the marks used in Fig. 3. Since the adatom back bonds are the preferable adsorption sites at the initial stage of oxidation,[21,30] the steep increase at small dosages indicates that the origin of the 0.0 eV component is the "ins" oxygen. Moreover, taking into account that the spectrum of the annealed surface is well reproduced by using the two O 1s components at 0.0 and 0.6 eV and that the ins and tri oxygen species were reported to be the most thermally stable species,[23,24] we attribute the origin of the 0.6 eV component to the "tri" oxygen.

The intensities of the two components observed after the annealing were slightly larger than the intensities of the 0.0 and 0.6 eV components of the spectrum recorded 2 h after the oxygen exposure. This means that the thermal reaction of the ins$\times n$-ad oxygen produces both ins$\times n$ and ins$\times n$-tri configurations. In case of considering the oxidation process that progresses through the two metastable oxygen species, the bonding configuration of the second metastable species should be ins$\times 2$-ad or ins$\times 3$-ad, and not ins-ad, since it is produced by the ins$\times n$-paul species that contains more than three oxygen atoms. Moreover, taking into account that the ins$\times 3$-ad oxygen can only produce the ins$\times 3$-tri species, whose adatom is bonded with four oxygen atoms and thus has no dangling bond, the second metastable species should be ins$\times 2$-ad in this case. Based on these conclusions, we propose two oxidation processes of the Si(111) surface, which make progress through the two metastable oxygen species (Fig. 4). The first process is "clean$\rightarrow$ins $\rightarrow ins$-$paul\rightarrow ins\times 2$-$ad\rightarrow$ins$\times 3$ and ins$\times 2$-tri." In this
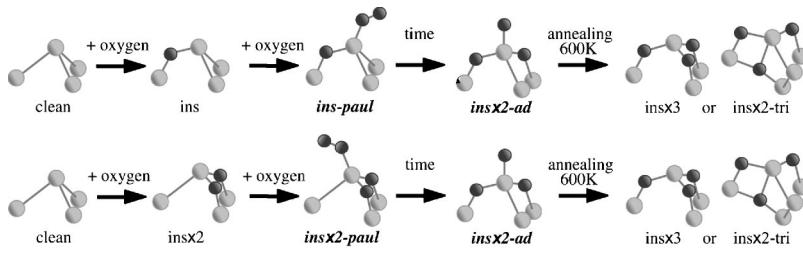
FIG. 4. Initial oxidation processes of the Si(111) surface, which progress through the two metastable oxygen species. Configurations written in italic letters indicate the metastable species.

process, the ins species would be formed by a site hopping of an oxygen atom; i.e., the ad oxygen of the ins-ad configuration, which is formed by the reaction of an oxygen molecule on a clean surface for example, hops to another adatom site and forms two ins configurations at the very initial stage of oxidation. The second process is "clean→ins×2→ins ×2-paul→ins×2-ad→ins×3 and ins×2-tri." The ins ×2-paul→ins×2-ad reaction in this process might result from the hopping of one oxygen atom of the paul species to another adatom site. According to these oxidation processes, it is quite clear that dangling bonds play an essential part in the oxidation process of a Si(111) surface since both metastable species contain oxygen adsorbed at the on top site. This suggests that a silicon dioxide film with a surface area in the nanoscale, for instance, can be achieved by preparing a surface with free dangling bonds in that area while the dangling bonds of the other part of the surface are terminated by hydrogen atoms.

Finally, we discuss the different relative intensities of the six components, which were $I_{-4.4 \text{ eV}}:I_{-1.3 \text{ eV}}:I_{0.0 \text{ eV}}:I_{0.6 \text{ eV}}:I_{1.5 \text{ eV}}:I_{3.2 \text{ eV}} = 0.08:0.13:1.00:0.39:0.28:0.04$ at 300 K and 0.22:0.34:1.00:0.21:0.09:0.11 at 100 K in Fig. 2, and the origin of the failure to observe the ins×n-paul species at 300 K in the literature. As shown in Fig. 3, the intensity of the −4.4 eV component decreases continuously after the saturation at around 2 L. The clear decrease observed above 2 L results from the relatively short lifetime of the ins×n-paul species at 300 K (1/15 of the lifetime at 100 K). At 100 K, the intensities of the ins×n-paul components hardly decrease. Since a shorter lifetime gives a smaller relative number of ins×n-paul oxygen after a certain time, we conclude that the different relative intensities of the six O 1s components observed at different temperature result from the temperature-dependent lifetime. Moreover, taking into account that the present result was obtained by continuously measuring photoemission spectra of the Si(111) surface exposed to O_2, the decrease in intensity of the −4.4 eV com-

ponent suggests that the failures to observe the ins×n-paul species at 300 K in the literature originate from the time lag between the completion of O_2 exposure and the data acquisition.

IV. CONCLUSION

In conclusion, the present photoelectron measurements indicate that two different metastable species exist on an oxygen-exposed Si(111)-(7×7) surface. The observation of two different metastable species reconciles the inconsistency reported in the former studies, in which the presence of only one metastable oxygen species was suggested. Of the two metastable species, one has finite lifetimes at 300 and 100 K and the other disappears at 600 K. Based on the relative binding energies of the time-dependent species, we conclude that it corresponds to the ins×n-paul configuration. From the disappearance of one O 1s component in the core-level spectra and the appearance of a new peak in the valence-band spectra after annealing the sample at 600 K, the bonding configuration of the second metastable species is concluded to be ins×n-ad. Based on the origins and the bonding configurations of the two metastable oxygen species, we proposed two models that explain the complex oxidation process of the Si(111) surface on an atomic level. Further, the observation of six O 1s components at relative binding energies of −4.4, −1.3, 0.0, 0.6, 1.5, and 3.2 eV at both 300 and 100 K suggests that the bonding configurations of the oxygen species are identical at both temperatures.

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*Electronic address: sakamoto@surface.phys.tohoku.ac.jp

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