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## Adsorption process of metastable molecular oxygen on a Si(111)-(7×7) surface

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The adsorption process of metastable molecular oxygen on a Si(111)-(7×7) surface is studied by ultraviolet photoelectron spectroscopy. At 120 K, three metastable states at 2.1, 3.8, and 5.1 eV grow up simultaneously following the decrease of the back-bond state as the dosage increases. After annealing at 600 K, we observed an unusual state attributed to the dangling bond. These results and the symmetries of the molecular orbitals lead to a conclusion that the metastable molecular species is adsorbed on top of an adatom stabilized by a coadsorbed atomic oxygen into the back bond. [S0163-1829(99)51636-6]

The initial stage of oxygen adsorption on silicon surfaces has been a topic of experimental and theoretical investigations, due to the technological importance of silicon oxides in the semiconductor device. However, the complex geometric and electronic structures of the silicon surfaces hinder the acquirement of a unique identification on the adsorbed structure and the reaction process on the silicon surfaces.

One of the most important issues of the initial chemisorption stage is the presence of the metastable oxygen adsorbed on the Si(111)-(7×7) surface, whose reported lifetime at 300 K varies from approximately 10 min (Refs. 1–3) to several hours.<sup>4–9</sup> The first observation of the metastable species was done using high-resolution electron-energy-loss spectroscopy (HREELS).<sup>10</sup> The result shows that the metastable species is a molecular species so-called “molecular precursor” that is chemisorbed with a “peroxy radical” configuration, as shown in Fig. 1. In the early ultraviolet photoemission spectroscopy (UPS) measurement,<sup>1,2</sup> the metastable states, which are extinguished after a 400 K annealing, are observed at binding energies of 2.1 and 3.9 eV in the valence spectra. These two states are ascribed to the O<sub>2</sub> π<sub>g</sub> derived orbitals with a “bridge” configuration from the theoretical calculations.<sup>11,12</sup> In the recent UPS studies,<sup>4–6,13</sup> the metastable state is observed at 3.8 eV,<sup>4,13</sup> and at 3.8 and 5.1 eV.<sup>5,6</sup> Based on the tight-binding (TB) calculations,<sup>14,15</sup> the 3.8-eV peak is ascribed to the π<sub>g</sub> derived orbitals with a “peroxy radical” configuration. The 5.1-eV peak is attributed to a second metastable species that has a “bridge” configuration from the polarization-dependent measurements.<sup>5,6</sup> Thus, the observation of the 5.1-eV peak suggests the existence of two different metastable species. Quite recently, a density-functional theory calculation shows that the metastable oxygen has an atomic configuration, i.e., no molecular species exists on the Si(111)-(7×7) surface, and suggests the “ad-ins” configuration.<sup>16</sup> The “ad” denotes an O atom bonding on top of the Si adatom and “ins” an O atom inserted into the back bond of a Si adatom as shown in Fig. 1. Up to now, despite the large number of experimental results and theoret-

ical calculations, the fundamental problem concerning the adsorption of oxygen on a Si(111)-(7×7) surface, in particular the origins of the metastable states observed in UPS and the configuration of the metastable oxygen, is still uncertain.

In this paper, we present the observation of three metastable oxygen states in one valence spectrum. The binding energies of these states are 2.1, 3.8, and 5.1 eV. Measuring the dosage-dependent intensities of these three states, we consider the metastable species to be a molecular oxygen stabilized by an atomic oxygen inserted into the back bond. The metastable states at 2.1 and 3.8 eV are ascribed to the O<sub>2</sub> π<sub>g</sub> derived orbitals, and the 5.1-eV peak as the O<sub>2</sub> π<sub>u</sub> derived one from the polarization dependent measurement and the semiempirical molecular orbital calculation.

The experiments were performed on the beamline BL-7B at the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan. An angle-resolved photoelectron spectrometer with a total-energy resolution of 150 meV at a photon energy of 21.2 eV and angular resolution of ±1°, was used for all UPS measurements. The analysis chamber was also equipped with a low-energy electron diffraction (LEED) system, an Auger-electron spectrometer (AES), and a quadrupole mass spectrometer (QMS). The base pressures were below 1 × 10<sup>-10</sup> Torr.

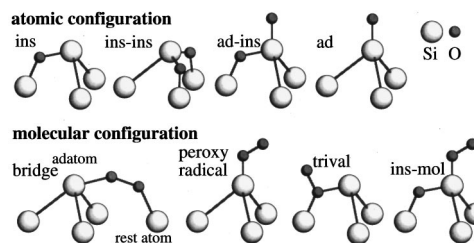


FIG. 1. Schematic illustration of the atomic and molecular configurations of oxygen adsorbed on a Si(111)-(7×7) surface.

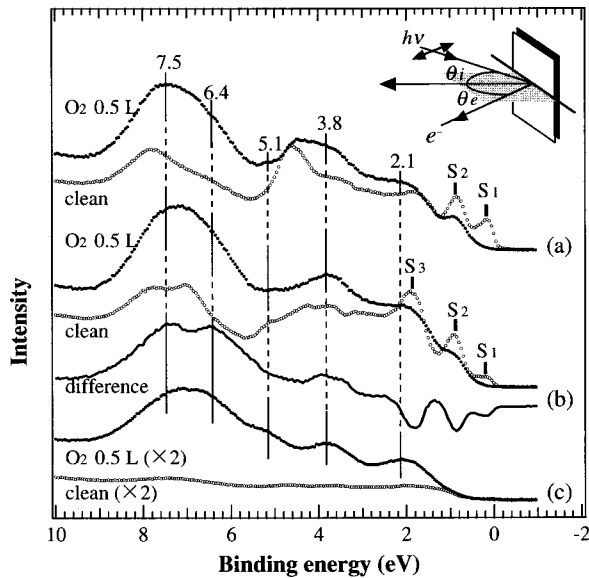


FIG. 2. UPS spectra of a Si(111)-(7 $\times$ 7) clean surface and the surface exposed to O<sub>2</sub> gas for 0.5 L. The open and filled circles represent the clean and oxygen adsorbed surfaces, respectively. (a) are recorded with geometry of ( $\theta_i=45^\circ$ ,  $\theta_e=15^\circ$ ), (b) ( $\theta_i=45^\circ$ ,  $\theta_e=20^\circ$ ), and (c) ( $\theta_i=0^\circ$ ,  $\theta_e=60^\circ$ ). The solid line in (b) is the subtracted spectrum of the surface covered with 0.5 L of oxygen and the clean surface. The inset shows the definition of  $\theta_i$  and  $\theta_e$  as well as the polarization of the SR light.

The Si(111) sample, cut from P-doped (*n*-type) Si wafers, has an electrical resistivity of 10 $\Omega$  cm and a size of 5 $\times$ 20 $\times$ 0.5 mm<sup>3</sup>. To obtain the clean reconstructed Si(111)-(7 $\times$ 7) surface, we heated up the chemically prepared sample to 1520 K for 3 s by direct resistive heating in the UHV chamber. We checked the quality of the surface structure by the observation of a clear (7 $\times$ 7) LEED pattern and verified the cleanliness by AES. The Si(111)-(7 $\times$ 7) sample was cooled down to 120 K using liquid N<sub>2</sub>, and then exposed to the O<sub>2</sub> gas to avoid the time-dependent attenuation of the metastable species at 300 K. No additional H<sub>2</sub>O and CO was detected by QMS during the exposure of O<sub>2</sub> gas. All measurements were done at 120 K.

UPS spectra were obtained by three different measurement geometries using the linearly polarized synchrotron radiation (SR) light of  $h\nu=21.2$  eV. The definition of the incident angle of the light ( $\theta_i$ ) and the emission angle of the photoelectron ( $\theta_e$ ) are shown in the inset of Fig. 2 as well as the polarization of the SR light. Taking into account the previous angle-resolved UPS study,<sup>17</sup> we adopted the geometries of ( $\theta_i=45^\circ$ ,  $\theta_e=15^\circ$ ) and ( $\theta_i=45^\circ$ ,  $\theta_e=20^\circ$ ) to observe clearly the behavior of the surface states against the oxygen adsorption. We also used the geometry ( $\theta_i=0^\circ$ ,  $\theta_e=60^\circ$ ) for the observation of the oxygen-induced states because the substrate features are very small at this condition. To obtain information on the polarization, the geometry ( $\theta_i=45^\circ$ ,  $\theta_e=15^\circ$ ) is used to the *p*-polarized measurement, and ( $\theta_i=0^\circ$ ,  $\theta_e=60^\circ$ ) to the *s*-polarized one.

Figure 2 shows the valence spectra of the Si(111)-(7 $\times$ 7) clean and O<sub>2</sub> gas exposed surfaces with different geometries. The amount of O<sub>2</sub> exposure is 0.5 langmuir (L). (a), (b), and (c) are measured with the geometries of ( $\theta_i=45^\circ$ ,  $\theta_e=15^\circ$ ), ( $\theta_i=45^\circ$ ,  $\theta_e=20^\circ$ ), and ( $\theta_i=0^\circ$ ,  $\theta_e=60^\circ$ ), respectively.

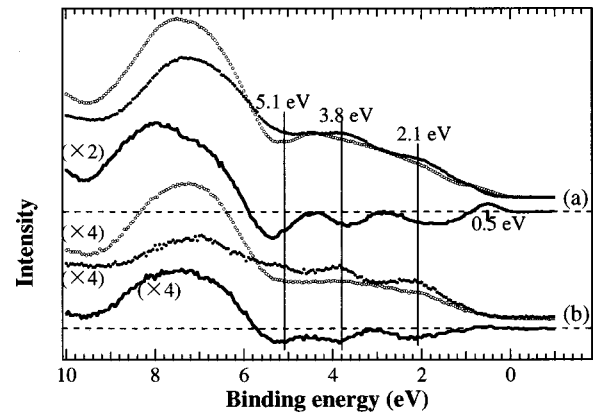


FIG. 3. UPS spectra of the Si(111)-(7 $\times$ 7) surface exposed to O<sub>2</sub> at 120 K (filled circles), those after annealing the sample at 600 K (open circles), and the subtracted spectra (solid lines). (a) is recorded for a Si(111)-(7 $\times$ 7) surface exposed with 10.0 L of O<sub>2</sub> in a geometry of ( $\theta_i=45^\circ$ ,  $\theta_e=15^\circ$ ), and that in (b) for a Si(111) surface exposed with 0.3 L of O<sub>2</sub> in a geometry of ( $\theta_i=0^\circ$ ,  $\theta_e=60^\circ$ ).

All spectra are normalized with the photon flux that is estimated from the photocurrent at the sample. For the clean surface, the surface states are clearly observed at  $S_1=0.2$  and  $S_2=0.9$  eV in (a), and  $S_2=0.9$  and  $S_3=1.8$  eV in (b). The states of  $S_1$ ,  $S_2$ , and  $S_3$  are mainly due to the dangling bond of the adatom, that of the rest atom, and the back bond of the adatom of the dimer-adatom-stacking fault structure.<sup>18</sup> After O<sub>2</sub> gas exposure, the intensities of the surface states decrease and oxygen-induced new states appear at 2.1, 3.8, 5.1, 6.4, and 7.5 eV. Especially, the 2.1-, 3.8-, and 5.1-eV peaks are clearly observed in one spectrum (c). The 6.4- and 7.5-eV peaks are observed after subtracting the spectrum of the clean surface from that of O<sub>2</sub> gas exposed surface as shown in (b).

Figure 3 displays the UPS spectra of the O<sub>2</sub> adsorbed Si(111)-(7 $\times$ 7) surface at 120 K and after annealing at 600 K. The subtracted spectra are to show clearly the annealing effect. The O<sub>2</sub> exposures are 10.0 L and 0.3 L in (a) and (b), respectively. The geometries are ( $\theta_i=45^\circ$ ,  $\theta_e=15^\circ$ ) and ( $\theta_i=0^\circ$ ,  $\theta_e=60^\circ$ ) in (a) and (b). In both cases, the 2.1-, 3.8-, and 5.1-eV peaks disappear after annealing and the intensities of the peaks around 7.0 eV increase. Since the metastable oxygen is quenched at 400 K and the stable one is observed at 700 K,<sup>1-3,10,19,20</sup> the disappearances of the 2.1-, 3.8-, and 5.1-eV peaks suggest the origins of these peaks to be the metastable species, and the increments of the peaks around 7.0 eV suggest their origins as the stable one. The stable oxygen atoms have the ‘‘ins’’ and/or ‘‘ins-ins’’ configurations as shown in Fig. 1.<sup>1-10,13,16,19,20</sup> The disappearance of the 2.1-, 3.8-, and 5.1-eV peaks indicates that three metastable states are observed simultaneously in Fig. 2(c). Taking into account the observation of only one metastable state at 3.8 eV in Figs. 2(a) and 2(b), the observations of one or two metastable states in the previous UPS spectra<sup>1,2,4-6</sup> are due to the complex substrate electronic structure. Moreover, a new state is observed at 0.5 eV in Fig. 3(a).

Although the origins of the 2.1-, 3.8-, and 5.1-eV peaks are suggested individually,<sup>1,2,4-6,13,16</sup> we are not able to explain the three metastable states observed in the present experiment. The previous suggestions are done for only one or

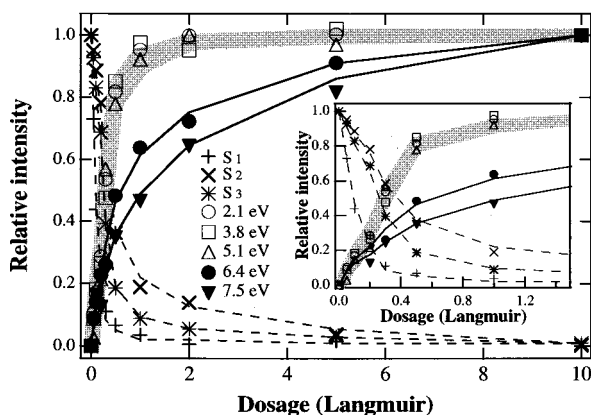


FIG. 4. Dosage-dependent intensities of the surface states and the oxygen-induced states. The intensity of each state, normalized with its maximum intensity, is obtained using the same measurement geometries as those in Figs. 2(a) and 2(b) for the surface states and those in Fig. 2(c) for the oxygen-induced states.

two metastable states observed simultaneously. In order to determine the origins of the three metastable states, we consider the configuration of the metastable species and the polarizations of the peaks. Since the adsorption of oxygen affects the surface electronic structure, we deliberate on the relation between the dosage-dependent intensities of the  $S_1$ ,  $S_2$ , and  $S_3$  states, and those of the 2.1-, 3.8-, 5.1-, 6.4-, and 7.5-eV peaks. The intensities of the surface states and the oxygen-induced states are obtained by first acquiring the subtracted spectra of the sample after  $O_2$  exposure and the clean surface to eliminate the substrate bulk features, and then using Voigt functions and an integrated background to analyze the spectrum by a standard least-squares-fitting method. The result shown in Fig. 4 is obtained using the same measurement geometries as those in Figs. 2(a) and 2(b) for the surface states, and those in Fig. 2(c) for the oxygen-induced states. The inset shows the enlarged figure from 0.0 to 1.5 L. The intensity of each state is normalized with its maximum intensity. With increasing the dosage, the  $S_1$  state disappears immediately at about 0.3 L, and those of the  $S_2$  and  $S_3$  states show decreases until 2.0 and 10.0 L, respectively. For the oxygen-induced states, the intensities of the stable states observed at 6.4 and 7.5 eV change gradually until 10.0 L. On the contrary, those of the metastable states at 2.1, 3.8, and 5.1 eV saturate at 2.0 L. The same dosage dependence in intensity suggests that the three metastable states come from one configuration. The presence of only one configuration is inconsistent with the previous UPS study,<sup>6</sup> in which the existence of two distinct metastable states are suggested by the different relative intensities of the 3.8-eV peaks to the 5.1-eV ones obtained at 30 and 300 K. The origin of the contradiction is due to the change in bond angle at different temperatures as discussed below.

The intensities of the metastable states increase at a dosage where those of the  $S_2$  and  $S_3$  states decrease. The change in intensity in the same dosage region suggests the adsorption of metastable oxygen to be affected with the dangling bond of a rest atom and/or with the back bond of an adatom. Here, we consider that the adsorption of the metastable species has correlation with only the  $S_3$  state, because the  $S_2$  state decreases in intensity even after the saturation of the

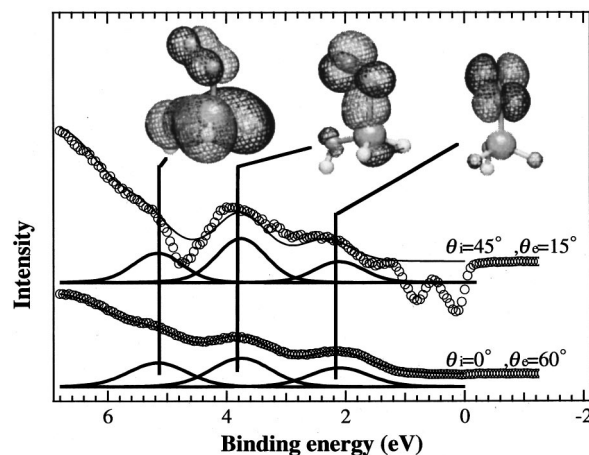


FIG. 5. The subtracted spectra of the Si(111) surface covered with 0.5 L of oxygen and the clean surface in geometries of ( $\theta_i = 45^\circ$ ,  $\theta_e = 15^\circ$ ) and ( $\theta_i = 0^\circ$ ,  $\theta_e = 60^\circ$ ), and the fitting results. Voigt functions and an integrated background are used to analyze the spectra by a standard least-squares-fitting method. The molecular orbitals are calculated by a semiempirical molecular orbital method.

metastable state above 2.0 L. In this case, three configurations are possible for the metastable species, i.e., the “trival,” the “ad-ins,” and the “ins-mol” configurations.

As shown in Fig. 3(a), a new state is observed at 0.5 eV after annealing the sample at 600 K. In the previous UPS study,<sup>1</sup> a state is appeared at 0.9 eV. Considering this binding energy, the metastable species is reported to interact with the dangling bond of a rest atom. In the present experiment, the spectrum of the annealed surface shows also a shoulder at 0.9 eV in Fig. 3(a). However, taking the difference between the spectra obtained before and after annealing, we understand that the binding energy of the new state is lower than that of the rest atom. Moreover, the dosage-dependent measurement suggests that there is hardly any relation between the metastable species and the rest atom. Since the adatom-like surface state of the “ins” and/or “ins-ins” configurations has a binding energy between 0.5 and 0.8 eV,<sup>13</sup> we attribute the new state as the dangling bond state of an adatom that is accompanied with one or two oxygen atoms inserted into the back bond. The appearance of the adatomlike surface state indicates the adsorption site of the metastable species as the on-top site of an adatom. Though the “ad-ins” configuration has an oxygen atom adsorbs on top of an adatom, this configuration is unsuitable. It leads to only two metastable states between 2.1 and 5.1 eV.<sup>16</sup> Hence, we conclude that the configuration of the metastable species is the “ins-mol” one. The presence of the molecular species is consistent with the HREELS results.<sup>9,10,19,20</sup> Furthermore, the large work function change, 0.4 eV for an exposure of 0.5 L, supports the existence of the negatively charged molecular oxygen adsorbed at the on-top site.

In order to measure the polarization dependence of the 2.1-, 3.8-, and 5.1-eV peaks, we have used the same method as that employed to obtain the result shown in Fig. 4. Figure 5 displays the subtracted spectra of the surface exposed with 0.5 L of oxygen and the clean surface, the fitting results, and the orbitals of the “ins-mol”  $O_2$  molecule calculated with a semiempirical molecular orbital method. The intensity ratio

of the 2.1-, 3.8-, and 5.1-eV peaks obtained with the *p*-polarized light to those with the *s*-polarized one are 0.93, 1.31, and 1.04, respectively. The semiempirical calculation shows that the three highest occupied molecular orbitals are composed by the  $p_x$ ,  $p_z$ , and  $p_x$  orbitals of an O atom in order of the binding energies. Here, we define the *z* axis normal to the surface and the *x* one normal to the O-O-Si plane. Considering the polarization dependence of the three metastable states and the components of the calculated molecular orbitals, the 2.1- and 3.8-eV peaks are attributed to the O<sub>2</sub>  $\pi_g$  derived orbitals, and the 5.1-eV peak to the O<sub>2</sub>  $\pi_u$  derived one. Since the O<sub>2</sub>  $\pi_g$  derived orbital at 3.8 eV interacts with the Si dangling bond, this consideration agrees well with the HREELS reports<sup>9,10,19,20</sup> in which the softened O-O stretching mode is considered to be due to the increase of the number of electron in the  $\pi_g$  orbital. Moreover, it is not surprising to consider the presence of “ins-mol” species with different O-O-Si angles, because two “peroxy radical” configurations with different O-O-Si angles are predicted by TB calculation.<sup>15</sup> This difference in angle should lead to different cross sections for the 2.1-, 3.8-

and 5.1-eV peaks. Therefore, we consider that the different relative intensities of the 3.8-eV peaks to the 5.1-eV ones reported previously,<sup>6</sup> might be come from the difference in O-O-Si angle at different temperatures.

In conclusion, we have investigated the initial chemisorption stage of oxygen on the Si(111)-(7×7) surface by UPS. The dosage-dependent intensities of oxygen-induced states, which are observed at 2.1, 3.8, and 5.1 eV, indicate the adsorption of the metastable oxygen has correlation with the back bond of the adatom. Taking into account the observation of the adatomlike surface state observed after annealing the sample at 600 K, we conclude that the metastable species has the “ins-mol” configuration. The 2.1- and 3.8-eV peaks are ascribed to the O<sub>2</sub>  $\pi_g$  derived orbitals, and the 5.1-eV peak to the O<sub>2</sub>  $\pi_u$  derived one from the polarization dependence of the metastable states and the calculated molecular orbitals.

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