

Adsorption of Oxygen on Si(001) Surfaces Studied by Reflection High-Energy Positron Diffraction*

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Structures of Si(001) surfaces in the initial oxidation processes at 110 K have been investigated by reflection high-energy positron diffraction (RHEPD). From the analyses of RHEPD rocking curves for various coverages of oxygen, it is found that the adsorbed oxygen atoms are located on top of the silicon dimer layer and in the dimer back-bonds. The distance between the surface oxygen and the dimer silicon, between the dimer silicon and the back-bond oxygen and between the back-bond oxygen and the bulk silicon is determined to be approximately 1.0 Å, 0.7 Å and 0.7 Å, respectively. The initial oxidation process is discussed from the change of specular spot intensity due to exposing oxygen. [DOI: 10.1380/ejssnt.2006.510]

Keywords: reflection high-energy positron diffraction, Surface structure, morphology, roughness, and topography, Oxidation, Silicon, Silicon oxides

I. INTRODUCTION

The initial oxidation of Si(001) surfaces is an important topic concerning the device applications. One of the most interesting points is how the atomic processes of the oxidation proceed in the surface. It is demonstrated that the adsorbed locations of the oxygen atoms are on the top of the surfaces and in the back-bonds of silicon dimers by positron-annihilation induced Auger electron spectroscopy (PAES) study [1, 2] and by high-resolution Si 2*p* photoemission study [3]. It is theoretically believed that O₂ molecules dissociate on the top of the surfaces and the oxygen atoms migrate into the back-bonds with almost barrierless [4–6]. To reveal the reaction path of the oxidation in detail, it is essential to determine the precise positions of adsorbed oxygen atoms in the initial oxidation process experimentally.

In this work, we report the structures of Si(001) surfaces at 110 K in the initial oxidation process using reflection high-energy positron diffraction (RHEPD) which is quite sensitive to the topmost surface structures [7–10]. We will demonstrate inevitable evidences for the adsorption of oxygen atoms on dimers as well as for the penetration into the back-bonds. Moreover, we will determine the atomic positions of oxygen and silicon atoms in the surface layer.

II. EXPERIMENTAL

Specimens (10×5×0.5 mm³) cut from an n-type Si(001) wafer with a resistivity of 10 Ωcm. These specimens were cleaned in pure ethanol and subsequently transferred to

an UHV chamber. After outgassing at approximately 700 K for several hours, the clean Si(001)-(2×1) surfaces were obtained by heating at 1500 K for 10 s a few times by a direct current flow. The cleaned Si(001) surface were exposed in oxygen gas with a purity of 99.9995% at 110 K. The partial oxygen pressure was below 1.3 × 10⁻⁶ Pa. RHEPD experiments were performed using a positron beam with an energy of 10 keV. The pressure during the measurements was below 5 × 10⁻⁸ Pa. Reflected positrons were observed using a micro-channel plate assembly (Hamamatsu F2226-24P) and a charge-coupled device (CCD) camera. The details of the RHEPD apparatus are described elsewhere [11]. RHEPD rocking curves were measured at the glancing angle from 0.1° to 6.0° with a step of 0.1°. The azimuthal angle was fixed at 24° from the [110] direction. This is so-called the one-beam condition where approximately only the specular beam is observed [12, 13].

III. RESULTS AND DISCUSSION

Figure 1 shows the observed RHEPD patterns of a cleaned Si(001) surface and the surface exposed to O₂ gas up to the coverage of 4 L at 110 K. The indices of three spots in Fig. 1(a) are assigned to the (0, 0), ($\overline{1}/2$, 0) and ($\overline{1}$, 0). After the O₂ exposure, the intensities of all spots are weakened as shown in Fig. 1(b). The decrease of the ($\overline{1}/2$, 0) and ($\overline{1}$, 0) spot intensities indicates that the structure of the silicon dimers is almost lost and the atomic structure is disorder.

We measured the specular spot intensity during O₂ exposure as shown in Fig. 2. The intensity decreases with increasing the amount of the O₂ exposure and approaches a constant at approximately 5 L. Our data is in good agreement with the Langmuir-type behavior by the formula of $(I - I_1)/(I_0 - I_1) = \exp(-\kappa l) (= 1 - \gamma)$, where I is the specular spot intensity, I_0 is the intensity at $l = 0$,

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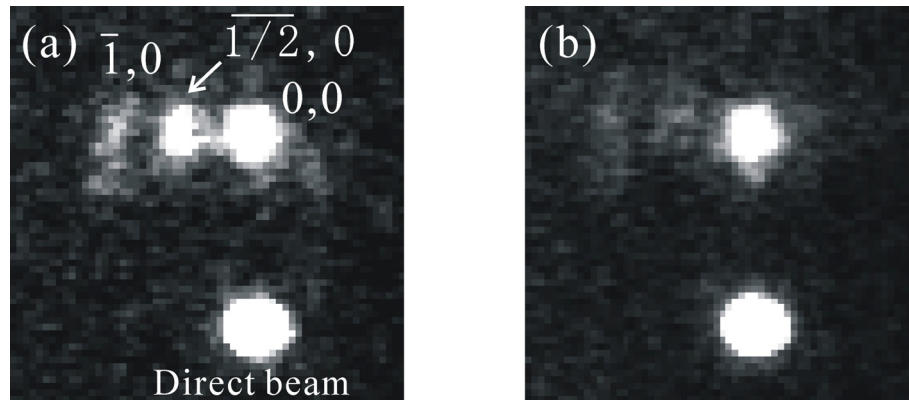


FIG. 1: RHEPD patterns of (a) a cleaned Si(001) surface and (b) the surface after exposing O_2 gas up to coverage of 4 L at 110K. The glancing angle is 1.8° at the total reflection condition ($< 1.99^\circ$) and the azimuthal angle is at 1.0° from the $[110]$ direction.

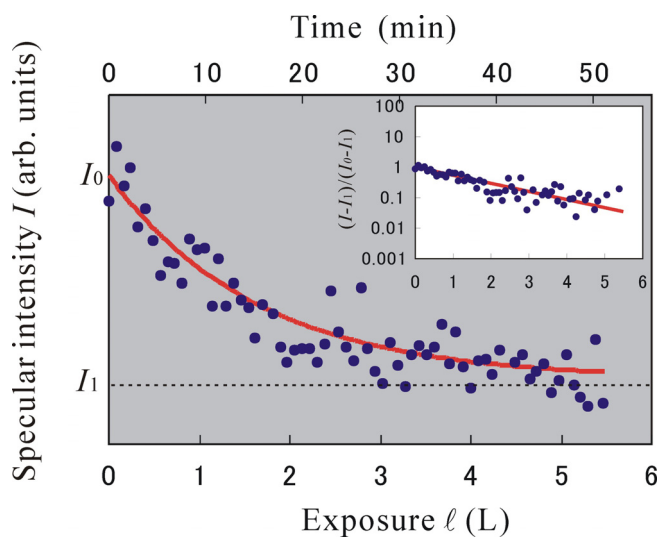


FIG. 2: Specular spot intensity during O_2 exposure at 24° away from the $[110]$ direction at the glancing angle 1.8° . Solid line denotes the curve fit by the formula of the Langmuir-type reaction. O_2 pressure is 2.4×10^{-7} Pa.

I_1 is the saturated intensity, κ is the reaction rate of oxidation (ML/L), l is the amount of the O_2 exposure (L) and γ is the oxygen coverage. The calculated curve with $\kappa = 0.6$ ML/L is denoted by solid line in Fig. 2. This saturating of Langmuir-type behavior is reported by the studies of the oxygen peak intensity during oxidation by PAES [1, 2] and Auger electron spectroscopy (AES) [4]. From their data, the oxidation reaction rate of PAES and of AES is estimated to be 0.3 at 193 K and 0.01 ML/L at room temperature, respectively. Our value is similar to PAES. In the PAES work, Ohdaira, *et al.* explain that the difference of the saturated coverage between PAES and AES is attributed to the different surface sensitivities of the measuring methods. In spite of this difference, they report the similar proposition that only the first surface layer is oxidized in the initial oxidation processes by O_2 exposure. Although it is not clear the reason of the difference between our oxidation reaction rate and one of AES, it can be considered that oxidation processes in our

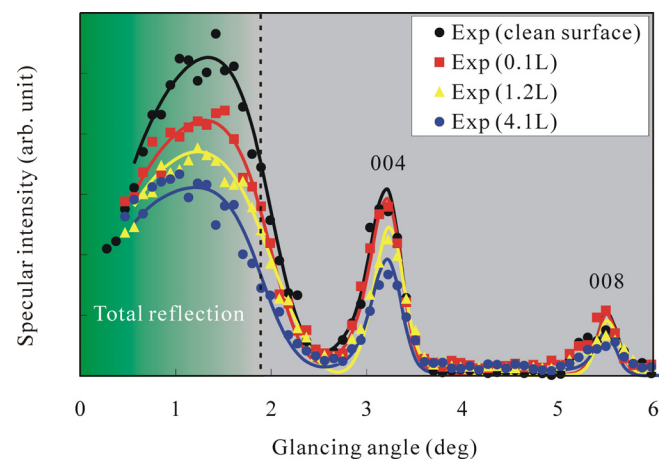


FIG. 3: Rocking curves of the specular spot at 24° away from the $[110]$ direction under the one-beam condition at 110K after O_2 exposure of 0.1 L, 1.2 L and 4.1 L. Solid lines are the curves calculated based on the dynamical diffraction theory.

experiment also occurs only in the first surface layer.

To investigate the structure of the oxidation surface, the rocking curves of the specular spot were measured under the one-beam condition [12, 13]. The experimental results are shown in Fig. 3 with the rocking curve of a clean Si(001) surface. The amounts of the O_2 exposure are varied to be 0.1 L, 1.2 L and 4.1 L. When the coverage of oxygen is assumed to be 1 ML where the intensity of the specular spot is saturated in Fig. 2, the coverages of 0.1 L, 1.2 L and 4.1 L are approximately estimated to be 0.1 ML, 0.4 ML and 0.8 ML, respectively. All rocking curves exhibit two large peaks at 1.5° and 3.3° , and one small peak at 5.6° . The first peak corresponds to the total reflection. The second and third peaks are assigned to the 004 and 008 Bragg reflections, respectively. The peak intensities of the total reflection and 004 Bragg decrease with increasing the oxygen coverage.

The experimental rocking curves were compared with those of dynamical calculations by the multi-slice method with appropriate atomic structures [13]. We examined the following three atomic models: (i) oxygen atoms are

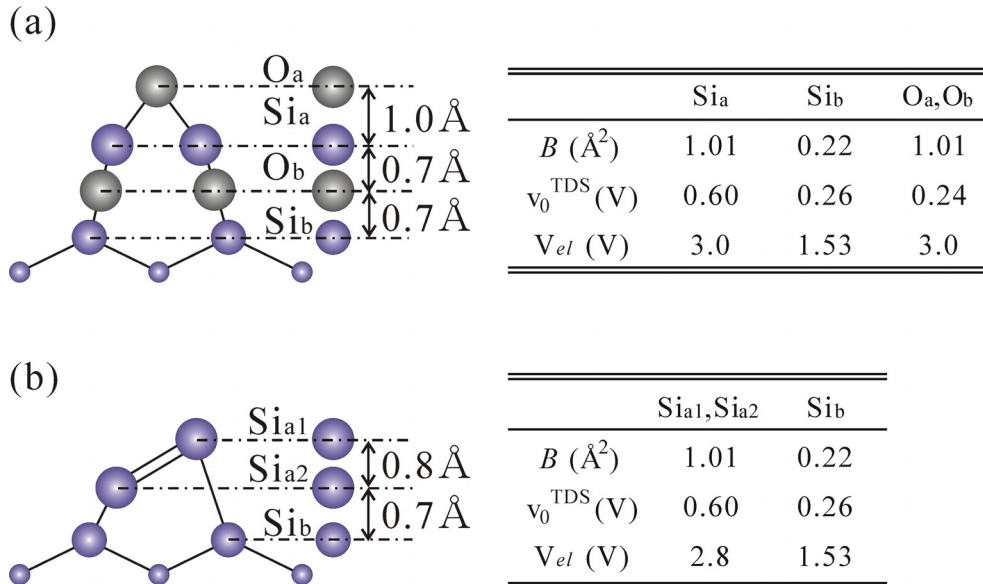


FIG. 4: Optimized atomic structure of (a) the region with oxidation and (b) the region without oxidation. Tables show the Debye parameter B , the imaginary potential for thermal diffuse scattering v_0^{TDS} and the imaginary potentials for electronic excitations V_{el} for each atom.

adsorbed only above the silicon dimer layer, (ii) oxygen atoms are inserted into the dimer back-bonds and (iii) oxygen atoms are adsorbed above the dimer layer and are inserted into the back-bonds. We evaluate the reliability factor R defined as follows:

$$R = \sqrt{\sum_{\theta} (I_{\theta}^{\text{exp}} - I_{\theta}^{\text{cal}})^2}, \quad (\sum I_{\theta}^{\text{exp}} = \sum I_{\theta}^{\text{cal}} = 100\%),$$

where I_{θ}^{exp} is the experimental intensity and I_{θ}^{cal} the calculated one at the glancing angle θ . From the calculations for the various vertical positions of oxygen and silicon atoms, it is found that the third mode is the best structure to explain the experimental results. Figure 4 shows the schematic illustration of the optimized surface atomic structures and parameters. As for the surface parts without oxidation, the asymmetric silicon dimer structure was assumed. The distance between O_a and Si_a , between Si_a and O_b , and between O_b and Si_b is determined to be approximately 1.0 \AA , 0.7 \AA and 0.7 \AA , respectively. The imaginary potentials for electronic excitations V_{el} for O_a, O_b and Si_a are determined to be 3.0 V. The other parameters are obtained from Ref [8, 14, 15]. R factors for each rocking curve are less than 2%. The rocking curves using the optimized atomic positions are denoted by solid lines in Fig. 3. The curves are in good agreement with the experimental results.

Our results show that oxygen atoms are located on top of the surface and in the back-bonds of silicon dimers. This result is consistent with the studies using positron-annihilation induced Auger electron spectroscopy [1, 2] and the study using high-resolution Si 2*p* photoemission [3]. As shown in Fig. 2, this oxidation reaction occurs from the initial stage of O_2 exposure. Although the reaction path of oxidation is not clear from our results, the penetration of oxygen atoms into the back-bonds progresses simultaneously with oxidation of the topmost sur-

face. This suggests that the penetration of oxygen atoms into the back-bonds is almost barrier-less reaction. Our suggestion is supported by the conclusion of the oxidation study by Watanabe, *et al.* using scanning reflection electron microscopy and Auger electron spectroscopy [4–6]. They proposed that the oxygen adsorption onto the topmost layer and oxygen migration to the back-bonds are barrier-less reaction. In the Si(001) surface even at low temperatures as 110 K, it is considered that barrier-less oxidation reaction occurs.

According to first-principles total-energy calculations, the most stable height is 0.09 \AA and the metastable height is 1.5 \AA [16]. The O_a height of 1.0 \AA is the mean value. It is known that there are some metastable oxygen sites [5, 6, 16, 17]. Considering that the atomic structure of the oxidized surface is disorder, it might be that the oxygen atoms of some stable and metastable distribute around the height of 1.0 \AA .

IV. SUMMARY

We have investigated the structures of Si(001) surfaces at 110 K in the initial oxidation process using RHEPD. The positions of oxygen and silicon atoms are determined by RHEPD rocking curves. It is found that the locations of oxygen atoms are on the topmost surface and in the back-bonds of silicon dimers. The distance between the surface oxygen atoms and the dimer silicon atoms, between the dimer silicon atoms and the back-bond oxygen atoms and between the back-bond oxygen atoms and the bulk silicon atoms is determined to be approximately 1.0 \AA , 0.7 \AA and 0.7 \AA , respectively. Since the two oxidation processes occur from the initial stage of O_2 exposure, we consider that the insertion of oxygen atoms into the back-bonds is barrier-less or almost barrier-less reaction.

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