Photoemission Study on the Surface Reaction Dynamics of Si(001) Oxidation by Supersonic O$_2$ Molecular Beams

In the surface reaction dynamics study, the roles of translational kinetic energy (E_t) of incident molecules are an area of current interest. For instance, the dissociative chemisorption of O$_2$ molecules takes place on Si(001) surfaces at room temperature (passive oxidation). In order to understand the roles of the incident energy in O$_2$ molecules, E_t dependencies of passive oxidation, induced by supersonic O$_2$ molecular beams (SSMBs), have been investigated by photoemission spectroscopy using high-energy-resolution synchrotron radiation (SR).

All experiments were performed at the experimental station for surface chemistry: SUREAC2000 [1,2] at **BL23SU**. The base pressure is less than 5×10^{-9} Pa when liquid N$_2$ is filled in the shroud and the manipulator. Monochromated SR beams of about 400 eV and 830 eV were used for

Si-2p and O-1s photoemission measurements with a surface sensitive condition (escape depth: 0.3 nm). The O$_2$ SSMBs are generated by the adiabatic expansion of a mixture of O$_2$, He and Ar using a high temperature nozzle. The maximum O$_2$ incident energy was calculated to be 3 eV. The typical SSMB flux density and the photon flux were estimated to be 2×10^{14} molecules•cm^{-2}•s^{-1} and 2×10^{10} photons•s^{-1}, respectively.

First, an H$_2$O-chemisorbed Si(001) surface was formed before O$_2$ exposure. Dangling bonds of the topmost Si dimers were terminated by H and OH in the H$_2$O-chemisorbed Si(001) surface. It was exposed to O$_2$ gas up to saturation. The oxidized surface was irradiated again by the O$_2$ SSMBs with respect to surface normal until the saturation coverage was achieved. The E_t dependence of the saturation coverage is shown in Fig. 1 [3]. Referring to the first-principles molecular dynamics calculation [4], the lower break was assigned to a potential energy barrier for the backbond oxidation of the topmost Si atoms, and the higher one was assigned to a potential energy barrier for the backbond oxidation of the second layer (subsurface) Si atoms.
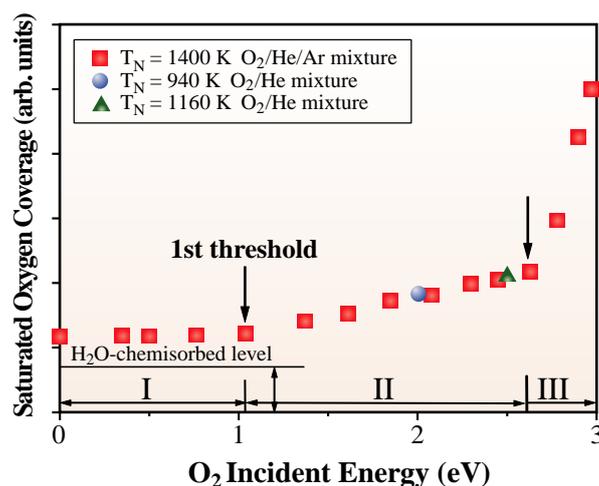
Fig. 1. The saturated oxygen coverage on the partially-oxidized (H$_2$O-chemisorbed) Si(001) surface as a function of translational kinetic energy of incident O$_2$ molecules. The symbol ■ represents the results obtained by varying mixing ratio of O$_2$/He/Ar keeping a nozzle temperature (T_N) of 1400 K. The symbol ● and ▲ represent the results obtained by different gas mixing ratios and nozzle temperatures of 940 K and 1160 K, respectively.

Different oxidation states are expected to appear in Si-2p photoemission spectra in each incident energy region. Representative Si-2p photoemission spectra are shown in Fig. 2 [5]. They were de-convoluted into bulk Si (Si-2$p_{1/2}$ and 2$p_{3/2}$), interface Si, H-terminated Si and oxidized Si: Si^{n+} (n = 1 - 4). The photoemission peak intensity ratio for the 2$p_{1/2}$ and 2$p_{3/2}$ components was measured to be 1:2 under a bulk sensitive condition so that the ratio was used for the de-convolution. The LS-coupling scheme may be no longer good due to crystal field effects even for the Si^{2+} component [6]. Therefore, the spin-orbit splitting was taken into account for bulk Si, distorted interface Si, H-terminated Si, and Si^{1+} components except Si^{2+}, Si^{3+} and Si^{4+} components. The Si-2p spectrum of the Si(001)

surface before O$_2$ exposure consists of bulk Si, Si-H and Si-OH (Si^{1+}) components as shown in Fig. 2(a). The spectral profile obtained after O$_2$ exposure with E$_t$ = 0.04 eV, representative in the region I, is very close to that before O$_2$ exposure. This fact implies that the Si-OH and Si-H bonds prohibit further oxidation by O$_2$ molecules. On the other hand, the spectral profile changed dramatically when the O$_2$ SSMBs with incident energy larger than the first threshold, 1.0 eV, were irradiated to the surface. An Si-2p spectrum for E$_t$ = 2.0 eV is shown in Fig. 2(c) as a representative in region II, indicating the Si^{4+} formation. The direct oxidation of Si dimer backbonds due to energetic O$_2$ collisions can take place in this incident energy region so that the topmost Si atoms can be surrounded
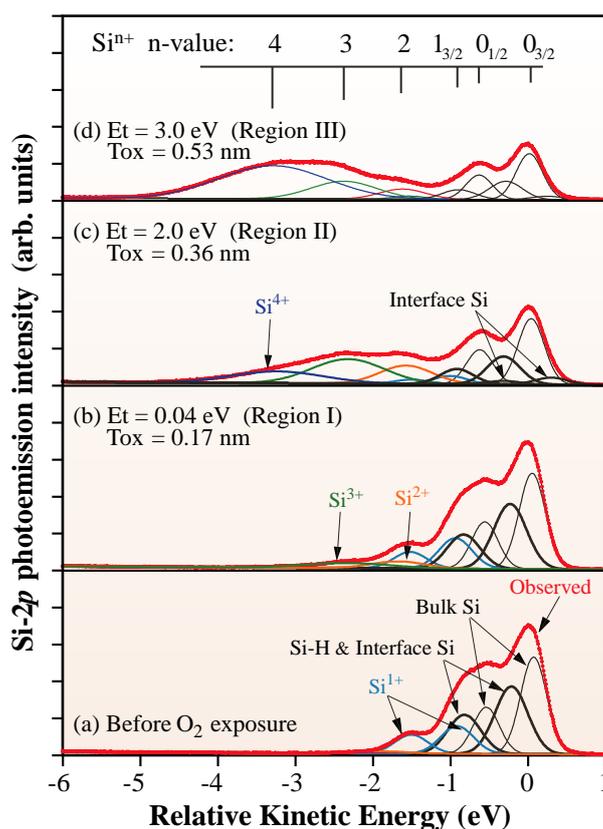
Fig. 2. Si-2p photoemission spectra for Si(001) surfaces oxidized up to saturation coverage at room temperature by O$_2$ molecules with various incident energies (E$_t$) : (a) for the initial (partially-oxidized) Si(001) surface, (b) for E$_t$ = 0.04 eV, (c) for E$_t$ = 2.0 eV and (d) for E$_t$ = 3.0 eV, respectively. T$_{ox}$ represents the oxide layer thickness.

by up to four oxygen atoms. The Si-2p spectrum for E_t = 3.0 eV shows that Si^{3+} and Si^{4+} contributions share a large part of the satellite peaks, as shown in Fig. 2(d). Such a large contribution is interpreted as the incident-energy-induced dissociative chemisorption of O_2 molecules at the subsurface backbonds in the energy region III as well as the topmost Si dimers bridge sites and their backbond sites. The oxide layer thickness was estimated approximately to be 0.53 nm. Consequently, the thickness of ultra-thin oxide layer, less than 1 nm, can be controlled at room temperature by controlling the translational kinetic energy of incident O_2 molecules in a hyperthermal energy region. Reaction models are also presented in Fig. 3.
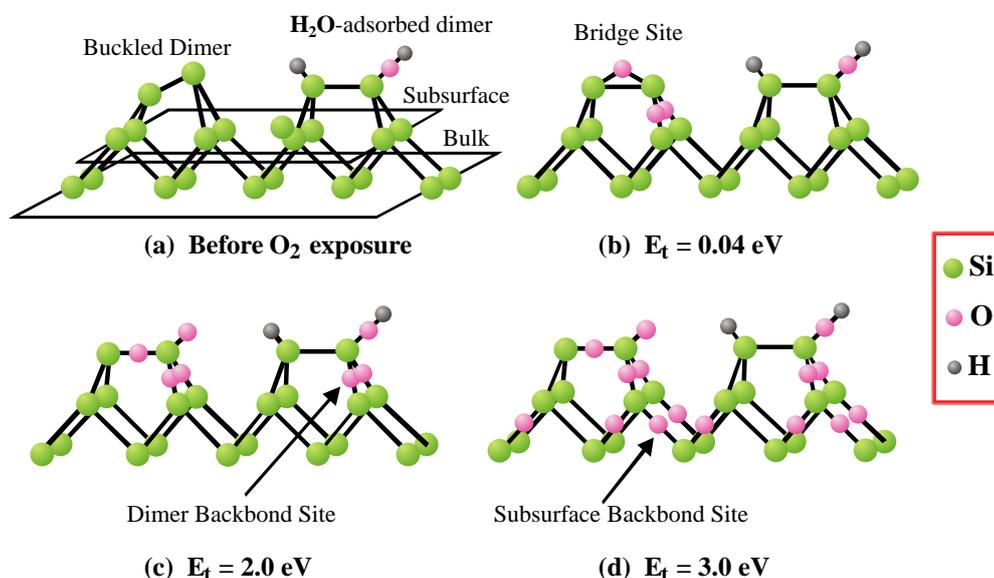
Fig. 3. Reaction models of incident-energy-induced oxidation processes: (a) for the partially-H_2O-chemisorbed Si(001) surface, (b) for the residual Si dimer oxidation by O_2 exposure, (c) for the Si dimer backbond oxidation by O_2 incident energy larger than the first threshold (1.0 eV), (d) for the subsurface backbond oxidation by O_2 incident energy larger than the second threshold (2.6 eV), respectively.

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