Real-time *in situ* photoemission spectroscopy for the analysis of Si(001) oxidation induced by supersonic O_2 molecular beams

The analysis of chemical phenomena occurring at the gas-solid interface is a fundamental step in research to understand and control surface chemical reactions. In particular, it is considerably essential to realize and control surface chemical reactions with respect to the recent development of nanotechnologies which require the atomicscale manipulation in terms of device sizes and chemical compositions. Photoemission spectroscopy combined with soft X-ray synchrotron radiation, which offers the advantages of energy resolution, intensity, beam size and wide energy regions, is a powerful experimental technique for observing the chemical composition and chemical bonds on solid surfaces. Furthermore, we can *in situ* monitor the time-evolution of chemical species on the solid surface in the core-level photoemission spectra during chemical reactions.

Here, we demonstrate the advantages of real-time *in situ* photoemission spectroscopy combined with a high-performance soft X-ray synchrotron radiation source for the monitoring of chemical reactions on solid surfaces. The real-time monitoring of oxidation on the Si(001) surface induced by translational kinetic energy of O_2 at room temperature is reported. This reaction system is an important subject, not only for the semiconductor industry, but also in terms of the reaction dynamics in surface science [1-4].

The SUREAC2000 [5], especially designed for the analysis of surface chemical reactions at beamline **BL23SU**, was used for all experiments. An important advantage of the SUREAC2000 is that *in situ* photoemission measurements with synchrotron radiation can be carried out under supersonic molecular beam (SSMB) irradiation on solid surfaces. The photon energy resolution was better than 100 meV and the photon flux was on the order of 10^{11} photons$\cdot$s^{-1}. Photoelectrons were collected with a 125 mm hemispherical electron energy analyzer (Omicron Nano Technology, GmbH) with five channeltrons. The excitation energies for the O-1*s* and Si-2*p* core levels were 830 eV and 409 eV, respectively. The analysis depth from the surface was roughly estimated to be 0.7 nm.

The O_2 beam with the kinetic energy of 2.2 eV was exposed to the n-type Si(001) substrate at 9 degrees from the surface normal at room temperature.

Figure 1 shows representative high-energy-resolution Si-2*p* photoemission spectra obtained by real-time *in situ* measurements taken during irradiation of the O_2 SSMB. The O_2 dose is indicated in Langmuir units (1L = 1.3×10^4 Pa$\cdot$s). It took approximately 40 s to obtain an Si-2*p* and an O-1*s* photoemission spectrum. Peak deconvolution was performed to obtain the components related to Si oxidation by the curve fitting procedure. The spin-orbit splitting between Si2$p_{1/2}$ and Si2$p_{3/2}$ was set to be 0.6 eV. Prior to the curve fitting, the backgrounds

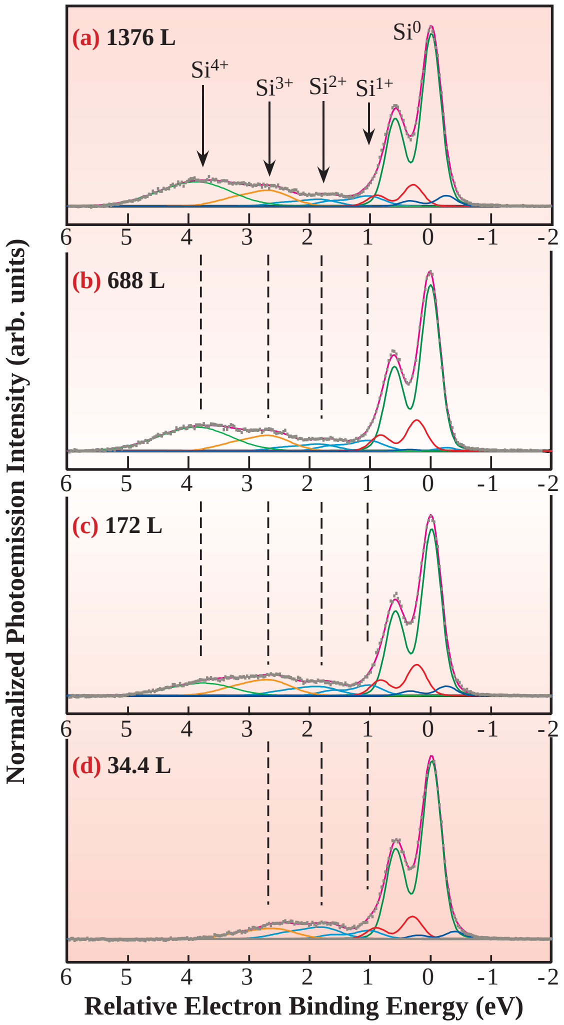

Fig. 1. Representative high-resolution Si-2*p* photoemission spectra for the real-time *in situ* observation of oxidation on a Si(001)- 2×1 surface induced by O_2 molecular beams at room temperature.

in the photoemission spectrum were numerically eliminated using the Tougaard method. The photoemission intensity ratio (Si2$p_{1/2}$/Si2$p_{3/2}$) was assumed to be 0.5 according to their statistical weights. Core level shifts related to the Si oxidation were estimated to be 1.00 (Si^{1+}), 1.82 (Si^{2+}), 2.62 (S^{3+}) and 3.67 (Si^{4+}) eV, with respect to the binding energy of the bulk Si-2$p_{3/2}$ peak position. Furthermore, α (0.23eV) and β (-0.26eV) were due to the slight distortion in the bond angles at the interface Si atoms. With increasing molecular beam exposure, the oxide components gradually increased without shifts of their peak positions.

Figure 2 shows the time evolution of (a) the oxide thickness, (b) the oxygen amount and (c)-(f) the intensities of each oxide component (Si^{4+}, Si^{3+}, Si^{2+} and Si^{1+}) normalized by the oxide thickness. As shown in Figs. 2 (a) and (b), the oxide thickness and the O-1*s* photoemission intensity drastically increased with irradiation doses less than 50L and then gradually increased. The saturated thickness of the oxide layers was estimated to be approximately 0.57 nm from the backbond oxidation of the subsurface Si layers. Time evolutions of the suboxide components are illustrated as a function of the O_2 dose in Figs. 2 (c) to (f). Since the Si^{4+} species is not observed at the early stage of molecular beam irradiation, up to 34.4L, the topmost Si dimer atoms are hardly surrounded by four oxygen atoms in the initial oxidation stage. As shown in Fig. 2 (d) and (f), the Si^{1+} and the Si^{3+} components gradually decrease with increasing the oxide thickness. This result indicates that the number of Si^{1+} and Si^{3+} atoms per unit oxide thickness is nearly constant, regardless of the oxide growth. The Si^{1+} species remain at the interface between the oxide layers and Si(001) substrate, whereas the Si^{3+} species are distributed over all oxide layers. As shown in Fig. 2(e), the amount of Si^{2+} species decreased with increasing amounts of Si^{4+}, whereas the amounts of Si^{1+} and Si^{3+} were virtually unchanged. This result indicates that the Si^{4+} species was directly converted from the Si^{2+} species.

Using real-time photoemission spectroscopy, we clarified the reaction mechanisms of oxidation on a Si(001) surface induced by the incident energy of O_2 at room temperature. In conclusion, we succeeded in showing that real-time photoemission spectroscopy using synchrotron radiation is a powerful method for investigating the surface chemical reactions from the viewpoints of kinetics and dynamics.

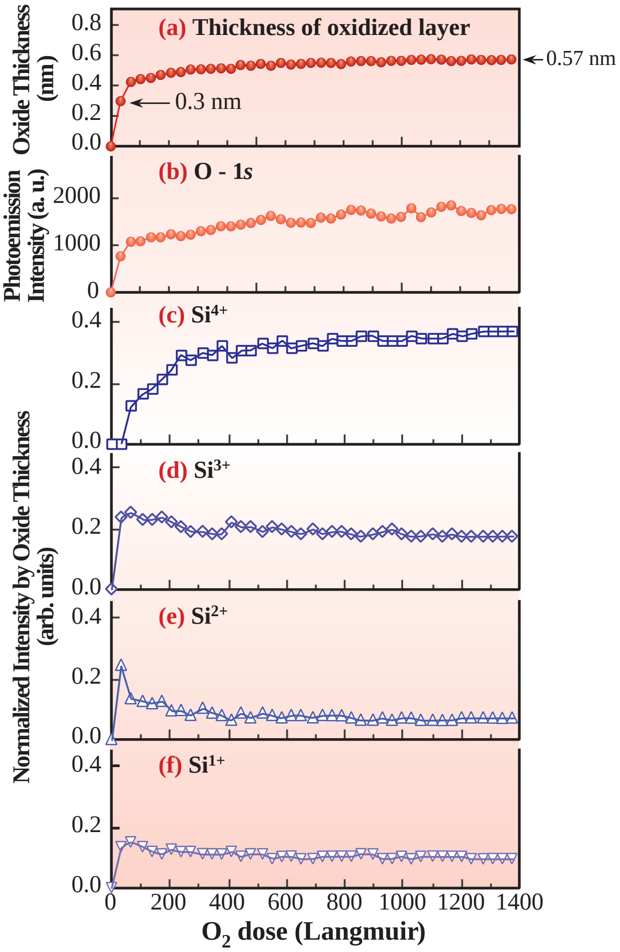

Fig. 2. Variation of **(a)** oxide thickness, **(b)** the O-1*s* photoemission intensity and **(c)-(f)** each Si-2*p* oxide component area intensity as a function of O_2 irradiation dose. Intensities for the Si-2*p* oxide components were normalized by the oxide thickness.

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