Real-time in situ photoemission spectroscopy for the analysis of Si(001) oxidation induced by supersonic \( \text{O}_2 \) 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 \( \text{O}_2 \) 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 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-1s and Si-2p core levels were 830 eV and 409 eV, respectively. The analysis depth from the surface was roughly estimated to be 0.7 nm.

The \( \text{O}_2 \) 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-2p photoemission spectra obtained by real-time in situ measurements taken during irradiation of the \( \text{O}_2 \) SSMB. The \( \text{O}_2 \) dose is indicated in Langmuir units (1L = 1.3 \times 10^4 \text{ Pa·s} ). It took approximately 40 s to obtain an Si-2p and an O-1s photoemission spectrum. Peak deconvolution was performed to obtain the components related to Si oxidation by the curve fitting procedure. The spin-orbit splitting between Si2p\(_{1/2}\) and Si2p\(_{3/2}\) was set to be 0.6 eV. Prior to the curve fitting, the backgrounds

![Fig. 1. Representative high-resolution Si-2p photoemission spectra for the real-time in situ observation of oxidation on a Si(001)-2x1 surface induced by \( \text{O}_2 \) molecular beams at room temperature.](image-url)
in the photoemission spectrum were numerically eliminated using the Tougaard method. The photoemission intensity ratio (Si2p1/2/Si2p3/2) 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 (Si1+), 1.82 (Si2+), 2.62 (Si3+) and 3.67 (Si4+) eV, with respect to the binding energy of the bulk Si2p3/2 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 (Si4+, Si3+, Si2+ and Si1+) normalized by the oxide thickness. As shown in Figs. 2 (a) and (b), the oxide thickness and the O-1s 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 O2 dose in Figs. 2 (c) to (f). Since the Si4+ 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 Si1+ and the Si3+ components gradually decrease with increasing the oxide thickness. This result indicates that the number of Si1+ and Si3+ atoms per unit oxide thickness is nearly constant, regardless of the oxide growth. The Si1+ species remain at the interface between the oxide layers and Si(001) substrate, whereas the Si3+ species are distributed over all oxide layers. As shown in Fig. 2(e), the amount of Si2+ species decreased with increasing amounts of Si4+, whereas the amounts of Si1+ and Si3+ were virtually unchanged. This result indicates that the Si4+ species was directly converted from the Si2+ species.

Using real-time photoemission spectroscopy, we clarified the reaction mechanisms of oxidation on a Si(001) surface induced by the incident energy of O2 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.

---

**References**