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In situ Si-*2p* core-level spectroscopy using synchrotron radiation for Si(001) initial oxidation induced by translational kinetic energy of O_2 molecules

Akitaka Yoshigoe and Yuden Teraoka
Japan Atomic Energy Research Institute (JAERI)
Synchrotron Radiation Research Center
1-1-1 Kouto Mikazuki-cho, Sayo-gun, Hyogo 679-5148, Japan
Fax: +81-791-58-2740, e-mail: yoshigoe@spring8.or.jp

In order to achieve the real-time "*in situ*" observation of surface chemical reactions on solid surfaces, we have designed and manufactured an experimental end-station at the soft x-ray beamline, BL23SU, in the SPring-8. This end-station realizes a simultaneous use of supersonic molecular beams (SSMB) and the synchrotron radiation photoemission spectroscopy. We studied the relation between the translatinal kinetic energy of O_2 and oxidation states (SiO_x) classified by the Si-*2p* core-level shifts and the time evolution of the Si-*2p* photoemission as well.
Key words: synchrotron radiation, supersonic molecular beams, real time " *in-situ* " observation, initial Si(001) oxidation, photoemission spectroscopy, translational kinetic energy of O_2

1. INTRODUCTION

In order to understand the interaction between gas molecules and solid surfaces, the translational kinetic energy of incident molecules is an important parameter in surface chemical reactions. Many interesting phenomena induced by the translational kinetic energy of gas molecules have been reported [1]. A new surface reaction analysis apparatus for surface reaction dynamics studies has been designed and manufactured as an experimental end-station at the soft x-ray beamline, BL23SU [2,3], in the SPring-8. This experimental end-station realizes a simultaneous use of supersonic molecular beams (SSMB) and the synchrotron radiation (SR) photoemission spectroscopy to achieve a real time "*in situ*" analysis of surface reactions to obtain more deeper understanding for elementary processes of chemisorption [4,5].

In this paper, we report that the real-time "*in situ*" observations using the SR photoemission spectroscopy were applied to the investigation of initial Si(001) oxidation induced by the translational kinetic energy of O_2 at room temperature. Oxidation on silicon surfaces is an important process in not only microelectronics manufacturing but also in surface science research [6]. Recent progress of a synchrotron radiation beamline with high energy resolution provides us the detail information on the oxygen adsorption states on Si surfaces [7-9]. Although these data may be useful for characterizing the oxygen chemisorption states and analyzing the oxidation processes, the effects of the translational kinetic energy for oxygen adsorption states have not been reported yet. On the other hands, there has been considerable work on O_2 adsorption process on Si(001) by molecular beam techniques [10-14]. These studies focus on the measurements of the initial sticking probability using the reactive molecular beam scattering and discussions for the adsorption mechanisms. However, the region of the translational kinetic energy was limited below 1.0 eV. Few studies on the relation between adsorbed states and the translational kinetic energy has been reported to our knowledge.

In order to make clear the relation between the translational kinetic energy of O_2, up to 3.0 eV region, and oxidation states (SiO_x), we have analyzed Si-*2p* core-level shifts in SR photoemission spectra. The dependence of Si-*2p* core-level spectra on SSMB exposure time is also reported.

2. EXPERIMENTAL

All experiments were performed at the surface chemistry end-station installed at the soft x-ray beamline, BL23SU, in the SPring-8 [2,3].

Figure 1 shows the top-view of the surface reaction analysis appratus which consists of an SR beam monitor chamber, a surface reaction analysis chamber, a supersonic molecular beam (SSMB) generator, a scanning probe microscope (SPM) chamber, a surface cleaning chamber and a load-lock chamber. Figure 2 shows the details of the surface reaction analysis chamber to explain how to perform the real time "*in situ*" SR photoemission spectroscopy during the SSMB exposure. The surface reaction analysis chamber has an electron energy analyzer and is connected to the SSMB

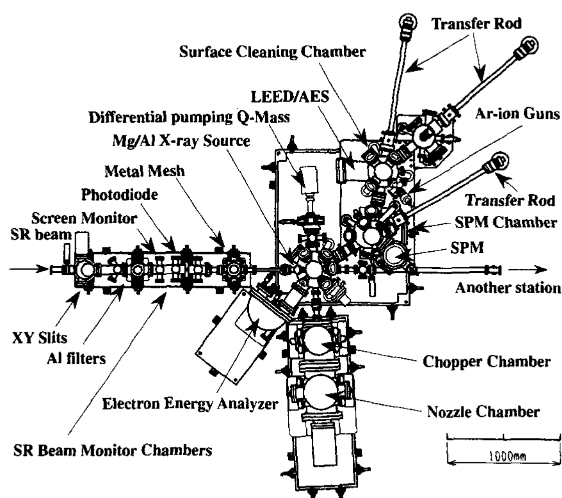

Figure 1. Top view of surface chemistry end-station installed at a soft x-ray beamline, BL23SU, at the SPring-8. Real time "*in situ*" observation of surface chemical reactions under SSMB irradiation was performed by using SR photoemission spectroscopy.

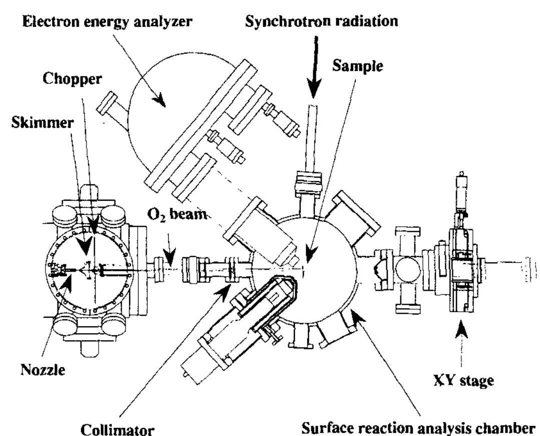

Figure 2. Details of experimental setup of surface reaction analysis chamber for real time " *in situ* " observation of surface reaction. SR photoemission spectroscopy can be simultaneously performed under SSMB exposure.

generator. The monochromated SR beam is introduced into the surface reaction analysis chamber through the SR beam monitor chamber which is also used as a differential pumping stage to prevent the reactant gas diffusion under the SSMB operation.

The translational kinetic energy of O_2 was varied with changes of the mixing ratios of the O_2, He and Ar gas under keeping the nozzle temperature at 1400 K. The adiabatic expansion of a mixture of the O_2 and the carrier gases generates the continuous SSMB. Owing to use the high temperature nozzle, the upper limit of the translational kinetic energy of O_2 can be achieved to be about 3.0 eV (caluculated value). The molecular beams pass through a skimmer into the chopper chamber and finally enter the surface reaction analysis chamber through a collimator. The typical O_2 beam flux density, estimated from the total pressure increase in the reaction analysis chamber, is about 2×10^{14} molecules/ $cm^2\cdot$ sec on a sample surface. An N^+-type Si(001) substrate was used in this study. Prior to the SSMB irradiation, the Si(001) substrate, pretreated by chemical methods [15], was heated up to 1300 K (flashing) to obtain the Si(001)-2x1 surface confirmed by a low energy electron diffraction technique (LEED) in the surface cleaning chamber.

3. RESULTS AND DISCUSSIONS

In order to clarify the influence of the translational kinetic energy of O_2 for the initial oxidation of Si(001) surfaces at room temperature, we have measured changes of the oxygen amount on the preoxidized Si(001) surface after exposing O_2 SSMB with various translational kinetic energies. For obtaining the preoxidized Si(001) surface, the Si(001) sample was firstly exposed to the O_2 residual gas (O_2 partial pressure: 1.3×10^{-7} Pa) in the surface reaction analysis chamber during the molecular beam operation by setting the sample out of the molecular beam axis. The relative oxygen increase on the Si(001) surface was estimated by measuring O-*1s* photoemission peak area intensities using an Mg-$K\alpha$ x-ray source. After flashing procedure, the O-*1s* peak which is due to OH species formed by dissociative H_2O chemisorption was observed. A time dependence of the oxygen amount on this surface showed a Langmuir-type adsorption curve. It took about two hours to obtain the first saturation coverage. We concluded that OH species may adsorb on the clean Si(001) surface with at least 60% coverage before the SSMB irradiation. After the first saturation was achieved, the Si(001) surface was directly irradiated by the O_2 SSMB for two hours to achieve the second saturation.

Figure 3 shows the translational kinetic energy dependence of the secondary saturated oxygen amount on the Si(001) surface. The photoemission intensity measured after 4 hours exposure to the O_2 residual gas was subtracted from the total saturated oxygen amount. Two breaks were clearly found at 1.0 eV and 2.6 eV. These values are very close to the predicted values (0.8 eV and 2.4 eV) from the first-principles caluculation [17]. The lower break (**A**) was, therefore, assgined to backbond oxidation of dimer Si atoms and the higher break (**B**) was assigned to subsurface Si oxidation, i.e. oxygen insertion between the second and the third Si layer. These facts lead us to expect different oxidation states at every translational kinetic energy regions: below 1.0 eV (region I), 1.0-2.6 eV (region II) and above 2.6 eV (region

III).

We have analyzed oxidation states by "*in situ*" Si-2*p* photoemission spctroscopy using the monochromated synchrotron radiation with the elliptic polarization. The detection angle of photoemission was 31 degrees with respect to the surface normal. Figure 4 shows the representative Si-2*p* photoemission spectra. The Si-2*p* core-level shifts due to the surface oxidation was indicated relatively to the bulk Si-$2p_{3/2}$ peak position in Fig. 4 on the basis of the recent report: 1.0 eV for Si^{1+}-$2p_{3/2}$, 1.6 eV for Si^{1+}-$2p_{1/2}$, 1.81 eV for Si^{2+}, 2.63 eV for Si^{3+} and 3.6 eV for Si^{4+} (SiO_2) [7-9].

The Si-2*p* photoemission spectrum on the Si(001) surface oxidized by the O_2 molecules with the translational kinetic energy of 0.63 eV is shown in Fig. 4(**a**) as representative in the region I in Fig.3. The surface oxidation seems to be mostly terminated in the oxidation number of +1. The slight contribution from Si^{2+} to the sub-oxide satellite peaks was recognized in the trace **a** in Fig. 4. According to the first-principles calculation [17], the migration of adsorbed oxygen atoms from an Si-O-Si bridge site in an Si dimer to a backbond site of the dimer Si atom is possible without sample heating. This prediction implies that an oxygen atom can be inserted into the backbond of dimer Si atoms even below the threshold energy of 1.0 eV.

The Si-2*p* photoemission spectrum of the Si(001) surface oxidized by the O_2 molecules with the translational kinetic energy of 2.0 eV (trace **b**) is shown as representative in the region II. According to the theory [17], direct backbond oxidation can take place in this translational kinetic energy region, thus a dimer Si atom can be surrounded by up to four oxygen atoms. The trace **b** indicates that the oxidation proceeds to the extent of Si^{3+} formation.

The O_2 molecules with the translational kinetic energy of 3.0 eV can dissociatively adsorb between the second and the third Si layer, according to the prediction of the theory [17]. The sub-surface (the second layer) Si atoms can be surrounded by oxygen atoms as well as dimer Si atoms in the region III. Thus, the fraction of Si^{3+} and Si^{4+} may drastically increase comparing to the trace **b** in the region II. The Si-2*p* photoemission spectrum for the 3.0 eV case indicates that the Si^{3+} and the Si^{4+} atoms mainly contribute in the satellite structure.

Figure 5 shows the O_2 SSMB exposure time dependence of Si-2*p* core-level spectra (**A**: 3.0 eV, **B**: 2.0 eV). The suboxide components gradually increased with increasing the SSMB exposure time. The spectra were obtained by real-time "*in situ*" measuremnts under O_2 SSMB exposure. It takes about 15 min to obtain one spectrum. The numerical values shown in the figure indicate the time passed from starting the exposure. The every photoemission measurement was finished until the indicated time. The spectra show that every oxidation states gradually increased with increasing the exposure time. In the case of 2.0 eV, Si^{3+} component slightly increased. On the other hand, not only Si^{3+} but also Si^{4+} component species increased in the case of 3.0 eV. These exposure time dependence indicates that oxidation processes progress by translational kinetic energy and creation rates of each oxidation state are different. We successfully monitored the time evolution of each different oxidation state due to the O_2 SSMB exposure by the real time "*in situ*" photoemission sepctroscopy.

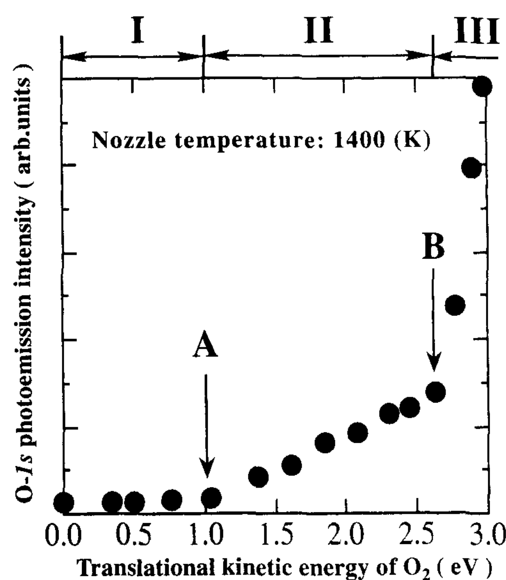

Figure 3. O-1*s* photoemission peak area intensities measured by Mg-$K\alpha$ x-ray source as a function of translational kinetic energy of O_2.

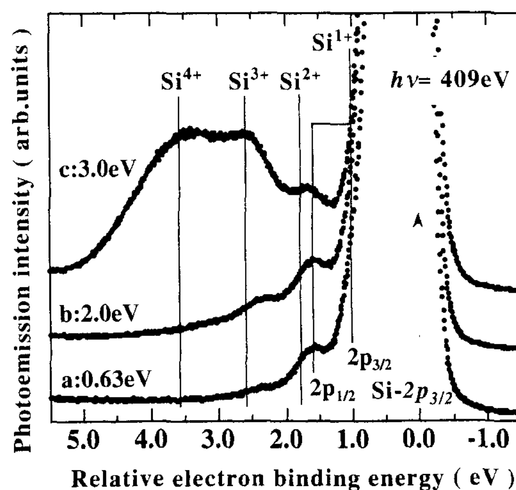

Figure 4. Si-2*p* photoemission spectra using synchrotron radiation for **a**) SSMB with 0.63 eV, **b**) SSMB with 2.0 eV, and **c**) 3.0 eV at room temperature.

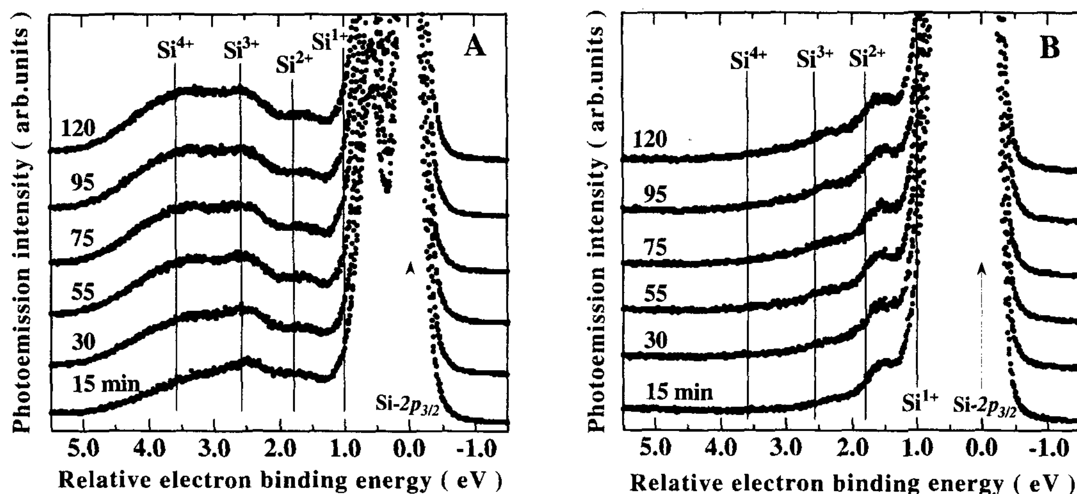

Figure 5. Exposure time dependence of Si-2*p* sub-oxide components with A) Et= 3.0 eV, B) Et= 2.0 eV. Et means the translational kinetic energy of O_2. Photon energy of monochromated synchrotron radiation was 409 eV.

4. Summary

We performed *"in situ"* observation for the initial Si(001) oxidation induced by the translational kinetic energy of O_2. By using photoemission spectroscopy with the synchrotron radiation, it was found that the characteristic oxidation states, as predicted by the first-principles caluculation, clearly depended on the translational kinetic energy. The top Si dimer sites were oxidized in the translational kinetic energy below 1.0 eV. The dimer backbond sites were oxidized with the translational kinetic energy lager than 1.0 eV. The sub-surface backbond sites were oxidized with the translational kinetic energy lager than 2.6 eV. We successfully monitored the time evolution of oxidation states under O_2 SSMB exposure condition by the real-time *"in situ"* photoemisson spectroscopy using the synchrotron radiation.

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