SR-PES and STM Observation of Metastable Chemisorption State of Oxygen on Si(110)-16×2 Surface

With the decrease in MOS device size down to the 65 nm node, the thickness of the SiO_2 gate insulator now falls into the region of 1.2 nm or less, which makes detailed understanding and precise control of the initial oxidation of Si surfaces even more indispensable. This situation applies not only to the conventional Si(001) surface but also to the Si(110) surface, which, from its higher hole mobility [1] and inevitable use in the multi-gated transistors [2], forms a key surface in next-generation CMOS technology. Despite this importance, knowledge of the kinetics of the initial oxidation of the Si(110) surface has been quite limited.

Among various aspects of kinetics in Si oxidation, one of the hot issues is the presence of metastable oxidation states. They are important because they form one of the crucial reaction pathways in Si oxidation. On the Si(111)-7×7 surface, molecularly adsorbed states of oxygen at adatom's dangling bonds are metastable [3], while on the Si(001)-2×1 surface the silanone species (Si=O) is metastable [3,4]. These metastable adsorption states change into more stable oxidation states after annealing. In contrast to the well-understood Si(111) and Si(001) surfaces, however, the Si(110) surface has no information as regards the presence/absence of the metastable adsorption states of oxygen on it. In this study, we conducted high-resolution photoelectron spectroscopy (PES) at SPring-8 to investigate the oxidation states of the Si(110)-16×2 clean surface after the room-temperature (RT) adsorption of oxygen molecules. The impacts of mild 300°C annealing have been investigated as well. Comparative scanning tunneling microscopy (STM) was also conducted to observe atomistic changes after the annealing.

PES measurements were conducted at the surface-chemistry endstation of beamline **BL23SU**. By chemical *ex situ* and thermal *in situ* treatments, we obtained a 16×2 reconstructed surface, which is indicative of the cleanliness of this Si(110) surface. Excitation photons with energies at 365 and 687 eV were used, and photoelectrons with a take-off angle of 20° were collected. Similar chemo-thermal treatment was applied as well for the STM [5].

Figure 1(a) shows the Si 2*p* spectrum of the Si(110)-16×2 clean surface after a RT exposure to 10 L (1 L = 1.0×10^{-6} Torr·s) oxygen molecules. In addition to the bulk peak, at least five components were observed in the spectrum: three suboxide species (Si^{n+}: $n = 1$ - 3) and two surface core-level shifts (SCLS) at α(+0.30 eV) and β(-0.33 eV). The SCLS components are related to the 16×2 surface reconstruction. The presence of higher suboxides like Si^{2+} and Si^{3+}, in addition to primitive Si^{1+}, suggests that the initial oxides are somewhat aggregated even for this small-dose (10 L), small oxygen coverage (0.4 ML), low-temperature (RT) adsorption.

The mild annealing at 300°C for 15 min drastically changes the oxide structure. The Si 2*p* spectrum after the annealing (Fig. 1(b)) shows a decrease in the level of Si^{2+} and an increase in those of the Si^{3+} components. The emergence of the Si^{4+} component is also observed. These results strongly suggest the onset of further aggregation of the oxides by the annealing. Furthermore, the binding energies of the Si^{2+} and Si^{3+} species shift towards higher energies,

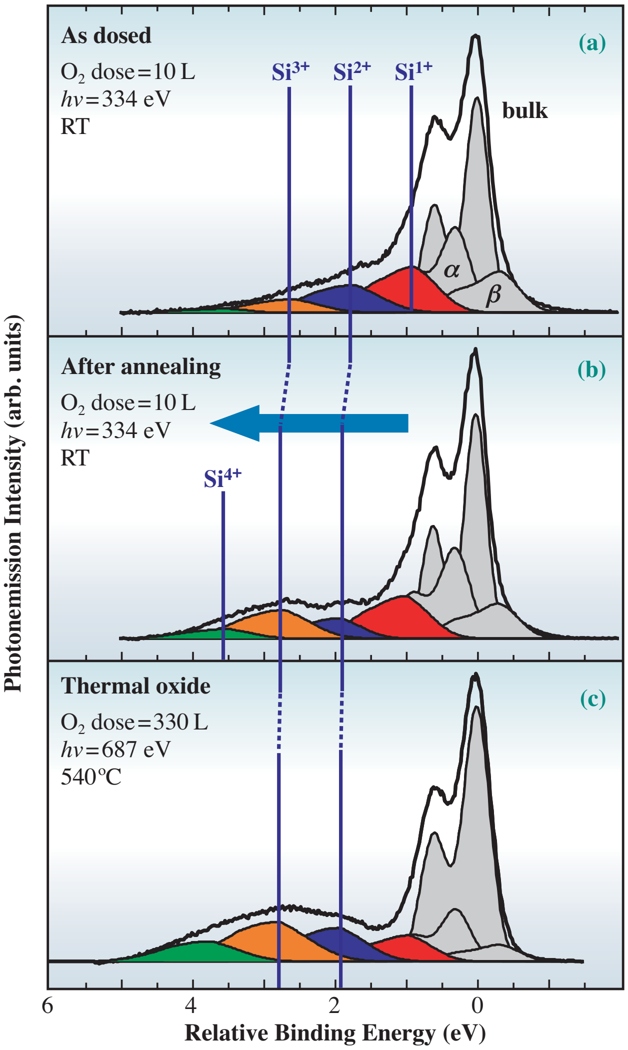

Fig. 1. Si 2*p* spectra of **(a)** as O_2-exposed, **(b)** as-annealed, and **(c)** as thermally oxidized (1 ML) Si(110)-16×2 surfaces.

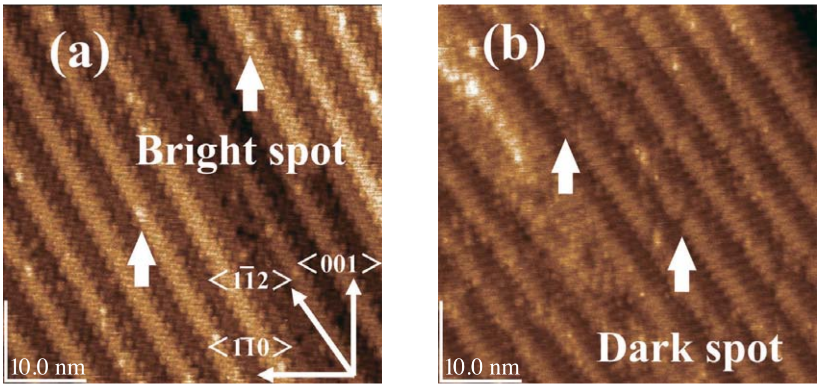

Fig. 2. Filled-state STM images of **(a)** as O_2-exposed and **(b)** as-annealed Si(110)-16×2 surfaces.

approaching those of thermal oxides shown in Fig. 1(c). Such peak shifts of Si suboxides have been already reported for the Si(001)-c(4×2) surface adsorbed with oxygen molecules at low temperatures [6]. According to Ref. [6], the shifts are attributed to deviations in the Si-O-Si angle or in Si-O bond length from the corresponding equilibrium values. Using this scheme, the peak shifts observed in the annealed Si(110):O surface (Fig. 1(b)) are understood to have arisen from the relaxation of locally strained oxidized structures into energetically more stable ones. In other words, the RT adsorption of oxygen molecules onto the Si(110)-16×2 surface results in metastable adsorption states.

This change in the oxidation states with annealing is observed by STM as well. Figure 2(a) shows the unoccupied-state STM image from the Si(110)-16×2 surface adsorbed with oxygen at RT. The small bright spots seen at the pentagon pairs (PPs), the unit for the Si(110)-16×2 surface reconstruction, correspond to reacted sites. Figure 2(b) shows an STM image of the surface after the 300°C, 15-min annealing. Dark spots larger than the bright spots in Fig. 2(a) can now be seen. Combining these with the results of the PES, the small bright spots at PPs before the annealing are related to metastable oxidation states, and the larger dark spots to stable oxidation sites. Figure 3 illustrates the possible oxidation structures before and after the annealing. In RT adsorption, energetically metastable oxidation states, such as adsorption at dangling bonds, are present (Fig. 3(a)). After the annealing, on the other hand, oxygen atoms move to more stable sites, most probably to the backbonds of PP adatoms (Fig. 3(b)). The actual oxidized states after the annealing could be more disordered, because a closer look at the dark spots in the STM image in Fig. 2(b) no longer shows the ordered PP structure. The oxidation caused by the annealing is accompanied by the collapse of the 16×2 reconstruction structure.

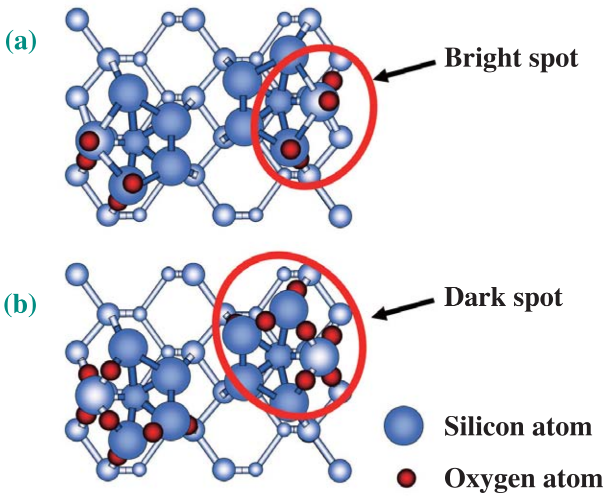

Fig. 3. Possible oxidation structure of **(a)** as O_2-exposed and **(b)** as-annealed Si(110)-16×2 surfaces.

Maki Suemitsu

Research Institute of Electrical Communication,
Tohoku University

E-mail: suemitsu@cir.tohoku.ac.jp

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