

Initial Stage of SiO₂/Si Interface Formation on Hydrogen-Terminated Silicon Surfaces

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Structural changes produced by the oxidation of hydrogen-terminated Si(111)-1 × 1 and Si(100)-2 × 1 surfaces at 300°C in dry oxygen under a pressure of 1 Torr was investigated by X-ray photoelectron spectroscopy (XPS) and multiple internal reflection infrared absorption spectroscopy (MIR-IRAS). Following results are obtained from the analysis of the experimental data: 1) the layer-by-layer oxidation reaction occurs locally at SiO₂/Si(111) interface, while that does not occur at SiO₂/Si(100) interface, however, 2) the oxidation proceeds more uniformly in atomic scale on Si(100) surface than on Si(111) surface.

1. INTRODUCTION

The control of oxide formation on an atomic scale is important for future metal-oxide-semiconductor (MOS) technology. Because the formation of native oxide can be suppressed by terminating Si surface with hydrogen atoms,^{1,2)} the hydrogen-terminated Si surface (abbreviated as H-Si surface hereafter) must be used instead of a clean Si surface for the control of oxide formation on the atomic scale. An atomically flat H-Si(111)-1 × 1 surface can be obtained by the treatment³⁾ in 40% NH₄F solution or that⁴⁾ in boiling water, while an atomically flat H-Si(100)-2 × 1 surface can be obtained by the annealing⁵⁾ in hydrogen atmosphere under pressures higher than 0.2 Torr at 700°C or by the annealing⁶⁾ at high temperature (>1100°C) in hydrogen atmosphere at 1 bar. The thermal oxidation of H-Si(111)-1 × 1 and H-Si(100)-2 × 1 surfaces has been studied by measuring oxidation-induced changes in Si 2p photoelectron spectra,⁷⁻¹¹⁾ while native oxide growth in moist air has been studied by scanning tunneling microscopy.¹²⁾

The oxidation of H-Si(111)-1 × 1 surface was performed in dry oxygen under a pressure of 1 Torr.⁷⁻¹⁰⁾ Following results were obtained from the analysis of Si 2p spectra: 1) the oxidation at 300°C does not proceed uniformly, however the oxidation proceeds more uniformly at 200°C, 2) by the oxidation at 300°C the interface layer becomes continuous at the oxide film thickness of 0.5 nm, and 3) at thickness greater than this the oxidation reaction at the interface occurs layer-by-layer at 600-800°C. The oxidation of H-Si(100)-2 × 1 surface was also performed in the same oxidation atmosphere.¹¹⁾ Following results were obtained from the analysis of Si 2p spectra: 1) the initial stage of interface formation at 300°C does not depend on the initial surface morphology, 2) by the oxidation at 300°C the interface layer becomes continuous at the oxide film thickness of 0.5 nm, and 3) at thickness greater than this the deviation from an atomically flat interface increases with the progress of oxidation, however, an abrupt compositional transition occurs.

In the analysis of changes in Si 2p spectra produced

by the oxidation at 300°C most of the spectra arising from Si-H bonds were neglected, because it was difficult to separate the hydrogenation-induced changes from oxidation induced changes in Si 2p spectra, because the electronegativity of Si is almost equal to that of hydrogen. According to the MIR-IRAS studies described in the following, the desorption of hydrogen does not occur by the oxidation in 1 Torr dry oxygen at 300°C. In the present study the oxidation process of surface Si was investigated from the measurement of oxidation-induced changes in infrared absorption spectra arising from stretching vibration of Si-H bonds. Consequently, the initial stage of oxidation process on H-Si(111)-1 × 1 surface determined previously only from the measurement of oxidation-induced changes in Si 2p spectra will be modified in order to satisfy the oxidation process of surface Si determined by MIR-IRAS studies. The same kinds of study was also performed on H-Si(100)-2 × 1 surface.

2. EXPERIMENTAL DETAILS

The silicon surfaces used for XPS and MIR-IRAS studies were prepared as follows. First, 200nm-thick-oxide films were formed in dry oxygen at 1000°C on 2-6 Ω · cm n-type Si(111) and 5-8 Ω · cm n-type Si(100) wafers for XPS studies and on 10-20 Ω · cm n-type Si(111) and 10-20 Ω · cm n-type Si(100) wafers for MIR-IRAS studies. The wafers used for MIR-IRAS studies have dimensions of 0.5 × 52 × 127 mm and have 45-degree bevels on each of the long sides. The H-Si(111)-1 × 1 surfaces used for XPS studies were prepared by the treatment in 40% NH₄F solution at 20°C for 6 min after removing 200-nm-thick oxide films. The H-Si(100)-2 × 1 surfaces were prepared by the epitaxial growth of silicon in a hydrogen atmosphere at 1100°C for 10 min after removing 200-nm-thick thermal oxide films by the treatment in 1% hydrofluoric acid solution. Here, silicon is epitaxially grown using SiHCl₃ and cooled to below 400°C in hydrogen atmosphere. MIR-IRAS was used as a sensitive tool to determine the microscopic arrangement of the H-Si(100) surface.¹¹⁾ For XPS studies a part of the

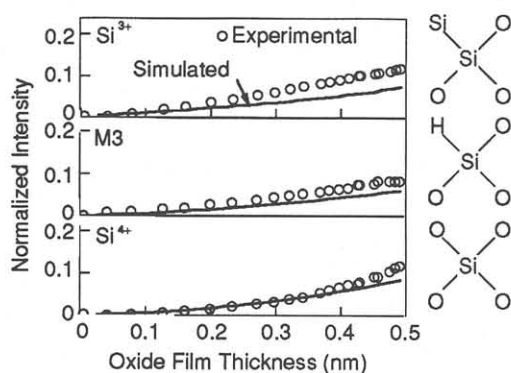


Fig. 1 Amounts of oxidation states as a function of areal density of bridging oxygen atoms for H-Si(111)-1 \times 1 surface. The simulated results are shown by solid curves.

silicon surfaces, whose area is 20 mm in diameter and central part of which were used for XPS studies, were heated optically, while for MIR-IRAS studies the silicon surfaces, central part of which were used for infrared studies, were heated uniformly by flowing current along the long sides of the wafers. Oxidation was performed in dry oxygen under a pressure of 1 Torr at 300°C. The dew point of oxygen gas used in the present oxidation process is below -93°C. The oxidation-induced changes in SiO₂/Si interface structures were studied by measuring Si 2p spectra excited by monochromatic AlK radiation at photoelectron take-off angles of 15, 30 and 90 degrees with an energy resolution of 0.37 eV and an acceptance angle of 3.3 degrees using ESCA-300 manufactured by Scienta Instruments AB. The area used for XPS studies is 6 \times 0.5 mm for the photoelectron take-off angle of 90 degrees. Infrared absorption spectra were measured multiple internal reflection using JIR-5500 manufactured by JEOL with a resolution of 1 cm⁻¹. The infrared radiation from the interferometer is focused at normal incidence onto the input bevel, and is internally reflected nearly 100 times, and exists the output bevel to be collected and refocused onto the photodetector. Here, the infrared absorption spectrum measured for native oxide formed in a mixed solution of H₂SO₄ and H₂O₂ (H₂SO₄:H₂O₂=4:1) was used as a reference spectrum. Other experimental details were described elsewhere.⁸⁾

3. INITIAL STAGE OF OXIDATION OF H-Si(111)-1 \times 1 SURFACE

The oxidation-induced changes in Si 2p and Si 2p_{3/2} spectra for H-Si(111)-1 \times 1 surface were measured until nearly one-molecular-layer thick oxide is formed. Because Si³⁺, M3 and Si⁴⁺ spectra can be separated from Si 2p spectra with rather small ambiguity, these spectra will be used for the following studies of oxidation process. Here, Si³⁺, M3 and Si⁴⁺ denote the Si atom bonded to one

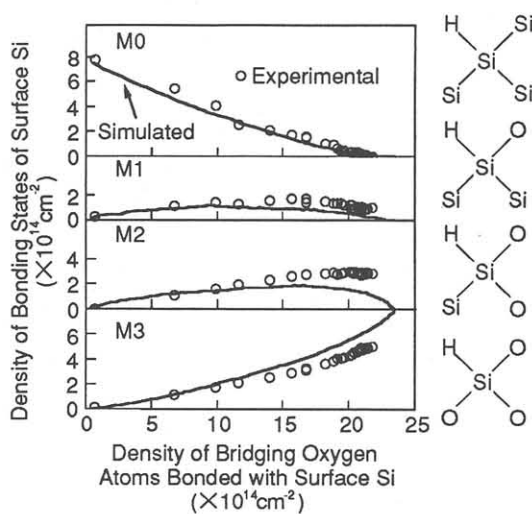


Fig. 2 Number of bonding states of surface Si as a function of number of bridging oxygen atoms bonded with surface Si for H-Si(111)-1 \times 1. The simulated results are shown by solid curves.

Si atom and three oxygen atoms, the Si atom bonded to one hydrogen atom and three Si atoms and the Si atom bonded to four oxygen atoms, respectively. Figure 1 shows the amounts of Si³⁺, M3 and Si⁴⁺ as a function of oxide film thickness obtained from the analysis of Si2p spectra. If the oxidation reaction occurs uniformly, the oxide consists only of Si⁴⁺ at the oxide film thickness of 0.3 nm, which corresponds to one molecular layer of SiO₂. However, according to this figure, this is not the case. This implies the non-uniform oxidation reaction at early stage.

The oxidation-induced changes in infrared absorption spectra for H-Si(111)-1 \times 1 surface were measured. According to the analysis of the spectra, the total amount of Si-H bonds is not affected by the oxidation, in other words, the desorption of hydrogen does not occur, if the oscillator strengths are the same for all kinds of stretching vibrations of Si-H bonds detected. Figure 2 is obtained from the analysis of the spectra and shows the amounts of oxidation states of surface Si as a function of areal densities of oxygen atoms bonded to surface Si. Here, the horizontal scales are calculated by considering bonding configurations of oxidized surface Si atoms.

The oxidation processes shown in Figs. 1 and 2 are simulated as follows: The three dimensional Si lattice consisting of 40 atoms \times 40 atoms in each layer on Si(111) plane is used for the simulation of oxidation. The bonding probabilities of Si atoms with oxygen atoms are adjusted until almost the same figures with those shown in Figs. 1 and 2 are obtained. For example, the Si atom bonded with oxygen atom is assumed to have higher bonding probability with oxygen atom as compared with Si atom, which do not bond with oxygen atom. The solid

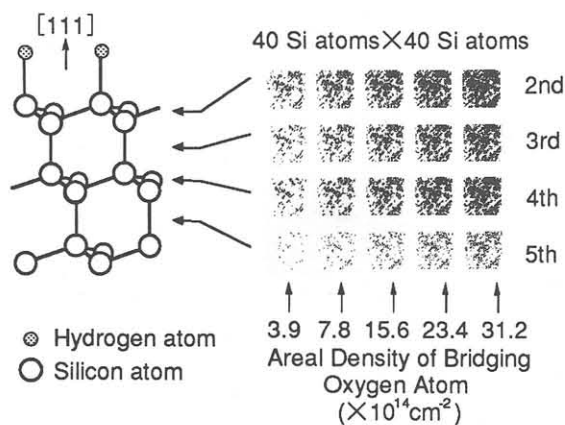


Fig. 3. Distribution of bridging oxygen atoms at and near the H-Si(111)-1 \times 1 surface.

curves in Figs. 1 and 2 are obtained for optimized simulation. The distribution of bridging oxygen atoms on each Si layer is shown in Fig. 3. From the top to the bottom of this figure, the topmost layer, the second layer from the top, the third layer and so on are shown in this order. From the left to the right the amount of bridging oxygen atoms increases. This figure indicates that once the isolated bridging oxygen atoms are produced the oxidation proceeds in lateral direction around these oxygen atoms. With oxidizing further the oxidation proceeds in vertical direction and results in the non-uniform oxidation.

4. INITIAL STAGE OF OXIDATION OF H-Si(100)-2 \times 1 SURFACE

As in the case of H-Si(111) -1 \times 1 surface, the XPS and MIR-IRAS studies on the initial stage of oxidation of H-Si(100)-2 \times 1 surface were performed until nearly one-molecular-layer thick oxide is formed. According to MIR-IRAS study, M3 is formed at the early stage of oxidation. This implies that the dimer bonds are bridged by oxygen atoms to form Si-O-Si bonds at the early stage of oxidation. Such bonds are considered in the simulation of changes in Si 2p spectral intensities with the progress of oxidation. The distribution of bridging oxygen atoms on each Si layer thus determined is shown in Fig. 4.

5. SUMMARY

Structural changes produced by the oxidation of H-Si(111)-1 \times 1 and Si(100)-2 \times 1 surfaces at 300°C in dry oxygen under a pressure of 1 Torr was investigated by XPS and MIR-IRAS. The oxidation induced changes in infrared absorption arising from stretching vibration of Si-H bonds were measured for the determination of oxidation processes of surface Si and are used to determine the oxidation process of surface Si on H-Si(111)-1 \times 1 and H-Si(100)-2 \times 1 surfaces. These are combined with

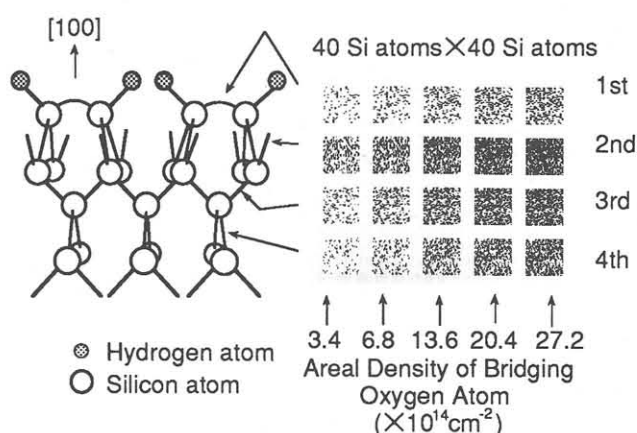


Fig. 4. Distribution of bridging oxygen atoms at and near the H-Si(100)-2 \times 1 surface.

the oxidation processes of bulk Si determined from the oxidation-induced changes in Si 2p photoelectron spectra. Following results are obtained from the analysis and simulation of experimental results: 1) the layer-by-layer oxidation reaction occurs locally at SiO₂/Si(111) interface, while that does not occur on SiO₂/Si(100) interface, however, 2) the oxidation on Si(100) surface proceeds more uniformly in atomic scale than that on Si(111) surface.

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