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Initial Stage of Oxidation of Hydrogen-Terminated Silicon Surface

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The initial stage of oxidation of 40% NH_4F treated Si(111) surface at 300℃ in dry oxygen with a pressure of 133 Pa and the subsequent oxidation at 600℃ and 800℃ were studied. It was found from the analysis of Si 2p photoelectron spectra that non-uniform layer by layer oxidation proceeds at 300℃. The experimental results suggesting layer by layer growth of oxide were obtained even for higher oxidation temperatures of 600℃ and 800℃.

1. Introduction

If the hydrogen terminated silicon surface can be oxidized without breaking Si-H bonds, so called backbond oxidation, the flatness of Si surface must be roughly preserved and almost uniform oxidation must be realized. Nagasawa et al. found such backbond oxidation on Si(100) surface at room temperature.[1] Recently Ohmi et al. found that nearly one molecular layer of silicon oxide formed on Si(100) surface by backbond oxidation at 300℃, so called preoxide, is stable up to 900℃ in dry argon.[2] This suggests that the desorption of hydrogen atoms on the surface of this preoxide weakly affect the surface structure. Higashi et al. discovered that an atomically flat and ultraclean Si(111) surface can be obtained by the treatment in 40% NH_4F solution.[3] It was found from the previous studies[4] on the initial stage of oxidation of 40% NH_4F treated Si(111) surface that the oxidation rate of p-type Si(111) is faster than that of n-type Si, the oxidation proceeds more uniformly on p-type Si than that on n-type and even on p-type Si interface is not abrupt. It is the purpose of the present paper to report the simulated results of the initial stage of oxidation of 40% NH_4F treated Si(111) surfaces at 300℃ in dry oxygen with a pressure of 133 Pa. Furthermore, the experimental results exhibiting layer by layer growth of thermal oxides at 600℃ and 800℃ in the same oxidation atomosphere are presented.

2. Simulation of Oxidation Process at 300℃

Figure 1 reproduces the oxidation induced changes in Si 2p photoelectron spectra measured at photoelectron take off angle of 15 degrees.[4] Here, Si^{1+}, Si^{2+}, Si^{3+} have almost the same binding energies with those defined in the literature.[5] Si^{4+} denotes Si atom bonded with four oxygen atoms. Figrue 2 shows the amounts of intermediate oxidation states as a function of number of bridging oxygen atoms obtained from the spectral analysis of Fig. 1. The number of bridging oxygen atoms indicated on the horizontal scale are calculated by considering the bonding configurations of intermediate oxidation states of Si atoms. According to this figure, at the early stage of oxidation the amount of Si^{1+} first increases and then the amount of Si^{4+} increases steeply. The latter implies the non-uniform oxide formation.

The oxidation processes thus measured are simulated as follows: The three dimensional silicon lattice consisting of 40 atoms × 40 atoms in each layer on (111) plane is used for the simulation of oxidation. The bonding probability of silicon atom with oxygen atom is adjusted until the almost the same figure with that shown in Fig. 2 is obtained. Because Fig. 2 implies that the oxidation proceeds non-uniformly, Si atom bonded with

oxygen atom is assumed to have higher bonding probability with oxygen atom as compared with other Si atoms. Figure 3 shows the simulated result. The distribution of bridging oxygens on each Si layer is shown in Fig. 4. From top to bottom on the left hand side of this figure the topmost layer, the second layer, the third layer and so on are shown in this order. From left to right on the right hand side of this figure the amount of bridging oxygen atoms increase. 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 layer by layer oxidation.

3. Layer by Layer Growth of Thermal Oxide

The oxidation was performed at 300 ℃ in dry oxygen with a pressure of 133 Pa up to the oxide film thickness of nearly 0.5 nm. Through this oxide the oxidation was performed at 600℃ in the same oxidation atomosphere up to the oxide film thickness of nearly 1.0 nm followed by the further oxidation at 800℃ in the same oxidation atomosphere up to nearly 1.5 nm. These oxidations were performed on an atomically flat H-terminated 2-6 Ω · cm n-type Si(111) surface prepared as follows. First, 200-nm-thick oxide film was formed on this surface in dry oxygen at 1000℃. Second, this oxide was removed by buffered hydrofluoric acid followed by the formation of native oxide by the treatment in H_2SO_4-H_2O_2 solution at 85-90℃. Third, this native oxide was removed by the treatment in 40% NH_4F solution followed by a rinse in deionized water. The method of oxidation is the same as that described elsewhere.[6)]

The amounts of intermediate oxidation states change with the progress of oxidation as shown in Fig. 5. Here, the oxide film thickness in the horizontal scale is calculated from the analysis of Si 2p photoelectron spectra assuming that electron escape depth in Si and that in silicon oxide is 2.6 nm and 3.4 nm, respectively. It should be noted that the incease and decrease in the amount of Si^{1+} and Si^{3+} are observed repeatedly with a period of 0.3 nm in thickness. Considering that the atomically flat SiO_2/Si interface formed on Si(111)

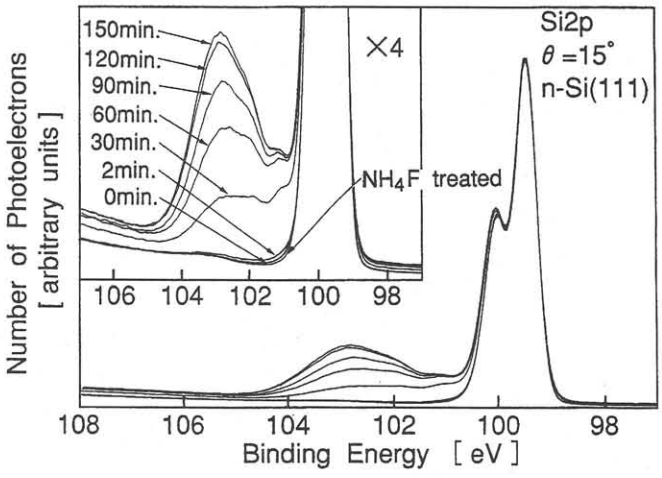

Fig. 1 Oxidation induced change in Si 2p photoelectron spectrum for n-type Si(111) surface.

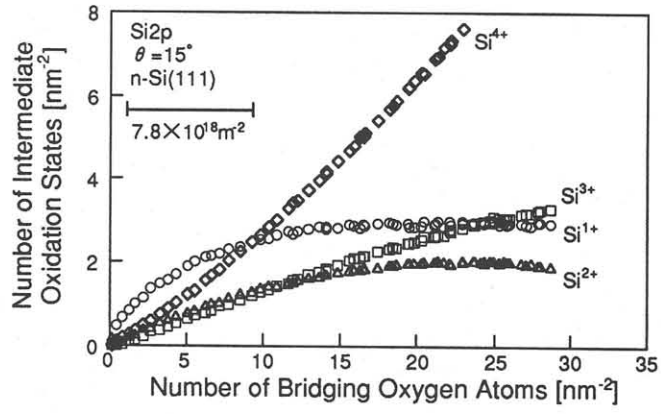

Fig. 2 Amounts of intermediate oxidation states as a function of number of bridging oxygen atoms.

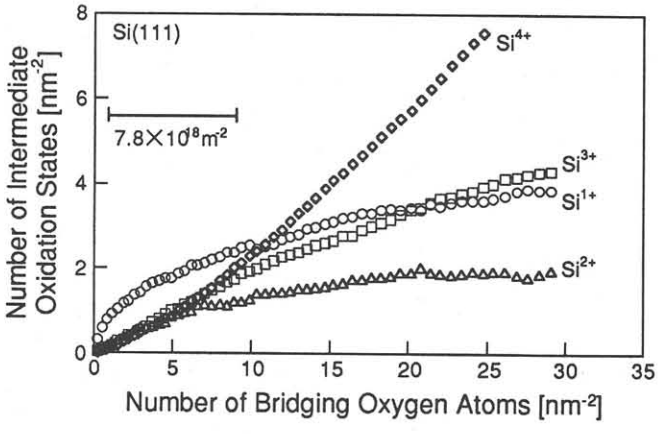

Fig. 3 Number of intermediate oxidation states as a function of number of bridging oxygen atoms, which is obtained from the optimized simulation of experimental data.

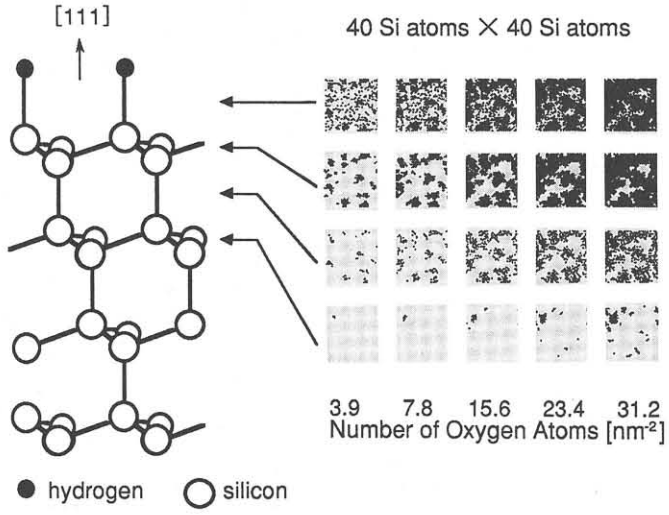

Fig. 4. Distribution of oxygen atoms at and near the hydrogen-terminated silicon surface corresponding to the simulated results in Fig. 3.

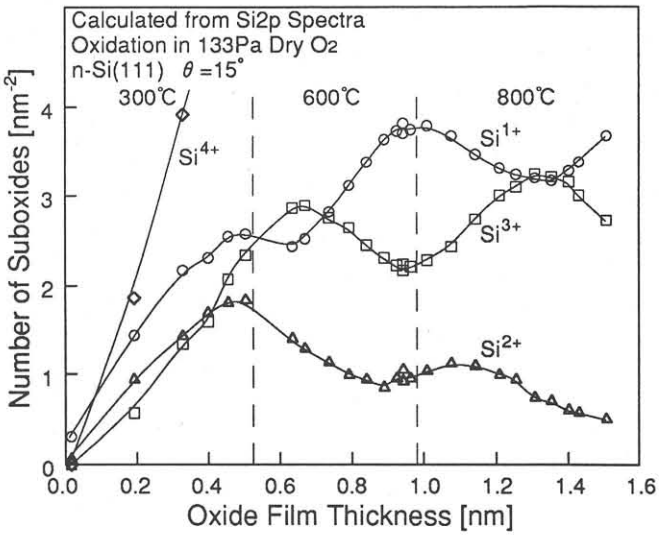

Fig. 5 Number of suboxides as a function of oxide film thickness obtained for oxidation at 600℃ after forming oxide at 300℃ and the subsequent oxidation at 800℃.

surface consists of Si^{1+} or Si^{3+}, Figure 5 implies that silicon oxide grows layer by layer even at higher oxidation temperatures of 600℃ and 800℃.

4. Summary

It was found from the analysis of the initial stage of oxidation of NH_4F treated Si(111) surfaces at 300℃ in dry oxygen with a pressure of 133 Pa that the non-uniform layer by layer oxidation proceeds at this oxidation temperature. Furthermore, the experimental results suggesting layer by layer growth of oxide were obtained even for higher oxidation temperatures of 600℃ and 800℃.

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