

## Surface and Interface Structures of Ultra-Thin Thermal Oxides on Si(100)

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### 1. Introduction

As a result of considerable progress in microfabrication technology for ULSI, it has become necessary to control oxide formation on an atomic scale in order to produce defect-free silicon oxide/silicon interface.[1] However, the observation of surface structure of ultrathin silicon oxide on an atomic scale, which is significant for the atomic scale control of oxide formation, has started only recently.[2]

If Si(111) surface is oxidized, Si<sup>+</sup> interface and Si<sup>2+</sup> interface appears alternately as a result of periodic change in bonding configuration along <111> direction.[3] Here, Si<sup>+</sup> and Si<sup>2+</sup> denote a Si atom bonded to one oxygen atom and three Si atoms and a Si atom bonded to three oxygen atoms and one Si atom, respectively. In accordance with the periodic changes in interface structure, the surface microroughness[2] was found to change periodically with the progress of oxidation. On the other hand, the periodic change in SiO<sub>2</sub>/Si(100) interface structure with the progress of oxidation can not be expected, if the interface consists only of Si<sup>2+</sup>. Here, Si<sup>2+</sup> denotes a Si atom bonded to two oxygen atoms and two Si atoms. However, it will be shown in the present paper that the surface microroughness of ultra-thin silicon oxide formed on Si(100) changes periodically with the progress of oxidation at 600°C in the oxide film thickness from 0.8 to 1.2 nm. This implies the layer-by-layer oxidation on Si(100) surface.

### 2. Experimental Details

The 5 μm thick n-Si layer epitaxially grown on (100) surface at 1100°C was terminated with hydrogen by the treatment in 0.5% hydrofluoric acid solution. By heating this hydrogen-terminated Si surface (abbreviated as the H-Si surface hereafter) in 4 Torr dry oxygen at 300°C, a thermal oxide layer with a thickness of about 0.6 nm was formed. In order to investigate the changes in surface morphology and interface structure with the progress of oxidation through this preoxide, we performed another oxidation, in 1 Torr dry oxygen at 600°C, and measurements of noncontact-mode atomic force microscope (NC-AFM) images and Si 2p photoelectron spectra. Since Si 2p spectra give structural information for an area larger than 6 mm × 0.5 mm and the root-mean-square roughness (Rms) of the SiO<sub>2</sub>/Si interface saturates for an area larger than 100 nm × 100nm,[4] the oxide-surface microroughness, defined by the average roughness (Ra), and Rms were measured over an area of 200 nm × 200nm using cantilever, with a force constant of 39 N/m and resonant frequency of about 300 kHz, and a single-crystalline silicon probe. Here, the effect of atomic steps on the surface

microroughness was minimized by using Si wafer with mis-alignment of less than 0.017 degrees from (100) surface. Other experimental details were described elsewhere.[2]

### 3. Experimental Results and Discussion

Figure 1 shows the surface morphology of oxide films with thicknesses of 0.8 and 1.2 nm measured over an area of 200 nm × 200 nm. The upper part of this figure shows no significant change in surface morphology produced by the change in thickness from 0.8 to 1.2 nm, while the lower part of this figure shows extremely smooth surface. The surface microroughness in Fig. 2 repeatedly increase and decrease with a period in thickness of 0.18 nm. This period in thickness is in good agreement with the thickness of one molecular layer of SiO<sub>2</sub> determined from the layer-by-layer oxidation on Si(100) surface in pure water at room temperature.[5] Figure 2 also shows the gradual increase in the surface microroughness with the increase in thickness, which must be produced by the gradual increase in interface roughness.[6]

The layer-by-layer oxidation implied by Fig. 1 was studied by measuring the change in interface structure with progress of oxidation. The upper part of Fig. 3 shows the Si 2p spectral intensity of Si<sup>4+</sup> and that of suboxides consisting of Si<sup>+</sup>, Si<sup>2+</sup> and Si<sup>3+</sup> normalized by the spectral intensity of Si substrate as a function of oxide film thickness. Here, Si<sup>4+</sup> denotes a Si atom bonded with four oxygen atoms. According to this upper part of Fig. 3, the normalized spectral intensity of suboxides saturates at a thickness of nearly 0.6 nm, while that of Si<sup>4+</sup> does not saturate at this thickness. Furthermore, the saturated normalized spectral intensity of suboxides is slightly larger than that calculated for an abrupt interface consisting of Si<sup>2+</sup>, which is shown by the dashed line in Fig. 3. The lower part of Fig. 3 shows the areal densities of Si<sup>+</sup>, Si<sup>2+</sup> and Si<sup>3+</sup> as a function of oxide film thickness. According to this figure, the interface consists not only of Si<sup>2+</sup>, but also of Si<sup>3+</sup> and Si<sup>+</sup>. Therefore, the interface structure must be the combination of the interface consisting of Si<sup>2+</sup>, the interface[5] consisting of Si<sup>+</sup> and Si<sup>3+</sup>, and the interface[7] consisting of Si<sup>3+</sup>. Therefore, the layer-by-layer oxidation must occur locally.

### 4. Summary

The periodic changes in surface microroughness of thermal oxide films formed on Si(100) surface in dry oxygen at 600°C with a period in thickness of 0.18 nm were discovered using NC-AFM. This observation combined with structural studies of the interface implies that the oxidation, a part of which is layer-by-layer oxidation, proceeds quite uniformly.

**References**

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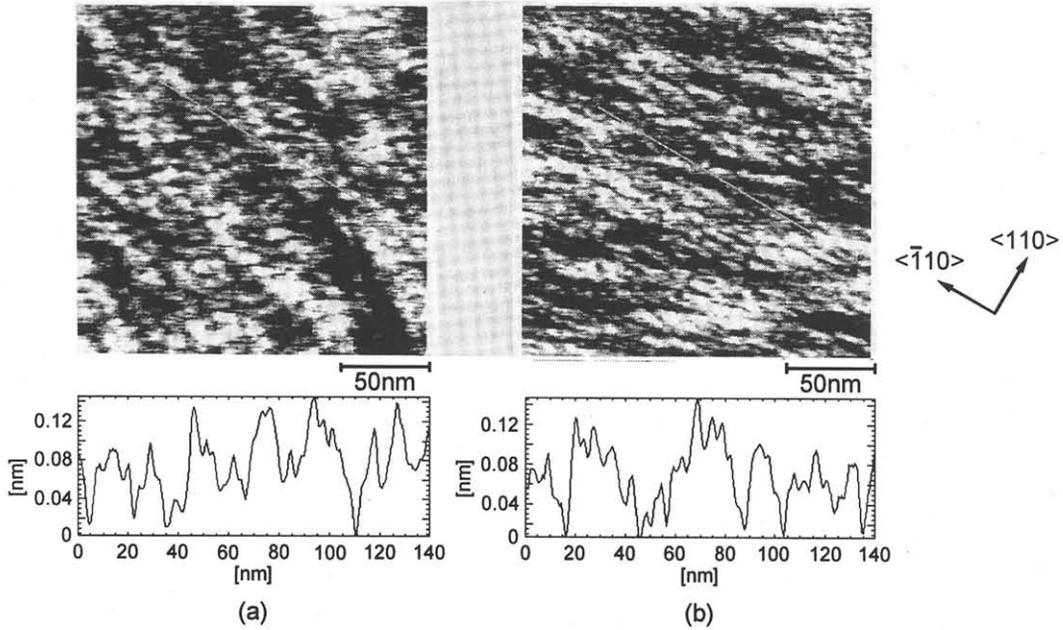


Fig. 1 Atomic force images and cross section of oxide films with thicknesses of (a) 0.8 nm and (b) 1.2 nm.

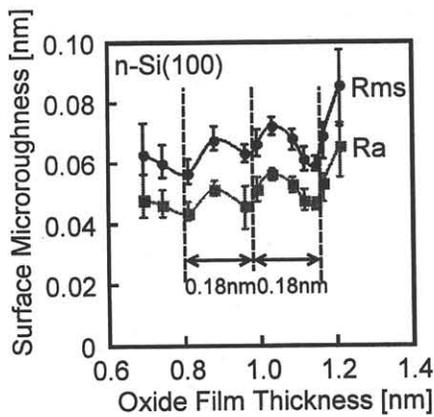


Fig. 2 Two kinds of surface microroughness of oxide surface.

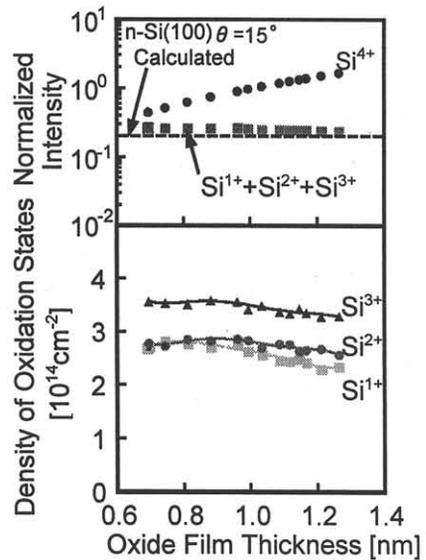


Fig. 3 Upper part shows normalized spectral intensity of  $\text{Si}^{4+}$  and sum of intensities of suboxides as functions of oxide film thickness. The dashed line shows the normalized intensity calculated for the interface consisting of  $\text{Si}^{2+}$ . Lower part shows the dependence of densities of  $\text{Si}^{1+}$ ,  $\text{Si}^{2+}$ , and  $\text{Si}^{3+}$  on the oxide film thickness. Si 2p spectra were measured at a photoelectron take-off angle of  $15^\circ$ .