Local Ordering and Layer Growth of the Initial Thermal Oxide of Si(001)

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The initial stages of the thermal (600 °C) oxidation of Si(001) clean surface were studied by scanning tunneling microscopy (STM). The oxides spread over the surface with the O2 exposure. At 120 L, almost all the surface was covered by the oxides. Steps still can be identified, and the apparent roughness had local minimum at this O2 exposure. These results indicate that the first layer is oxidized quite uniformly. Some local orderings of the initial oxides were observed on the terraces. Such local orderings may enhance the oxidation in lateral direction, and thus initial oxidation of Si(001) proceed layer by layer even at 600 °C.

1. Introduction
Gate Oxides' thickness of the future LSI will be less than 6 nm. In realizing such devices, it is important to reduce oxide-Si interface roughness[1,2]. At room temperature (native oxide growth), the oxidation proceeds by layer by layer. Above around 400 °C or 500 °C (thermal oxide growth), the oxide growth is qualitatively different from that at room temperature, because Si-Si bonds are easily broken above this temperature. For example, scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) results suggested that the initial thermal oxide growth of Si(111) at 600 °C proceeds by island oxide formation[3,4]. On the other hand, transmission electron microscopy (TEM) results suggested layer by layer oxidation of Si(111) at high temperatures[5]. In this paper, we will show that the initial thermal oxide growth of Si(001) proceeds layer by layer rather than by island oxide formation even at 600 °C.

2. Experimental
The sample was an n-type (0.05-0.09 Ω cm) Si(001) CZ wafer with a misorientation of 0.4° toward [110]. Similar results were also obtained on a p-type wafer. A clean surface was obtained by heating up to 1200 °C in ultrahigh vacuum (UHV). Oxide was formed at 600 °C and at O2 pressure of 1.33 × 10^-6 Pa. The exposure was varied from 15 L to 1200 L (1L = 1.33 × 10^-6 Pa s) by varying the exposure time. These exposure corresponds to the coverage up to more than 1 mono-layer (ML)[6]. All the STM measurements were performed in the same UHV chamber after cooling the sample down to room temperature.

3. Results and discussion
Fig. 1 shows STM topographs of the Si(001) surface exposed to O2 at 600 °C. At 15L (fig. 1 (a)), the O2 exposure produced oxides (A ~ C) and Si islands (D) among the Si dimers. The oxides appeared as "dark site" (A), "sequence of dots" (B), and "dot (with dark surroundings)" (C). Among them, "dark site" (A) is not stable, while "sequence of dots" (B) and "dot (with dark surroundings)" (C) are stable[7]. Steps are indicated by arrows.

At 60 L (fig. 1 (b)), the oxides spread over the surface with O2 exposure. Si dimer rows are still observed at this stage. The oxidation starts on both step edges and terraces, and step edges do not seem to be important for the growth of the oxides on this experimental condition. This is in contrast to the oxide growth from the step edges which is reported in case of native oxide growth in water[8].

At 120 L (fig. 1 (c)), almost all the surface was covered by the oxides. This suggests that the O2 coverage is roughly 1 ML, which is in agreement with XPS results[6]. Steps still can be identified. These results indicate that the first layer is oxidized quite uniformly. Some local orderings of the "sequence of dots" (oxide B) were observed on the terraces.

At 600 L (fig. 1 (d)), "sequence of dots" (oxide B) covers the surface. This may be explained by the transformation of "dark site" (A) (not stable) into "sequence of dots" (B) and "dot (with dark surroundings)" (C) (stable oxide). Unlike Si(111), since all Si atoms on Si(001) have 2 back bonds, it is easier for the initial thermal oxides of Si(001) to have some local orderings. In order to estimate the uniformity of the oxides, we calculated the apparent roughness Ra and RMS from the STM topographs (fig. 2). We note that the STM topographs reflect both the electronic state (which changes upon oxidation) and the morphology of the surface. Therefore, although apparent roughness does not directly reflect the oxide-Si interface roughness, we consider that the apparent roughness contains some information of the oxide-Si interface roughness[9].

As a whole, the apparent roughness increases with the O2 exposure. In addition, it has local minimum at 120 L which indicates that the first layer is oxidized quite uniformly[10]. Figure 3 schematically explains the apparent roughness observed above. Figure 3 (b) corresponds to the O2 exposure of 60 L: the apparent roughness increases because of the co-existence of the oxidized surface and clean (not oxidized) surface. Figure 3 (c) corresponds to the O2 exposure of 120 L: the apparent roughness decreases again because the first layer is oxidized quite uniformly. The apparent roughness at 120 L is larger than that at the clean surface. This indicates that
the oxide-Si interface is not perfect: there exist some Si islands, the first layer which is not oxidized yet, and the second layer which is oxidized already. This agrees with the previous results that the oxide-Si interface initially becomes rougher during the thermal oxidation of Si(001)[11-13].

Oxidation is ruled by the following process: (1) nucleation of the oxides; (2) lateral (parallel to the surface) growth of the oxides; (3) vertical (normal to the surface) growth of the oxides; (4) transformation of the oxides into the stable oxides; (5) etching of the oxides. Si islands are also formed during these processes. Among these processes, we will neglect the etching of the oxides[7], because etching rate of the Si surface decreases abruptly above the critical O₂ pressure[14]. On the clean (not oxidized) surface, nucleation of the oxides seem to be the fastest process. In addition, the lateral and vertical growth of the oxides at 600°C may be comparatively important than those at room temperature: the lateral growth may be enhanced by the local ordering of the stable "sequence of dot" (oxide B), while vertical growth may be enhanced by the larger O₂ or O diffusion rate. The layer by layer growth of the oxides indicates that the lateral growth is faster than the vertical growth. Therefore, the local ordering of the stable "sequence of dot" (oxide B) seem to play an important role in the initial oxidation of Si(001) which proceed layer by layer even at 600°C.

Fig. 1. Si(001) surface exposed to O₂ at 600°C. 1L=1.33x10⁻⁴Pa s. Arrows indicate steps.
(a) Oxides (A~C) and Si island (D) are observed among the Si dimer rows. The Oxides appear as "dark site" (A), "sequence of dots" (B) and "dot (with dark surroundings)" (C).
(b) The oxides spread over the surface with the exposure. Si dimer rows are still observed.
(c) Almost all the surface was covered by the oxides. O₂ coverage is considered to be roughly 1ML. Steps still can be identified. Some local orderings of the "sequence of dots" (oxide B) were observed on the terraces.
(d) The "sequence of dots" (oxide B) covers the surface.
4. Conclusions

The initial stages of the thermal (600°C) oxidation of Si(001) clean surface were studied by STM. The oxidation starts on both step edges and terraces. The oxides spread over the surface with the O₂ exposure. As a whole, the apparent roughness increases with the O₂ exposure. At 120L, almost all the surface was covered by the oxides. Steps still can be identified, and the apparent roughness had local minimum at this O₂ exposure. These results indicate that the first layer is oxidized quite uniformly. Some local orderings of the "sequence of dot" (stable initial oxide) were observed on the terraces. Such local orderings may enhance the oxidation in lateral direction, and thus initial oxidation of Si(001) proceed layer by layer even at 600°C. STM is an useful technique to study the initial oxidation process.

Acknowledgements

We acknowledge Professors T. Sakurai and T. Hashizume for collaboration in developing the STM apparatus.

References