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

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The initial stages of the thermal (600℃) oxidation of Si(001) clean surface were studied by scanning tunneling microscopy (STM). The oxides spread over the surface with the O_2 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 O_2 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℃.

1. Introduction

Gate Oxides' thickness of the future LSIs will be less than 6nm. In realizing such devices, it is important to reduce oxide-Si interface roughness[1,2]. At room temperature (native oxide growth), the oxidation proceeds layer by layer. Above around 400℃ or 500℃ (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℃ 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℃.

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℃ in ultrahigh vacuum (UHV). Oxide was formed at 600℃ and at O_2 pressure of 1.33×10^{-4}Pa. The exposure was varied from 15L to 1200L (1L = 1.33×10^{-4}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 O_2 at 600℃. At 15L (fig. 1 (a)), the O_2 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 60L (fig. 1 (b)), the oxides spread over the surface with O_2 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 120L (fig. 1 (c)), almost all the surface was covered by the oxides. This suggests that the O_2 coverage is roughly 1ML, 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 600L (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 O_2 exposure. In addition, it has local minimum at 120L 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 O_2 exposure of 60L: the apparent roughness increases because of the co-existence of the oxidized surface and clean (not oxidized) surface. Figure 3 (c) corresponds to the O_2 exposure of 120L: the apparent roughness decreases again because the first layer is oxidized quite uniformly. The apparent roughness at 120L 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 O_2 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℃ 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 O_2 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℃.

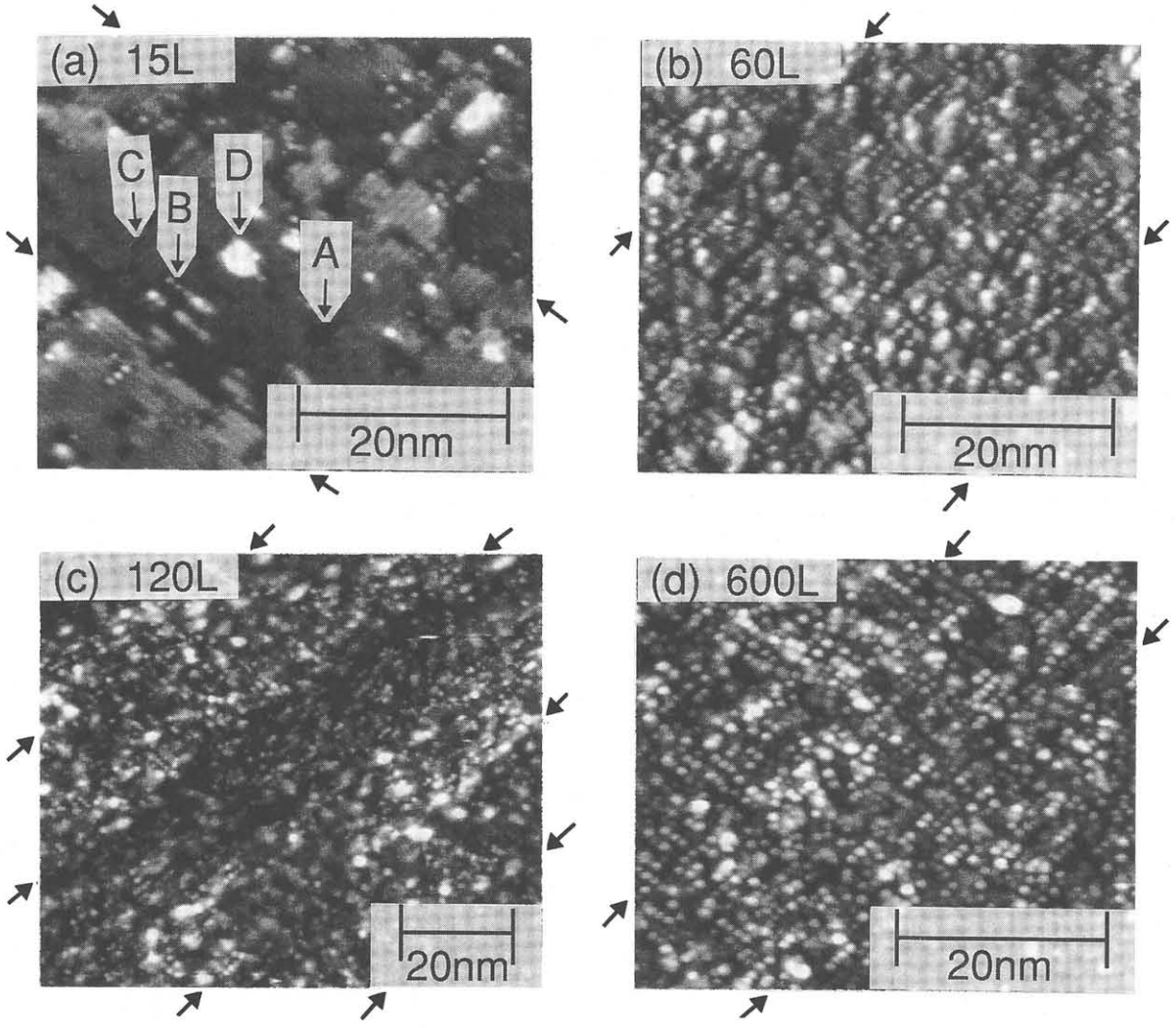

Fig. 1. Si(001) surface exposed to O_2 at 600℃. 1L=1.33×10^{-4}Pa s. Arrows indicate steps.
(a) Oxides (A～C) and Si island (D) are observed among the Si dimer rows. The Oxides appear as "dark site" (A), "sequence of dots" (B) and "dot (with dark surroundings)" (C).
(b) The oxides spread over the surface with the exposure. Si dimer rows are still observed.
(c) Almost all the surface was covered by the oxides. O_2 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.

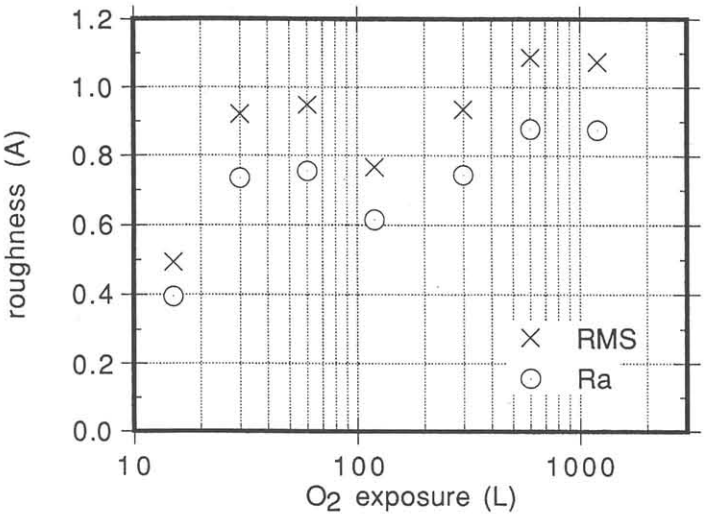

Fig. 2. Apparent roughness calculated from the STM topographs. As a whole the apparent roughness increases with O_2 exposure. In addition, it has local minimum at 120L.

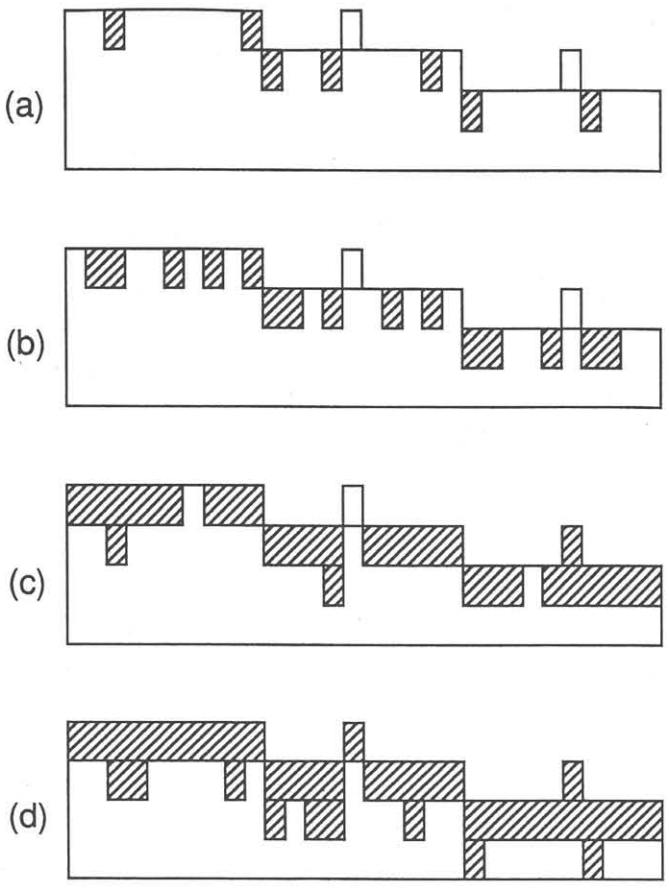

Fig. 3. Schematic representation of Si(001) oxidation process. Shaded region represent the oxidized region.
(a) Nucleation of oxides.
(b) Lateral growth and additional nucleation of oxides. The apparent roughness increases because of the co-existence of oxidized surface and clean (not oxidized) surface.
(c) The apparent roughness decreases again because first layer is oxidized quite uniformly.
(d) Oxide growth proceeds to second layer.

4.Conclusions

The initial stages of the thermal (600℃) 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 O_2 exposure. As a whole, the apparent roughness increases with the O_2 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 O_2 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℃. STM is an useful technique to study the initial oxidation process.

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References

[1] Y. C. Cheng and E. A. Sullivan, Surf. Sci. 34 (1973) 717.
[2] T. Ohmi, K. Kotani, A. Teramoto and M. Miyashita, IEEE Electron Device Letters, 12 (1991) 652.
[3] Y. Ono and M. Tabe, 1992 Int. Conf. Solid State Devices and Materials, Tsukuba, (1992) 196.
[4] M. Tabe, T. T. Chiang, I. Lindau and W. E. Spicer, Phys. Rev. B 34 (1986) 2706.
[5] F. M. Ross and J. M. Gibson, Phys. Rev. Lett. 68 (1992) 1782.
[6] F. Lutz, J. F. Bischoff, L. Kubler and D. Bolmont, Phys. Rev. B 40 (1989) 10356; ibid. B 40 (1989) 11747.
[7] M. Udagawa, M. Niwa and I. Sumita, Jpn. J. Appl. Phys. 32 (1993) 282.
[8] M. Hirose, T. Yasaka, M. Takakura and S. Miyazaki, Solid State Technology (Dec. 1991) 43.
[9] A. H. Carim, M. M. Dovek, C. F. Quate, R. Sinclair and C. Vorst, Science 273 (1987) 630.
[10] U. Neuwald, H. E. Hessel, A. Feltz, U. Memmert and R. J. Behm, Appl. Phys. Lett. 60 (1992) 1307.
[11] A. H. Carim and R. Sinclair, J. Electrochem. Soc. 134 (1987) 741.
[12] T. Ohmi, K. Matsumoto, K. Nakamura, K. Makihara, J. Takano and K. Yamamoto, Appl. Phys. Lett. 62 (1993) 405.
[13] M. Niwa et al., Appl. Phys. Lett., in press (1993).
[14] J. J. Lander and J. Morrison, J. Appl. Phys. 33 (1962) 2089.