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The Initial Stages of the Thermal Oxidation of Si(001) 2×1 Surface Studied by Scanning Tunneling Microscopy

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The initial stages of the thermal oxidation of Si(001) 2×1 surface were studied by scanning tunneling microscopy (STM). The O_2 exposure at 600℃ produced a random distribution of Si islands, "dark sites", "sequence of dots", and "dots with dark surroundings". The "sequence of dots" and the "dots with dark surroundings" seem to remain on the surface even after the successive heating. The "dark sites", the "sequence of dots", and the "dots with dark surroundings" are considered to be initial forms of oxides. From the experimental results, a possible model of the "sequence of dots" was proposed. Also in the discussion, some relations between the SiO_2/Si interface and the initial forms of the thermal oxides have been suggested.

1. Introduction

The minimum feature size of the recent VLSIs have been reduced down to sub-micron. In the near future, the requirement of the gate oxides' thickness of the metal-oxide semiconductor (MOS) field-effect transistors (FETs) will be less than 10nm. Accordingly, the understanding of the initial oxidation process and the structure of the SiO_2/Si interface will be significantly important in realizing deep sub-micron MOS FETs. As such, many works have been made on the initial stages of the thermal oxidation of Si surfaces. Despite these efforts, the initial stages of the thermal oxidation of clean Si surfaces are still not fully understood because of the lack of the spatial resolution of the traditional surface analytical techniques.

In contrast, STM has atomic or near-atomic resolution, and hence is an useful technique to study the initial stages of the oxidation of Si surfaces. In fact, many groups have recently used STM to study the initial stages of the oxidation of Si surfaces[1-6]. Here, we report a new STM measurement on the initial stages of the thermal oxidation of Si(001) 2×1 surface which is primarily a research in the field of surface science, and also in the long run, a clue to elucidate the initial oxidation process in Si technology.

2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 7×10^{-9}Pa using an apparatus similar to that described elsewhere[7]. The sample was an n-type (0.05-0.09 Ω cm) Si(001) CZ wafer. A clean 2×1 surface was obtained by degassing the sample at 800℃ by resistive heating for several hours, followed by a series of short heatings up to 1200℃. The O_2 exposure was performed at 600℃ using a nozzle faced to the sample at the distance of 10mm. The average O_2 pressure during the exposure was 1.33×10^{-4}Pa, which was previously calibrated at room temperature by comparing samples exposed to O_2 using the nozzle and samples exposed to O_2 near the ion gauge. The sample was expected to have some oxides under the pressure and the temperature[8]. The O_2 exposure was 15L (1L=1.33×10^{-4}Pa s). The sample was quickly cooled down to room temperature just before stopping the O_2 exposure. We also examined the sample which was quickly cooled down to room temperature just after stopping the O_2 exposure and obtained similar results. All the STM measurements were performed at room temperature. Another sample was kept at 600℃ for 3 minutes after stopping the O_2 exposure to see the effect of heating. This sample was also quickly cooled down to room temperature after the heating.

3.Results and discussion

Fig.1 shows an STM topograph of the Si(001) surface exposed to O_2 at 600℃ and imaged at room temperature at -2V sample bias voltage (filled state image). The surface still has dimers with 2×1 reconstruction. In addition to the dimers, the O_2 exposure produced Si islands (a), "dark sites" (b), "sequence of dots" (c), and "dots with dark surroundings" (d). The Si island (a) has its long axis perpendicular to the dimer row direction. The "sequence of dots" (c) aligns along the direction perpendicular to dimer row direction, and has its bright dots in between the dimer rows. The "dot with dark surroundings" (d) appears on the dimer rows.

The surface is expected to have some oxides under the O_2 exposure condition. In order to discriminate oxidized sites from normal dimers, bias voltage dependence of the corrugations of the sites was examined, as shown in fig.2. The Si island (a) did not change its height at the different bias voltage, and its height was one monolayer of Si(001) surface (0.136nm). In contrast, the "dark sites" (b), the "sequence of dots" (c), and the "dots with dark surroundings" (d) changed their height at the different bias voltage. From the bias voltage dependence, the sites labeled b-d are considered to be oxidized sites, because the sites having different electronic states from those of the normal dimers may appear to change their height with respect to the normal dimers by changing the bias voltage. The gradual change of the corrugation with the position observed in the "dark site" (a) can be explained by O

atoms perturbing the electronic states of not only the atoms directly bonded or adsorbed but also the other surrounding atoms. The differences of the height between each "dot" of the "sequence of dots" can also be explained by the same effect.

While some of the "dark sites" may be atomic-sized defects[9], most of them seem to be oxidized sites. The "sequence of dots" resembles the "diluted-dimer" observed in the case of Si deposition on Si(001)[10], but the bias voltage dependence of the corrugation cannot be explained by the "diluted-dimer". In addition, the "diluted-dimer" was not observed at either high temperature growth or after annealing at high temperatures(>350℃).

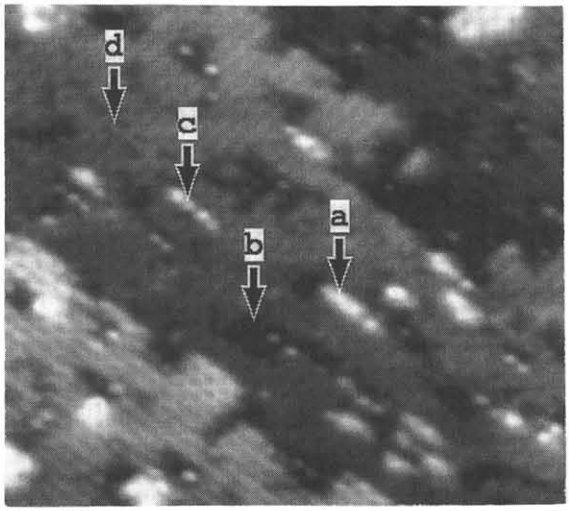

Fig.1 Si(001) surface exposed to O_2 at 600℃ and imaged at room temperature at -2V sample bias (filled state image). The O_2 exposure produced Si islands (a), "dark sites" (b), "sequence of dots" (c), and "dots with dark surroundings" (d).

On the sample kept at 600℃ for 3 minutes after stopping the O_2 exposure, the "sequence of dots" (c), the "dots with dark surroundings" (d), Si islands (a), hollows (b), and complicated shapes of steps with "inlets" (e) were observed, as shown in fig.3. The "sequence of dots" and the "dots with dark surroundings" seem to remain on the surface even after the heating, while most of the "dark sites" seem to be removed. Some of the oxygen on Si surfaces seem to act as "glue" that stabilizes the surface atoms[11]. These sites could be removed by the heatings up to 1200℃ to obtain clean 2×1 surface. Hollows and complicated shapes of steps with "inlets" are considered to be identical to the results of the "formation of hollows" and the "crossings of steps with hollows" observed in the case of the O_2 exposure at low O_2 pressures by reflection electron microscopy (REM)[12].

It is interesting to mention that the "sequence of dots" resembles the structure observed on the SiO_2-stripped Si(001) surface after the thermal annealing[13]. A possible explanation is as follows: some oxides (SiO_x) remained on the SiO_2-stripped surface even after the HF treatment, and some of the remaining oxides were removed by the successive heat treatment, and as a result the "sequence of dots" remained on the surface because they are harder to remove than the "dark sites". Further investigation may bring forth a clue to elucidate the structure of SiO_2/Si interface.

Another interest may be on the structure of the initial forms of thermal oxides. The "dark sites" may be explained by O atoms bonded or adsorbed to the dangling bonds, because the surface states related to the dangling bonds disappear by the elimination of the dangling bonds. In contrast, the dimers with O atoms inserted into the bridging bonds may appear as bright sites[14]. However, it seems to be difficult to explain the "sequence of dots", because the dimer with O atom inserted into the bridging

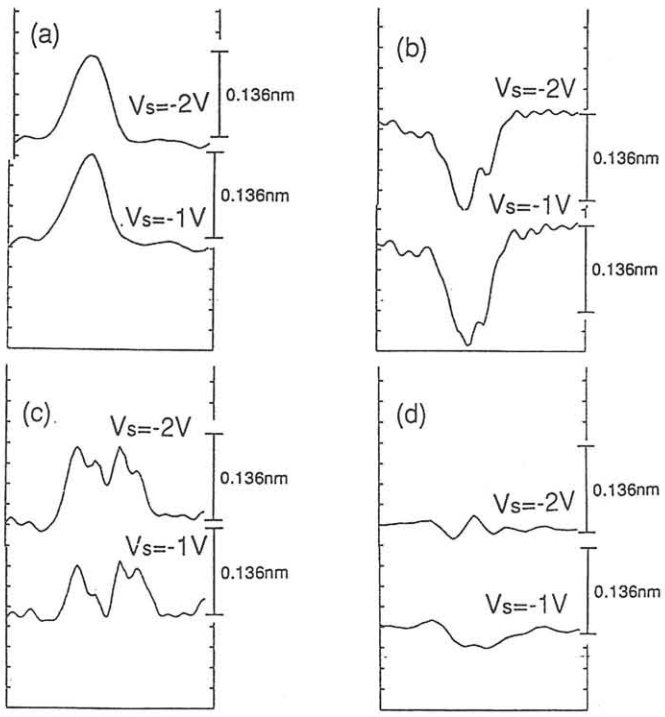

Fig.2 Sample bias voltage dependence of the corrugations of the sites in fig.1. One monolayer of Si(001) surface corresponds to 0.136nm.

bond should appear on the dimer row while the bright "dots" of the "sequence of dots" appear in between the dimer rows.

Instead, we propose a model of the "sequence of dots" as shown in fig.4. The open and filled circles represent Si and O atoms, respectively. The atoms at upper layer are shown by larger circles. This model consists of -O-Si-O- units in between the dimer rows. The Si atom in the -O-Si-O- unit has two dangling bonds, and it may appear as bright dot if there are surface states related to the dangling bonds. Although the bond lengths and bond angles may need some modifications, the -O-Si-O- unit seems natural because a unit similar to the model exists in β-cristobalite. The misfit of the ideal SiO_2(β-cristobalite)/Si interface proposed by Herman[15] is 6%. This interface structure has never been observed, probably because the strain caused by the misfit is unfavored. However, the local -O-Si-O- unit on the surface may be stabilized by modifying the bond lengths and bond angles. Although definite mechanisms of formation of the "sequence of dots" are still not clear, some facts related to them are as follows: (1) surface diffusion of Si atoms are activated at elevated temperatures; (2) Si(001) surface is anisotropic; (3) the influences of O atoms reach to not only the atoms directly bonded or adsorbed but also to the other surrounding atoms; (4) the bond energy of the Si-O bond is about twice as large as the Si-Si bond. The fact 1 explains the source of the Si atom in the -O-Si-O- unit, and it may be the reason why the "sequence of dots" is not observed on the surface exposed to O_2 at room temperature. The facts 2,3 may explain the origin of the ordering of the "sequence of dots". The fact 4 may explain why Si atom in the -O-Si-O- unit is strongly bonded to the surface than the dimering Si atoms, and hence, the "sequence of dots" is harder to remove than the "dark sites". The model shown in fig.4 suggests some relations between the SiO_2/Si interface and the initial forms of the thermal oxides.

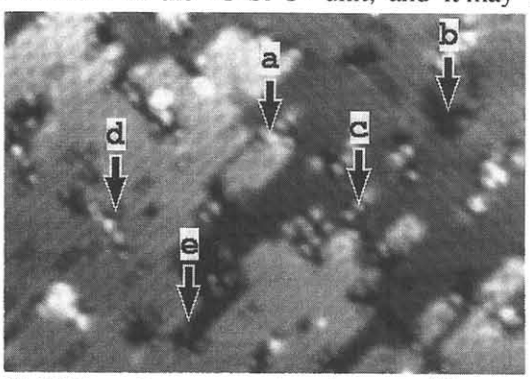

Fig.3 Si(001) surface exposed to O_2 at 600℃ and kept at the same temperature for 3 minutes after the exposure. The surface was imaged at -2V sample bias. The "sequence of dots" (c), the "dots with dark surroundings" (d), Si islands (a), hollows (b), and complicated shapes of steps with "inlets" (e) were observed.

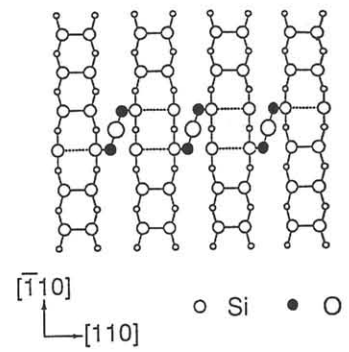

Fig.4 A possible model of the "sequence of dots". A -O-Si-O- unit similar to that in the model exists in β-cristobalite.

4.Conclusions

The initial stages of the thermal oxidation of Si(001) 2 $\times$1 surface were studied by STM. The O_2 exposure at 600℃ produced a random distribution of Si islands, "dark sites", "sequence of dots", and "dots with dark surroundings". The "sequence of dots" and the "dots with dark surroundings" seem to remain on the surface even after the successive heating. The "dark sites", the "sequence of dots", and the "dots with dark surroundings" are considered to be initial forms of oxides. From the experimental results, a possible model of the "sequence of dots" was proposed. Also, some relations between the SiO_2/Si interface and initial forms of the thermal oxides have been suggested. Further investigation may bring forth a clue to elucidate the structure of SiO_2/Si interface.

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