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High Temperature STM Observation of Layer-by-Layer Etching of Si(111) with O_2 Flux

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The variation of Si(111) surface by exposing to the O_2 flux at elevated temperature was investigated by high temperature type STM. The surface was etched from the step edges with layer-by-layer manner, where the step edges showed complex wavy shape accompanied by pinning cluster. Real time monitoring of the surface changes revealed the appearance of pinning cluster which support the mobile adparticle for the mechanism of the etching from the step edges.

1. Introduction

The control of the flatness of Si wafer surface has attracted attentions which is partially due to the thinning of the gate oxide which makes the roughness of the initial wafer more critical for the MOS characters. It has been shown successfully that atomically flat Si(111) surface can be obtained only by a chemical treatment with NH_4F.[1] The result suggested that the anisotropic etching of the surface is the key process for the realization of the atomically flat surface. It has been shown that O_2 can etch the Si surface with the condition of low O_2 pressure and high substrate temperature. If the etching proceeds in layer-by-layer manner, it might be possible to apply this technique to the flattening of Si surface. This technique has an advantage of good process compatibility where the effect can be expected only by tuning the gas pressure and substrate temperature in oxidizing furnace. In this report, we want to show the behavior of Si(111) surface which is etched by O_2 flux observed by high-temperature type scanning tunneling microscope (STM) which enables the real time monitoring of the surface. The result shows clearly the step motion together with the pinning sites at elevated temperature.

2. Experimental

The experiment was executed in UHV condition with the base pressure below $1x10^{-10}$ torr. The wafer was Si(111) (p-type, B doped) and 7x7 reconstructed surface was prepared by flashing at 1150 °C for 1min after long time degassing. The heating of the wafer was done by running the current through wafer. Figure 1 shows an expected phase diagram of the SiO_2 growth as the functions of the O_2 pressure and the substrate temperature. The solid line above 900 °C is derived from the previous report,[2] and the rest of the line is a simple extrapolation. Below the solid line, the surface is expected be in the oxygen-free condition whereas the region above corresponds to the SiO growth mode. The condition we used in the current experiment is marked by an open circle in the figure.

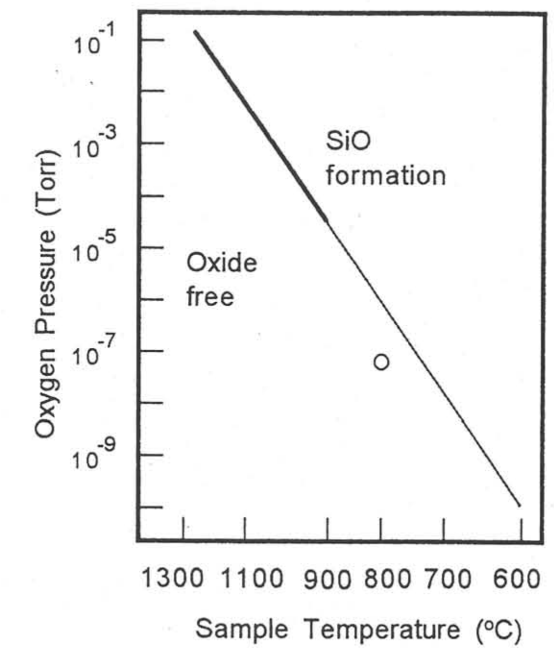

Fig. 1. Diagram for the SiO_2 growth on Si(111) surface where the data above 900 °C is from Ref. 2 and the rest is the extrapolation of this line. The region above/below the line is expected for the SiO_2 growth/oxide-free conditions.

3. Results and Discussion

First we show the Si(111) surface changes after the reaction with O_2 obtained after quenching to room temperature for large area in Fig. 2. (1x1 μm^2) The frames are shown as the function of the exposing time of the Si(111) surface to the O_2 with the conditons of the substrate temperature of 800 °C and the O_2 pressure of $1x10^{-7}$ torr. After turning off the O_2 flux, the sample was held at 800 °C for another 1min and then cooled down to room temperature for the STM

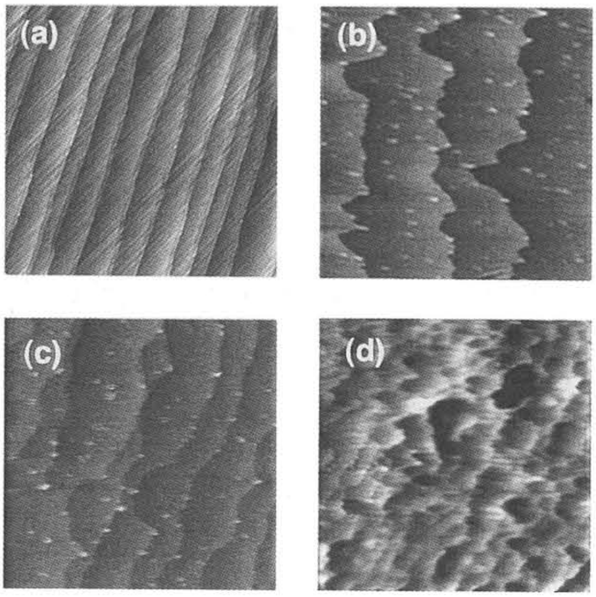

Fig. 2. Si(111) surface variation with exposing oxygen ($1x10^{-7}$ torr) to the 7x7 surface at elevated temperature (800 °C). The images are all for 1x1 μm^2. The clean surface was exposed to oxygen for 0 (a), 10 (b), 30 (c) and 100 sec (d). The monoatomic steps changed their shape with the step edges were recessed in layer-by-layer manner.

observation. The initial surface is shown in (a) where quite straight steps are running parallel with each other. These steps are with the height difference of ~0.3 nm which is corresponding to the bilayer step of Si(111) surface. The surface showed big change after exposed to O_2 for 10 sec (1 L). The steps are with the height of ~0.3 nm but they became complex zigzag in shape. The terrace parts were still oxygen free and clear 7x7 structures were observed. There can be seen whites dots in the terrace parts as well at the step edges, and apparently the kinks of the step edges are accompanied by these dots.

Further introduction oxygen makes complex shape of the surface, where the surface after exposing 30 sec (3 L) and 100 sec (10 L) are shown in (c) and (d), respectively. Though the step edges showed curved structure than the case of (b), the surface remained step-and-terrace structure.

The behavior of the step edges as shown above can be understood by the recession of the step edges which might be due to the reaction of the Si surface with O_2 to form SiO which is volatile and desorbed from the surface. And the curved and zigzag shape structure were formed mainly by the presence of the pinning sites which are observed as white dots in the images, which pinned the motion of the step edges and formed complex shape of the step edges. However, the process of the reaction of the O_2 with Si at step edges are not trivial issue. As was indicated by room

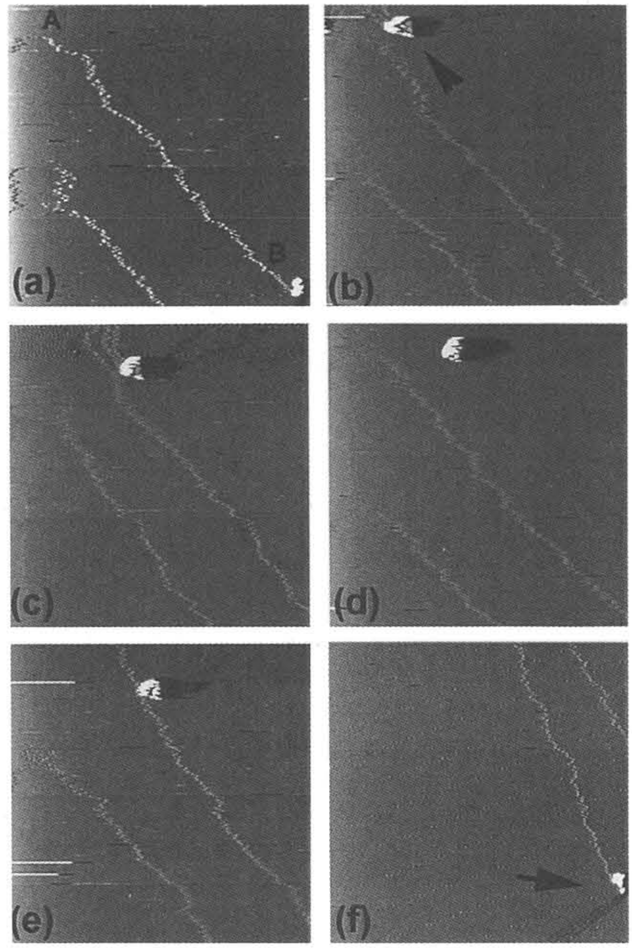

Fig. 3. *In*-situ observation of the Si(111) surface as the function of exposure time to the O_2 obtained at elevated temperature of ~800 °C with the interval of ~20 sec in each frame. (area for 280x280 nm^2) The images were taken with constant height mode with the scanning from left to right. ('A'-'B' in (a) is the step edge and the marks are on the upper terrace)

temperature STM observation on the adsorption of O_2 on the Si(111)-7x7 surface, the adsorption of the O_2 atoms occur in the middle of the terrace as well and there was no preferential adsorption and growth of the oxidized species at the step edges.[3] So in order to explain the recession of the step edges by the desorption of SiO species, there should be mass transfer in either two following models; [4,5] (1) formation of vacancies in the middle of the terrace followed by the migration of those vacancies to the step edges to form complex shape step edge structure. (2) migration of adparticles, may be SiO, to the step edges which desorbed at the step edges. In either case, the step edges were recessed as the function of the time of exposure to the O_2 flux. The whites dots observed on the surface after exposing to the O_2 flux, which pinned the motion of the step flow, is probably related to the SiO species which assembled to form a cluster of SiO_x. Since the shape of the surface morphologies obtained after exposing the Si surface to O_2 flux is apparently determined by the presence of these pinning sites, the control of the appearance of those pinning species will be the key for the realization of atomically flat surface by this technique.

Next, we shall show the STM images of the surface at elevated temperature with exposing to the O_2 flux in Fig. 3. The observation was executed with high temperature type STM at the sample temperature of ~800 °C and O_2 pressure of 1×10^{-8} torr. The images were taken with constant-height mode with scanning from left to right; so the white stripe appeared in the image corresponds to the step edges stepping up to the right. Each image was taken with the time interval of ~30 sec. It can be seen atomic step is running on the line 'A'-'B' where marks of A and B are on the upper terrace. The O_2 introduction was initiated after the thermal drift was diminished, so there hardly was the thermal drifting in those images.

In the following frame (b), we can identify the appearance of a cluster as is shown by an arrow in the image. We want to point out here that this is not STM tip induced structure. In the high temperature observation, the STM tip occasionally touch the surface and transfer Si atom to the surface. However, since the substrate temperature is high enough, those Si atoms form atomically flat island which is surrounded by monoatomic steps which was confirmed in the images before O_2 introduction. So the cluster seen in the image is apparently oxygen induced structure and we want to attribute it to the SiO_x cluster where some mobile adparicles were assembled. In this view point, the image may support the model of the migration of adparticle to the step edge as the origin of the step recession in the two models stated above.

In frame (c), we can notice newly appeared island which is accompanying steps which are corresponding to several layers. This layered island may be formed by the pinning of the step flow. Apparently the step edges were quite mobile in this condition which can be seen in the next frame (d), where the layered islands were disappeared. And the adjacent step in (d) appeared further from the cluster compared with (c). It can be understood, since the steps were expected to be recessed by the SiO etching, the approaching step in (d) is different from the one in (c). This implies that the pinning effect by this cluster is not perfect and the pinned step edges were released after certain amount of the steps were piled at the pinning site, and also in some case the step run over the cluster without pinned by this structure. This may explain the lack of the multi layer step at the pinning site shown in Fig.2. In (f) we can clearly see another pinning of the step edges with a structure as is shown by an arrow.

Here we point out the step flow rate with O_2 introduction comparing the step flow on the clean surface. It has been reported that the step can flow at elevated temperature, whose direction depend on the direction of the electric field of the heating current.[6] However, the step-flow rate of the current experiment observed at ~800 °C is much higher than the clean surface case at ~860 °C, where the former case is corresponding to ~100 nm/sec in average.

4. Conclusion

In summary we observed the Si(111) surface variation when the surface at elevated temperature was exposed to low-pressure O_2 flux. The surface after quenching to the room temperature showed curved monoatomic step edges which were often pinned by clusters. The high temperature STM observation in real time manner showed the appearance of a cluster around the step edges which support the model of the migration of adparticle for the mechanism of the recession of the step edges. It was monitored that these clusters pin the step motion, but the bunched step edges around the pinning center disapeared after cerain amount of the layers were piled up, which is consistent with the lack of step bunching of multi layers at the pinning center. The O_2 etching technique for the realization of atomically flat surface seems feasible from the view point that the etching proceed by layer-by-layer manner. However it may be critical to control the pinning center for the perfect step-and-terrace structure.

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