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Wafer-Scale Self-Organization of Periodic Step/Terrace Structure on Hydrogen-Terminated Si Surface

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1. Introduction

Takahagi, one of authors of the paper, revealed the hydrogen-termination and hydrogen-passivation phenomena of the HF-etched Si surface, which have become an essential concept for the development of a preparation technique in Si device production.[1,2] Higashi et al.[3] and Jakob and Chabal[4] developed a novel preparation technique to obtain an atomically flat Si(111) surface with Si-H hydrogen-termination by the treatment using a buffered HF or NH_4F aqueous solution. But the surface has many defects on a terrace and a step edge.[5] The preparation method of silicon surface without any defects is expected to be developed. Silicon wafer with ordered terrace and step surface structure may be an useful substrate for nano-fabrication process.[6] No worker has developed a wet process to prepare atomic-scale completely regular Si(111) surface until now.

In this work, we tried to develop a wet process to be able to bring us the atomically flat surface with the periodic step/terrace structure and without defects like a kink and an etch-pit all over the Si(111) wafer surface.

2. Experiment

We used a polished n-type Si(111) wafer. The samples were cut various angle off the (111) plane in the two type directions of $\langle 11\bar{2}\rangle$ and $\langle \bar{1}\bar{1}2\rangle$. The native oxide layer on the Si surface was removed by immersion in a 5% HF solution after supersonic washing in an acetone. Finally, the Si wafer was immersed in a 40% NH_4F solution. We examined the effect of treatment-temperature and oxygen concentration of the NH_4F solution to the Si surface morphology. The surface morphology was observed by UHV-STM and AFM and a chemical structure of the surface was also measured using polarized FT-IR-ATR.

3. Results and discussion

Figure 1 shows the STM images of the Si(111) surfaces prepared by NH_4F-treatment. The Si surfaces cut off in the $\langle 11\bar{2}\rangle$ direction have an atomically flat surface. Treatment times, which were optimized at the solution temperature of 20°C and 72°C, were 6min and 30sec, respectively. The step/terrace structure is observed on both conditions. A bilayer step with height of 0.31nm was observed and a bunching step structure was not observed. However, at the condition of 20°C, many irregular structures, that are kinks and etch-pits, are observed in a step edge and a terrace. On the other hand, the step edges on the surface treated at 72°C are almost straight and have little kink structure, and a period of the step/terrace is uniform. Topmost hydrogen atoms can be observed clearly at an enlarged STM image as shown in Fig.1(c). Hydrogen atoms in step edge are ordered in a straight line along $\langle \bar{1}10\rangle$ direction. The result shows that a periodic characteristic can be improved by using hot NH_4F aqueous solution. The following data were obtained using Si wafer treated by NH_4F at a temperature of 72°C.

Figure 2 shows the AFM images observed at 9 points on the surface of a 4 inch wafer with off-angle of 1° in $\langle 11\bar{2}\rangle$ direction. The same regular morphology are observed at all points. Similar result was confirmed on the wafer inclined to $\langle \bar{1}\bar{1}2\rangle$ direction. It was confirmed that the periodical structure in a wafer-scale could be formed by wet process. We examined the surface morphology of the samples having various off-angle in both directions of $\langle 11\bar{2}\rangle$ and $\langle \bar{1}\bar{1}2\rangle$. Figure 3 shows a relationship of an average terrace width in AFM images and the off-angle measured by XRD. The terrace width is decreasing with increasing the off-angle. A solid line in Fig.3 is the terrace width calculated from the off-angle assuming uniform step/terrace and bilayer step surface structure. The result shows that the uniform step/terrace structure on Si(111) surface is self-organized, and its period depends on only an off-angle of

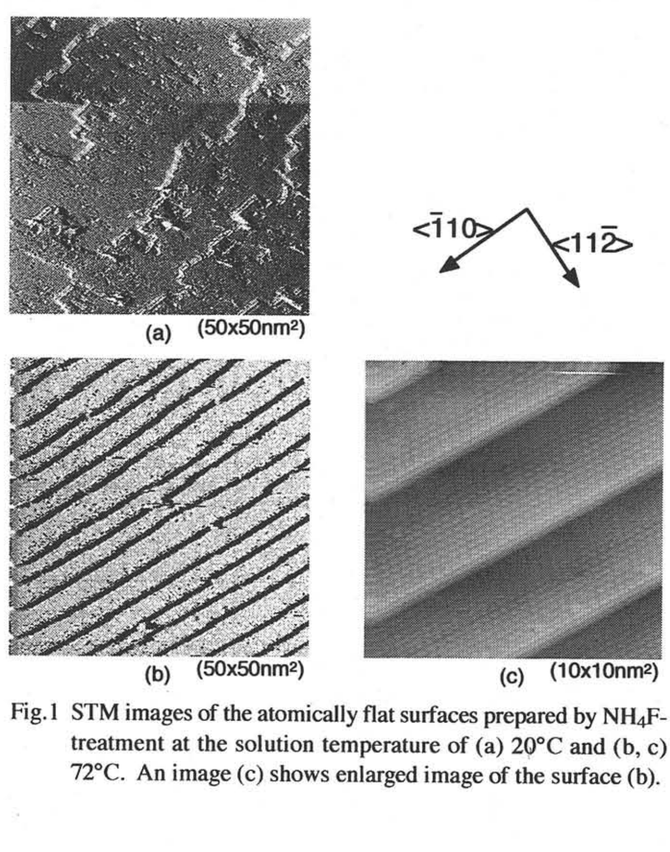

Fig.1 STM images of the atomically flat surfaces prepared by NH_4F-treatment at the solution temperature of (a) 20°C and (b, c) 72°C. An image (c) shows enlarged image of the surface (b).

Si wafer surface. FT-IR-ATR measurement of these surfaces revealed that chemical structures of the step edge on the surfaces miscut in <11$\bar{2}$> and <$\bar{1}\bar{1}$2> directions were mono-hydride and di-hydride, respectively.

Next, we tried to make clear an origin of the reduction of crystallographical defects such as kinks and etch-pits on the surface by the hot NH_4F treatment. A dissolved gas concentration in aqueous solution is considered to decrease with increasing solution temperature. It was found that the dissolved oxygen concentration (DOC) in NH_4F solution at 72°C was lower value of 1.8ppm than that of 5.0ppm at 20°C. In order to confirm the effect of the dissolved oxygen, we tried treatment using the NH_4F solution with low DOC prepared by nitrogen gas bubbling. Figure 4 shows STM images of a wafer treated by NH_4F solution with DOC of 0.1ppm at the temperature of 20°C. The step edges are almost straight, and a period of the step/terrace is uniform. The periodicity of the step/terrace structure is drastically improved by reduction of DOC. Similar improvement was observed by putting an oxygen scavenger such as $(NH_4)_2SO_3$ into NH_4F solution. The dissolved oxygen is considered to form partially oxidized structure, whose etching rate may be different from silicon. Oxygen dissolved in NH_4F solution was proved to reduce a regularity of Si surface.

4. Conclusions

The formation of the periodic step/terrace structure with regular step edge was achieved by NH_4F aqueous solution at low DOC condition. The dissolved oxygen is considered to play a role of a formation of partially oxidized structure. It was found that the Si(111) surface was self-organized to the step/terrace structure which period was fixed by value of the off-angle of wafer. We got the new wet process to prepare the periodical structure of Si(111) surface in a wafer-scale.

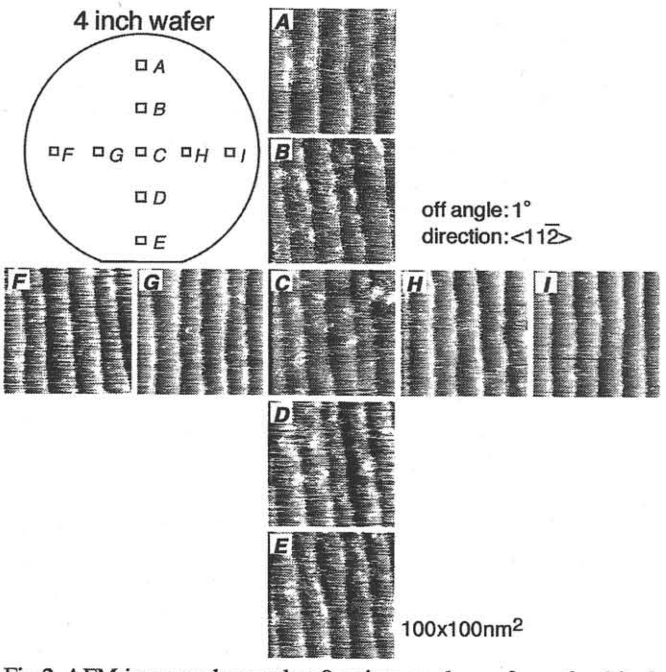

Fig.2 AFM images observed at 9 points on the surface of a 4 inch wafer with off angle of 1° in <11$\bar{2}$> direction.

Acknowledgments

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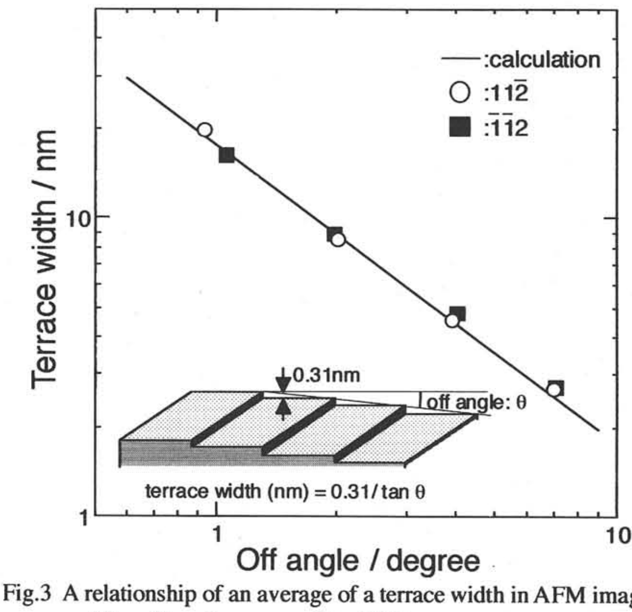

Fig.3 A relationship of an average of a terrace width in AFM images and the off angle measured by XRD.

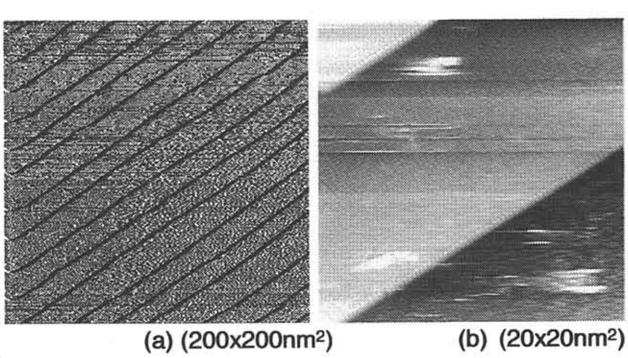

Fig.4 STM images of a wafer treated by NH_4F solution with DOC of 0.1ppm prepared by nitrogen gas bubbling at the solution temperature of 20°C.