Surface Observation and Modification of Si Substrate in Solutions

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Topographical changes during surface etching of oxidized p-Si(111) substrate in 0.3M NH₄F solution have been investigated by atomic force microscopy (AFM). During etching of oxide layers, a fiber structure along the <1TO> direction was observed. After the oxide layers were completely etched, anisotropic surface etching proceeded, which is similar to the case in dilute alkaline solutions. We have also demonstrated surface modification of hydrogen-terminated p-Si(111) substrate on a nanometer scale with Electrochemical scanning tunneling microscopy (ESTM) in a dilute H₂SO₄ solution.

1. INTRODUCTION

Silicon is one of major semiconductor materials which is widely used for many kinds of electronic devices. Recently, it was pointed out that atomic-scale surface flatness of the Si substrate is important for fabricating microstructural electronic devices using the Si ULSI technologies¹⁾. As one of the methods to obtain an ideal Si surface, wet processes such as H-termination in a NH₄F solution²⁾ have been of interest. For further studies about wet processes to obtain an ideal Si surface, in situ observation during H-termination of Si substrates is important. A few investigations during H-termination of Si substrates were reported by Electrochemical Scanning Tunneling Microscopy (ESTM)^{3,4)}. Though ESTM is a very useful method for in situ observation, it is impossible to apply ESTM to a specimen covered with thick insulating layers such as SiO,. On the contrary, the Atomic Force Microscopy (AFM) technique is a powerful method to study in situ observation with a possible application to insulating materials, as it has been presented before⁵⁾

Surface modification processes on a nanometer scale are also necessary for fabricating microstructural electronic devices. STM has been expected an ideal tool because of its atomic resolution. After STM-based device fabrication process was investigated by Dagata et al.⁶, there have been many attempts to fabricate nonometer scale structures on Si substrate using STM in air⁷⁻⁹, UHV-STM^{10,11}, AFM in air¹²⁻¹⁴) and non-contact mode AFM¹⁵. However, there has been few attempts in solutions¹⁶. To apply the process above mentioned to the environment in solutions, more attempts are needed.

In this paper, we investigate surface observation during surface etching and H-termination process of oxidized p-Si(111) substrate in $0.3M \text{ NH}_4\text{F}$ solution by AFM. We also demonstrate surface modification of H-Si(111) substrate on an nanometer scale with ESTM in a dilute H,SO₄ solution.

2. EXPERIMENTAL

Highly B-doped (1x10¹⁸/cm³) p-Si(111) specimens (Shin-

had vicinalities less than $\pm 0.1^{\circ}$ from the (111) direction. After degreasing with acetone in ultrasonic cleaner, the specimens were boiled in a 2:1 solution of H₂SO₄:H₂O₂ at 100°C for 10 min. For AFM observation, the specimens were dipped in 25% HF solution for 30s and reoxidized in the 2:1 solution of H₂SO₄:H₂O₂ at 100°C for 2 min to form thin oxide layers on the surface. For ESTM modification, the specimens were dipped into a 40% NH₄F solution for 40 min to terminate the surfaces by hydrogen atoms²). After above-mentioned treatments, all specimens were placed into sample cell and then were covered with ultrapure water (>18.3 MQ·cm, Millipore-Q) for AFM observation and a dilute H,SO₄ solution for ESTM modification, respectively. To observe etching process of oxidized p-Si(111) surface, a 0.68M NH₄F solution was dropped into the ultrapure water that covered the surface of the specimen. The concentration of NH₄F during AFM observation was about 0.3M. A dilute H,SO₄ solution and a 0.68M NH₄F solution were prepared from reagent solutions (superpur grade, KANTO Chem. Co., Ltd.) and ultrapure water. AFM and ESTM experiments were performed with commercial units (AFM; SPA300, ESTM; STE330, Seiko Instruments Inc.). All images shown in this study are topographic ones. The Si cantilevers with a microfabricated Si tip (Nanoprobe Co., Ltd.) were used for AFM observation. The typical value for curvature of tip apex and spring constants were 15 nm and about 0.2 N/m, respectively. The reference force during AFM observation was maintained at the order of 10° N. The ESTM tips were prepared by electrochemical etching of a Pt wire, subsequently by insulating with apiezon wax. The ESTM tip bias voltage and p-Si(111) bias voltage reported in this study are referred to a Ag/AgCl electrode. The procedure for modification experiments was as follows. First, the ESTM tip was moved to the surface with a condition for observation (ESTM tip bias voltage was +0.63 V and the tunneling current was 0.8 nA, respectively). Secondly, a more positive bias voltage was applied the tip. Thirdly, tip was repeatedly scanned lines under feedback control. After tip scanned, the tip condition was changed to that used for observation.

Etsu Semiconductors Co., Ltd.) were used. Those surfaces

3. RESULTS AND DISCUSSION

3.1. AFM IMAGES in 0.3M NH₄F SOLUTION

Figure 1 (a) shows a typical AFM image of as-prepared oxidized Si(111) surface in ultrapure water. The scanning area of the image is $200 \times 200 \text{ nm}^2$. The surface consists of dome-shaped structures and this overall feature is characteristic SiO, surface.



Fig.1. Typical, 200 x 200 nm², AFM images of oxidized p-Si(111) surface in ultrapure water (a) and in 0.3M NH₄F solution.

Though etching process of the oxide layers started just after the NH₄F solution was dropped in the ultrapure water, similar AFM images as shown in Fig. 1 (a) were observed. This result indicates that the morphology in the oxide layers is homogeneous. As the etching proceeded, the topography changed as shown in Fig. 1 (b). The scanning area of Fig. 1 (b) is also $200 \times 200 \text{ mm}^2$. A one-dimensional fiber structure along the $<1\overline{10}>$ direction is observed. Similar structure was observed at n-Si(111) surface covered with a thin oxide layer in 1% HF solution by ESTM³⁾. Because ESTM proves not surface topography of oxide layer but SiO,-Si interface, the ESTM image reflects Si substrate. These results suggest that the fiber structure observed in Fig. 1 (b) seem to be very thin oxide layer on Si substrate and that the topography of Si substrate affects the formation of the structure. Some triangular pits are also observed in Fig. 1(b). As the etching proceeded, these pits became larger and another topography suddenly appeared as shown in Figs. 2.

Figures 2 (a) and (b) show continuous AFM images

during surface etching process of H-Si(111) in 0.3M NH₄F solution. The area of these images is 400 x 400 nm² and the interval of observation between two images is about 1 min. All step edges are monolayer-height and toward the $<11\overline{2}>$ direction. All triangular holes observed on the terraces are monolayer-depth and the directions of those sides are toward the $<11\overline{2}>$ direction.



Fig.2. Typical, 400 x 400 nm², continuous AFM images during etching process of H-Si(111) surface in 0.3M NH₄F solution. The interval of observation between two images is about 1 min.

As the etching proceeded, the size of the holes became larger with holding the direction of their sides and their monolayer-depth. We also observed that the step edges moved backward and new triangular holes with monolayer-depth were formed on the terraces. Continuous AFM measurement suggests that the etching proceeds laterally and slower at <112> step edges than at <112> step edges. This anisotropic etching process of Si(111) surface was also observed by ESTM³⁾ and it is similar to the case observed in a dilute NaOH solution by AFM⁵⁾ and ESTM¹⁷⁻¹⁹⁾. This result is consistent to the fact that the 0.3M NH₄F solution is a alkaline solution.

3.2. SURFACE MODIFICATION by THE ESTM TIP

The modified line formed by the ESTM tip in a dilute H_2SO_4 solution is shown in Fig. 3. The area of the image is 240 x 240 nm² and the arrows indicate step edges. The modification condition was as follows; tip bias voltage was +1.43 V and p-Si(111) bias voltage was -0.37 V. The

scanning speed was 100 nm/s and a 100 nm line scanning was repeated 10 times. The pattern can be observed as depressed line, which suggests the modified part is less conductive. The width of the line shown in Fig. 3 is 12 - 30 nm. When the condition except the tip bias voltage was kept at the value above mentioned, a threshold tip bias voltage of around +1.4 V was observed for the modification.



Fig.3. Typical, 200 x 200 nm² ESTM image of H-Si(111) in a dilute H_2SO_4 solution after surface modification by the ESTM tip. The modified part is observed as depressed line. Arrows indicate step edges.

The size modified by the ESTM tip depended on a line scanning times, the tip bias voltage and a scanning speed. Therefore, we confirmed that this modification was not caused by mechanical one such as scratching by the tip. Though this dependence was reproducible, absolute modified size was not always the same. The mechanism during this ESTM modification is not yet clear, because it was also depended on the shape and the curvature of the tip apex exposed to the solution. More experiments are needed to further understand this modification process.

4. CONCLUSION

Topographical changes during surface etching of oxidized Si(111) in 0.3M NH₄F solution have investigated by AFM. During etching of oxide layers, a fiber structure along the <1 $\overline{10}$ > direction, which its formation seems to be affected by the topography of Si substrate, was observed. After the oxide layers were completely etched, anisotropic surface etching was observed. We also demonstrated surface oxidation of H-Si(111) on nanometer scale in dilute H₂SO₄ with ESTM. The modified line of width as small as 12 nm has been achieved by applying above +1.4 V vs. Ag/AgCl electrode to the ESTM tip.

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