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ESTM/AFM Observations on Si(111) in Several Solutions

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Electrochemical scanning tunneling microscopy (ESTM) and atomic force microscopy (AFM) measurements were performed to observe topographies on hydrogen-terminated Si(111) surfaces in several solutions. In a dilute H_2SO_4 solution, AFM images were similar to ESTM ones. This result indicates that the AFM observation is a useful method to study topographies with a possible application to insulating materials. We have also shown AFM images of H-Si(111) in ultrapure water and in a dilute NaOH 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 solve this problem, wet processes have been of interest. To examine surface flatness of Si(111) treated by a wet process, many studies have been performed by using ultrahigh vacuum scanning tunneling microscopy (UHV-STM)²⁻⁷⁾ and atomic force microscopy (AFM)⁸⁾. These studies are mainly ex situ observations. For further studies about wet processes of Si substrates, study on topographic change during a wet process is important and in situ observation of Si surfaces in solutions is necessary. A number of studies about in situ observation of Si(111) surfaces have been reported using electrochemical STM (ESTM)⁹⁻¹⁵⁾. Though ESTM is a very useful method for in situ observation in solutions, it has some disadvantages. The bias voltage is limited to observe surfaces with stability and without surface modification. Moreover, it is impossible to apply ESTM to a specimen covered with thick insulating layers such as SiO2. On the contrary, AFM is a powerful method for observation under such conditions. From this point of view, AFM observation of Si surfaces in solutions is important but only a few studies have been reported¹⁶⁾. As the first stage of our studies, we have demonstrated the performance of AFM observation for observing the images of H-terminated p-Si(111) surfaces in a dilute H₂SO₄ solution, in ultrapure water and in a dilute NaOH solution.

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2. EXPERIMENTAL

Highly B-doped (1x10¹⁸/cm³) p-Si(111) specimens (Shin-Etsu Semiconductors Co., Ltd.) were used for observation. Those surfaces had vicinalities less than \pm 0.1° 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. After these processes, the specimens were dipped into a 40% NH₄F solution for 40 min to terminate the surfaces by hydrogen atoms. After above-mentioned treatments, all specimens were placed into sample cell in a glove bag purged with dry N_2 gas and then were covered with ultrapure water (>18.3 M Ω ·cm, Millipore-Q). These preparations enabled us to examine surfaces without exposing to air. A dilute H₂SO₄ solution and a dilute NaOH solution were prepared by dropping reagent solutions (superpure grade, KANTO Chem. Co., Ltd.) into the ultrapure water that covered the surface of the specimen. ESTM and AFM observations were performed with commercial units (ESTM; STE330, AFM; SPA300, Seiko Instruments Inc.). All images shown in this study were topographic ones. The ESTM tips were prepared by electrochemical etching of a Pt wire, subsequently by insulating with apiezon wax. Cantilevers (a spring constant of 0.09 N/m) with a microfabricated silicon nitride tip (Olympus Optical Co., Ltd.) were used for AFM observation. The reference force during AFM measurement was maintained at the order of 10⁻⁹ N.

3. RESULTS AND DISCUSSION

3.1. ESTM and AFM IMAGES IN A DILUTE H2SO4 SOLUTION

ESTM and AFM images on H-Si(111) surfaces in a

dilute H_2SO_4 solution are shown in Figs. 1 (a) and (b), respectively. The scanning area of the two images is 450 x 450 nm². Few absorbed contaminants are observed on these surfaces. The ESTM and AFM images exhibit some common features as the follows: The surfaces consist of successive monolayer-height terraces toward the $\langle \overline{112} \rangle$ direction. There are triangular monolayerdepth holes whose sides are toward the $\langle 112 \rangle$ direction. These characteristic features of the AFM image are also in good agreement with the previous STM studies on H-Si(111)²⁻⁷⁾. This result indicates that the AFM image seems to reflect the topography of Si surface and we can compare the AFM result with the ESTM one.



Fig.1 Typical, 450 x 450 nm², ESTM (a) and AFM (b) images of H-Si(111) in a dilute H2SO4 solution.

3.2. AFM IMAGES IN ULTRAPURE WATER

Figure 2 (a) shows typical, 450 x 350 nm², AFM image of as-prepared specimens in ultrapure water. The overall feature of this image is similar to that shown in Fig. 1 (b). The ESTM measurement is difficult in ultrapure water because of insufficiency of electrolytes. AFM images in ultrapure water could be obtained easily. This is one of advantage points of AFM measurement compared with ESTM method.

From continuous AFM measurement, we found the change of step edge. Figure 2 (b) was observed 1 hour



Fig. 2. Typical, 450 x 350 nm² AFM images of H-Si(111) in ultrapure water: The interval of two images is about 1 hour.

later after the observation of Fig. 2 (a). The area of this image is also 450 x 350 nm². White arrows in Figs. 2 (a) and (b) indicate the same points. The overall feature of these images is similar but the change of step edge can be clearly observed at an area indicated by the white arrow. It was also observed that the other step edges partially backed about 10 nm. The tendency of step changes is independent on reference forces and interval of AFM measurement. We confirmed that this change was not caused by mechanical modification such as scratching by tip. However the effect of mechanical modification still remains and we can not discuss in detail because the resolution of the AFM image shown in Fig. 2 (b) became worse during continuous measurements, which suggests cantilever tip might be damaged.

3.3. AFM IMAGES IN A DILUTE NaOH SOLUTION

We also performed AFM observation in a dilute NaOH solution. As soon as NaOH reagent was dropped, the first stage of the etching process occurred. We observed at first that there were triangular holes whose sides consisted of a few monolayer-height terraces toward the $<11\overline{2}>$ direction. We can not reveal the sites where the etching starts, because the stability of AFM measurement became worse for a few minutes because of NaOH diffusion. As the etching proceeded, these holes became larger. Figure 3 (a) is typical, 500 x 500 nm², image observed during surface etching proceeding. All triangular holes observed on the terraces are monolayer-depth and the directions of those sides are toward the $<11\overline{2}>$ direction. As the etching proceeded, the size of the holes became larger with holding the



Fig.3. Typical, 500 x 500 nm² AFM images of different B-doped Si(111) in a dilute NaOH solution:
(a) 1x10¹⁸/cm³, (b) 1x10¹³/cm³.

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 in alkaline solution has been elucidated by the difference in the number of hydrogen-silicon bonds between at $<11\overline{2}>$ step edges and at <112> step edges [4]. The formation mechanism of new triangular holes on terraces still remains uncertain. To examine the effect of dopants on new triangular holes formation, we performed AFM observation on dopantschanged Si specimen (1x10¹³/cm³). Figure 3 (b) shows a typical, 500 x 500 nm², image of dopants-changed Si surface in a dilute NaOH solution. The significant changes were not observed as compared with Fig. 3 (a). For the formation mechanism, further studies are necessary.

The anisotropic etching process of Si(111) was investigated by Allongue *et al.*^{14, 15)}, who observed the initial stage of *n*-Si(111) etching at near open circuit

potential (OCP) by ESTM. They reported that *in situ* ESTM measurement was difficult at the OCP because of the surface reactivity. By using AFM, we could stably and continuously perform *in situ* observation on unbiased Si(111) specimen. This suggests that AFM measurement is useful to observe under the conditions which ESTM measurement is difficult.

4. CONCLUSION

Hydrogen-terminated Si(111) surfaces in several solutions were studied by using ESTM and AFM and we demonstrated the performance of AFM observation in solutions. The AFM technique is a powerful method to study surface dynamics during chemical reactions with a possible application to insulating materials. In this paper, we showed AFM images of H-Si(111) in a dilute H2SO4 solution, in ultrapure water and in a dilute NaOH solution. The detailed studies on Si surfaces in solutions are now in progress.

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