

Atomic Structure of Hydrogen-Terminated Si(111) Surfaces by HF Treatments

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Atomic structure of hydrogen-terminated Si(111) surface has been studied by using scanning tunneling microscopy (STM). The STM images of a 1%-HF treated sample exhibit regular dots with distance of 2.2 Å, which is characteristic of the trihydride (SiH₃) phase. In contrast, on the surface prepared by boiling in the hot water after 1 %-HF dipping, we obtain regular dots with distance of 3.8 Å which are originating from the monohydride (SiH) phase.

1. INTRODUCTION

Hydrogen-termination of silicon surface has recently been attracted from the points of both device technology and the surface science since the surfaces are resistant against oxidation even in air. In order to make clear the mechanism of hydrogen-termination and its resulting structure, many studies such as infrared spectroscopy (IR),^{1,2} ultraviolet photoelectron spectroscopy (UPS),³ scanning tunneling microscopy (STM)⁴ have been made so far on Si samples prepared by both the dry and wet processes. Special attention has recently been paid for the wet processes,^{1,2,5} i.e., the dilute-HF and pH-modified buffered-HF treatments. In the case of dilute (1-10%) HF treatment, there exist three types of hydrogen configurations on the Si surface:^{1,2} mono- (SiH), di- (SiH₂), and trihydrides (SiH₃). Among them, the mono- and dihydrides are located at defect sites such as atomic steps and point defects, and the trihydride is mainly on the flat part of the (111) surface. In contrast, on the Si(111) surface treated by pH modified buffered HF, only monohydride exists on the entire surface.⁵

The STM was also used to study the hydrogen states on the HF-treated Si(111) surfaces, since it was shown that the tunneling current was stable even in air on this sample.⁶ The

first STM image with atom-like features were shown in air by Nakagawa et al.⁷ on both Si(001) and Si(111) surfaces prepared by the dilute HF treatment following ultraviolet radiation. Recently, Becker et al.⁸ have shown clear atomic images with the 1x1 structure of the monohydride phase on the flat part of the (111) surface prepared by the pH modified buffered HF treatment.

Here we have made STM observation on the Si(111) surfaces prepared by dipping into 1%-HF solution and by repetition of dipping into HF solution and boiling in hot water for 10-times. In this letter, we shall present the STM images showing the presence of both the trihydride and monohydride phases on the Si(111) surface and discuss their origins based on atomic structure models.

2. EXPERIMENTS

Samples (5x5x0.38 mm³) were cut from B doped p-type Si(111) wafers (0.1-0.3 Ω·cm) within a misorientation angle of ±0.1°. The samples were cleaned by the conventional RCA method and then was boiled in a solution of HCl:H₂O₂:H₂O=1:1:4 for 10 min and a clean oxide layer with about 20 Å in thick was grown on the surface. In the final stage of cleaning, one type of the sample was dipped into the 1%-HF solution diluted with deionized water for 30 sec, and the oxide layer

was removed moderately. It was rinsed by the deionized water for 30 sec and then vented with the dry nitrogen gas. Another type of the sample was boiled in the hot water after 1%-HF dipping. This process was repeated for 10 times. At the final sequence the sample was dipped into the 1%-HF solution and was rinsed by the deionized water for 30 sec and then vented with the dry nitrogen gas. In order to avoid the oxidation during period of experiment, the STM measurement has been carried out in an ultrahigh vacuum chamber ($< 1 \times 10^{-10}$ Torr). When the pressure reached 1×10^{-8} Torr after pumping for 2 hours without baking, the sample was transferred to an STM chamber. The STM observation was started as soon as the pressure in the STM chamber reached 1×10^{-10} Torr without any treatments of the surface ("as-prepared" surface). Mechanically ground Pt-tip was used without any cleaning. The xy piezos for tip scanning were calibrated within a few percent by measuring the atomic image of graphite in UHV just after measuring the Si sample.

3. RESULTS AND DISCUSSION

Figure 1 shows a $25 \times 16 \text{ \AA}^2$ STM image (empty states) of the Si(111) surface prepared by simple dipping into the 1%-HF solution. We can clearly see the regular arrangement of atom-like dots with the three-fold symmetry. In this image the distance between dots measures 2.2 \AA . This is definitely smaller than the distance of 3.8 \AA between the topmost Si-atoms on the Si(111)- 1×1 . We also imaged the filled states by applying positive voltage to the tip. The image also exhibited atom-like dots with the three-fold symmetry and the distance of 2.2 \AA .

Figure 2 shows a $81 \times 40 \text{ \AA}^2$ STM image (empty states) of the Si(111) surface prepared by repeated processes of 1%-HF dipping and boiling in the hot water. We can see the atomic steps and the regular arrangements of atom-like dots with the separation of 8.8 \AA which correspond to the distance between the topmost Si-atoms on the Si(111)- 1×1 surface.

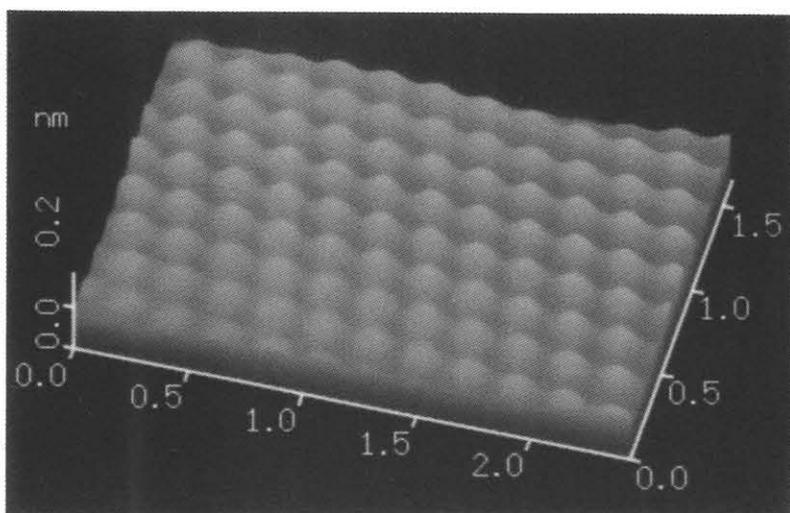


Fig. 1. A $25 \times 16 \text{ \AA}^2$ STM image of the Si(111) surface prepared by dipping 1%-HF solution. The tip was biased at -2.0 V (the empty states) and the tunneling current was maintained at 0.2 nA .

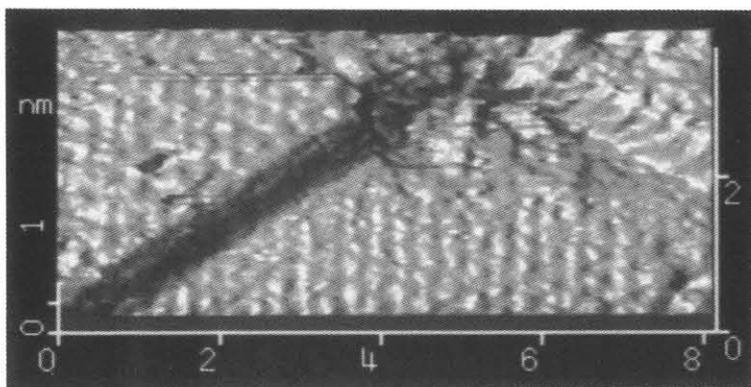


Fig. 2. A $81 \times 40 \text{ \AA}^2$ STM image of the Si(111) surface prepared by combination of the 1%-HF dipping and boiling in the hot water. The tip was biased at -2.0 V (the empty states) and the tunneling current was maintained at 0.2 nA .

We shall discuss the origin of the dots appeared in the STM images. The tunneling current for the present samples is stable after exposing to air and the IR measurements on the sample prepared by the same dilute HF treatment exhibit the existence of mono-, di-, and trihydrides on the Si(111) surfaces. Hence we shall concentrate our attention to hydrogen-related structures. On the Si(111) surface the dihydride does not exist so that its possibility can be ruled out. Therefore we shall consider two hydride phases, monohydride and trihydride phases.

Pandey *et al.*³ have proposed a structure model for the trihydride phase on the surface by comparing their data with the theoretical calculation. In this model, shown in Fig. 3, the distance between H atoms belonging to the same SiH₃ radical is 2.4 Å and the length of Si-H bond is 1.5 Å. And the SiH₃ radicals on the Si(111) surface are rotated by 30° from the ideal or staggered configuration. The direction of rotation is taken to be the same to each other, forming the single domain structure.

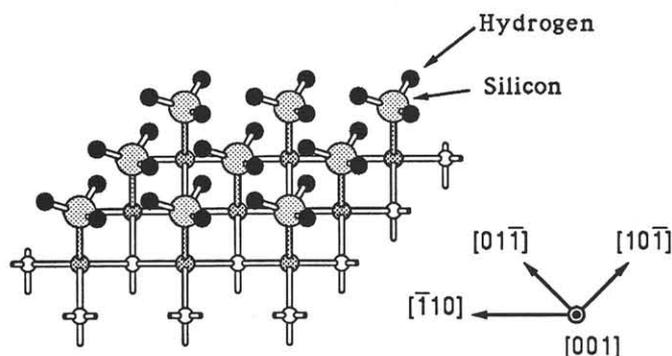


Fig. 3. Schematic view along the [001] direction of SiH₃ phase on the Si(111) surface.

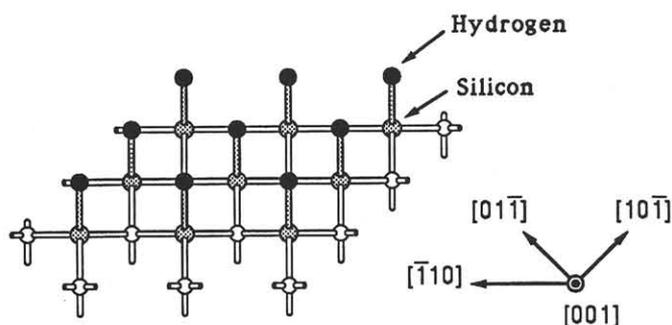


Fig. 4. Schematic view along the [001] direction of SiH phase on the Si(111) surface.

As a result, the H-H distance on the neighboring Si atom becomes 2.1 Å. Then the arrangement of the H atoms is likely to exhibit the three-fold symmetry apparently, and the average distance between H atoms is taken to be 2.2 - 2.3 Å. This value is in good agreement with the measured value in Fig. 1. Therefore we can ascribe the origin of the dots in Fig. 1 to the hydrogen atoms of the trihydride phase on the Si(111) surface. In the case of monohydride phase, H atoms are located on-top sites of the topmost Si atoms whose feature is shown in Fig. 4. Therefore they exhibit the same separation as that of the Si atoms. This is exactly seen in the STM image in Fig. 2.

4. CONCLUSION

In summary, atomic images are clearly observed by the STM on the as-prepared Si(111) surfaces treated by the 1%-HF and the combination of 1%-HF dipping and boiling in hot water. These images are originated from the H atoms and can be explained by the trihydride and monohydride structural models, respectively. Present experiments indicate that the H-termination of Si(111) surface is dependent on the H-termination process.

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