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Scanning Tunneling Microscopy Observation on the Atomic Structures of Step Edges and Etch Pits on NH_4F-Treated Si(111) Surface

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The atomic structures of the step edge and the etch pit on the NH_4F-treated Si(111) surface were studied by UHV-STM observation and also by FT-IR and XPS measurements. The atomic image of the area nearby the step edge on the surface of hydrogen terminated 1x1 Si(111) prepared by the NH_4F treatment was obtained using STM with care for the organic contamination on the observed sample surface. Hydrogen atoms terminating topmost Si atoms on the terrace were observed to be closely packed with threefold symmetry. Various size pits with triangle shape on the terrace were seen to be aligned their one vertex pointing to $[1\bar{1}2]$. An existence of one -atom size etch pits was also confirmed. The step edge was confirmed to contain some kinks. We succeed to observe a hydrogen atom of the Si-H bond projecting in an oblique direction from endmost Si atom at the step edge.

1. INTRODUCTION

In the previous studies, one of us revealed the hydrogen-termination and hydrogen passivation phenomena of the HF-etched Si surface, which have become an essential concept for development of preparation technique in Si device production process.[1,2] Following the works, many researchers tried to analyze chemical structures of the hydrogen (H)-terminated Si surface using XPS, FT-IR, STM and so on. Chabal and coworkers developed novel preparation technique to obtain an atomically flat Si(111) surface using buffered HF or NH_4F aqueous solution.[3,4] They vigorously analyzed chemical structure of the surface mainly using FT-IR. Several researchers studied on the morphology and atomic arrangement of the H-terminated surface by STM and AFM observation.[5-9] These studies revealed that NH_4F-treated Si(111) surface has unreconstructed 1x1 surface crystal lattice. However, organic contaminations prevented them to obtain an atomic-resolved and wide area STM image of the surface enough to discuss atomic structure of a step and an etch pit in detail. In the present study, we studied the atomic structures of the step edge and the etch pit on the NH_4F-treated Si(111) surface by UHV-STM observation with care for the organic contamination on the STM sample surface and also by FT-IR and XPS measurements.

2. EXPERIMENT

We used polished p-type Si(111) wafer having miss-orientation angle of 0.2° . The native oxide layer on the Si surface was removed by immersion in 1% HF solution after a supersonic washing in acetone. Finally, the Si wafer was immersed in 40% NH_4F solution for 7 min before well rinsing in ultra-pure water. The Si surface was confirmed to have a chemical structure of a monohydride termination, an atomic-scale step/terrace morphology and a negligible surface organic contamination using FT-IR-ATR, AFM and XPS, respectively. It was introduced into the UHV chamber of STM instrument through the load-lock chamber. A tungsten-tip which was etched in KOH aqueous solution was used in STM measurement. The x and y axes in the STM image were calibrated using data of the measurement of the atomic image of 7x7 structure of reconstructed Si(111) surface just before. STM observation was carried out in vacuum of 1×10^{-8} Pa. Most of images were taken under the condition of the tip bias of about -1.5 V and tunneling current of 0.2 nA.

3. RESULTS AND DISCUSSION

Figure 1 shows STM current image of the NH_4F treated H-terminated Si(111) surface with 45 nm x 45 nm area. Only a small part of the STM image has an atomic-resolution structure and other part shows an irregular structure. The XPS measurement suggested that an organic contamination with an average thickness of about 0.13 nm existed on the Si surface. In order to find out the origin of the surface organic contamination, the chemical compositions on the Si sample surfaces at each steps in the experiment were analyzed using XPS. Figure 2 shows XPS spectra of surfaces just after NH_4F treatment, after holding in transfer vessel made of PTFE at 30 min and after evacuating in load-lock chamber at 30 min. The transfer vessel was used to hold the Si sample until setting it on the STM sample holder after the wet treatment. Intensities of C_{1s} and O_{1s} peak did not change during keeping in the transfer vessel, however, these peaks increased during

evacuation process as shown in Fig.2. This result suggests that the organic contamination did not occur during the wet treatment and the sample transfer process in atmosphere, but occurred during evacuation process. This contamination considered to originate with oil mists from turbo-molecular-pump evacuating load-lock chamber. In order to protect the surface from the contamination arising from oil mist, the sample surface was covered with a Si wafer which was prepared by the same wet treatment as the sample wafer during evacuation process in the load-lock chamber. Then, the Si wafer cover was taken away from the sample surface in the UHV measurement chamber just before a start of STM observation. Figure 3 shows STM current image of the H-terminated Si(111) surface observed using sample introducing method above described. Area size of the image is same as the image in Fig.1. We can see a clear step/terrace structure with etch pits and the regular arrangement of atoms with threefold symmetry on the terrace.

Figure 4 shows an atomic topographic image of an area with size of 18 nm x 18 nm nearby the step edge. The distance among atoms arranged with threefold symmetry on the terrace measures 0.38 nm, which well agrees with the distance between H atoms terminated the topmost Si atoms on the Si(111) surface. Result of FT-IR-ATR measurement confirmed that the dominant structure of the sample surface was monohydride terminated structure. The observed dots are considered to be hydrogen atoms of Si-H groups which terminate surface dangling bonds of Si atoms. There are various size etch pits on the terrace. The most of them have right triangle shape indicated with "A" and a part of them has deformed triangle shape indicated with "B". A vertex of each triangle points to $[11\bar{2}]$ direction. There are also extremely small etch pits indicated with "C" which consist of one or few atomic holes on the terrace. We can observe atomic images in bottom of larger pits. Atomic steps containing some kink structures indicated with "D" mainly run along $<\bar{1}10>$ direction. A row of lower bright atomic dots is observed at the step edge indicated with "E". Figure 5 shows an atomic image and a line-height-profile observed along $<10\bar{1}>$ direction across the step edge. The step height measures 0.31 nm which well agrees with a bi-atomic layer height. A peak like a landing of stairs is observed between an upper terrace

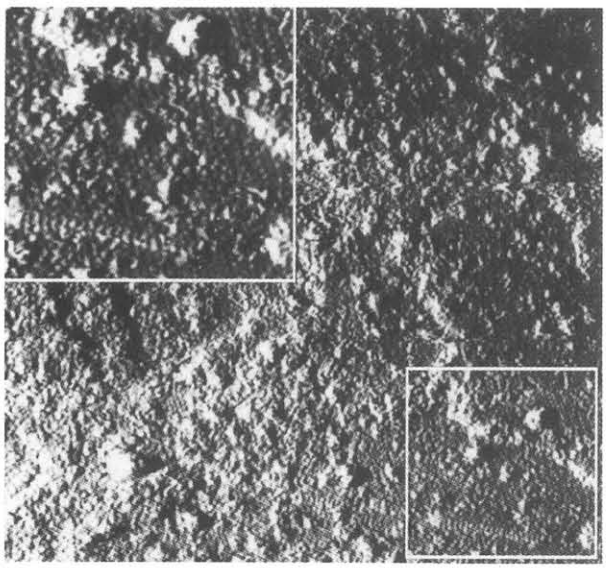

Fig.1 STM current image of the NH_4F treated H-terminated Si(111) surface with 45 nm x 45 nm area.

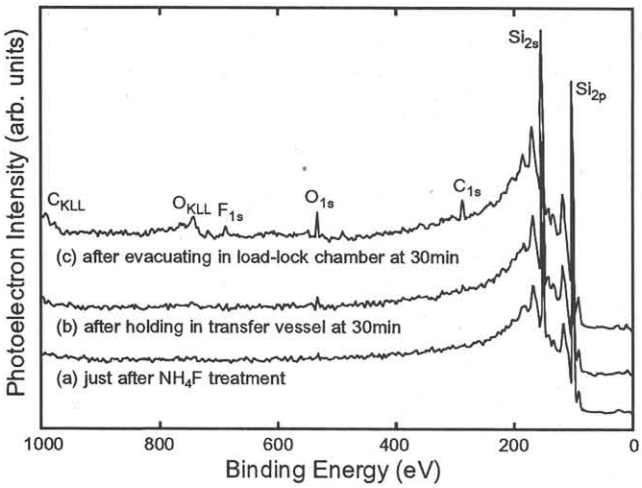

Fig.2 XPS spectra of surfaces (a) just after NH_4F treatment, (b) after holding in transfer vessel made of PTFE at 30 min and (c) after evacuating in load-lock chamber at 30 min.

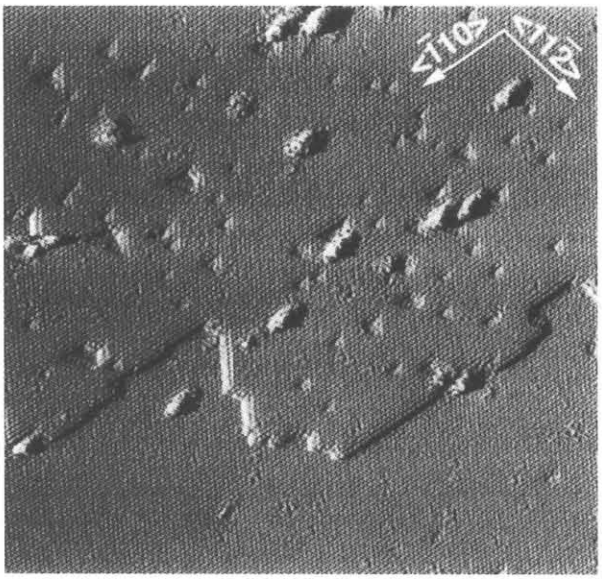

Fig.3 STM current image of the H-terminated Si(111) surface with care for the organic contamination on the STM sample surface. Area size of the image is same as the image in Fig.1.

and a lower terrace in the line profile. The landing-peak corresponds to the lower bright atomic dots at the step edge. A height of the landing-peak from the lower terrace measures 0.12 nm. The lower bright atomic dot at the step edge is considered to be the image of a hydrogen atom of the Si-H bond projecting in an oblique direction from endmost Si atom at the step edge as show in Fig. 6.

4. CONCLUSION

We successfully obtained the atomic image of the area nearby the step edge on the surface of hydrogen terminated 1x1 Si(111) prepared by NH_4F treatment. Hydrogen atoms of Si-H on the terrace were observed to be closely packed with threefold symmetry. Various size pits with triangle shape on the terrace were seen to be aligned their one vertex pointing to $[11\bar{2}]$. An existence of one -atom size etch pits was also confirmed. The step edge was confirmed to contain some kinks. We succeed to observe medium height hydrogen atoms projecting in an oblique direction from endmost Si atom at step edge.

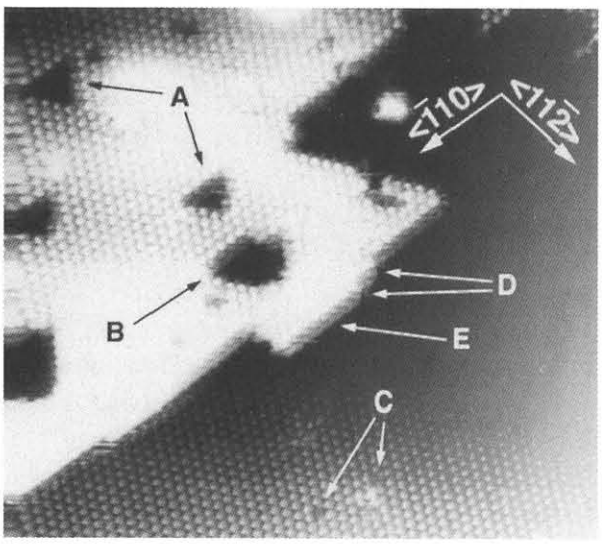

Fig.4 An atomic topographic image of an area with size of 18 nm x 18 nm nearby the step edge.

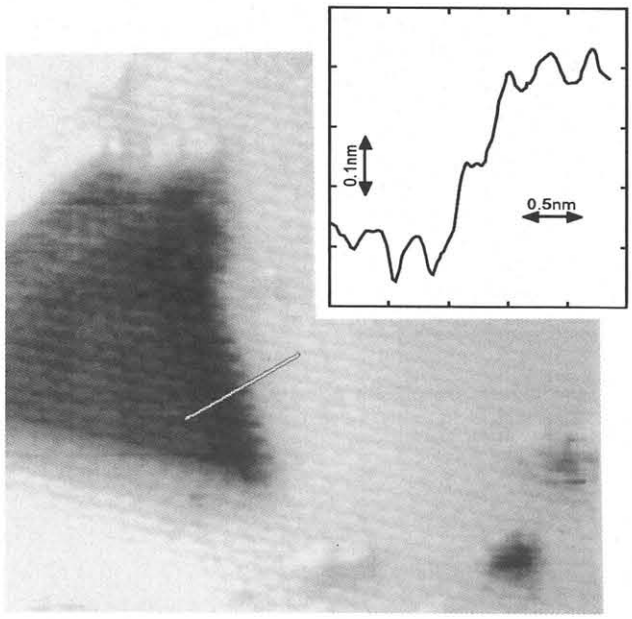

Fig.5 An atomic image and a line-height-profile observed along <101> direction across the step edge.

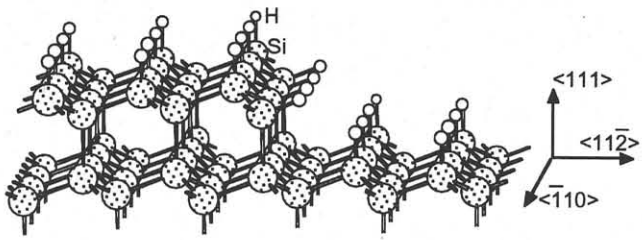

Fig.6 Geometrically structural model of H-terminated Si(111) surface.

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