Atomic-scale defect control on hydrogen-terminated silicon surface at wafer scale

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(Received 17 July 2000; accepted for publication 15 November 2000)

We have developed a wet preparation method for an atomically defect-free Si wafer surface. In the conventional atomically smooth treatment using ammonium fluoride aqueous solution, dissolved oxygen has been revealed to form defects on the Si (111) surface. We have been able to create an extremely atomically smooth hydrogen-terminated surface with a good periodic step/terrace structure. Moreover, the ordered surface structure was confirmed to be fabricated all over the wafer surface. The atomic-scale defect-free hydrogen-terminated wafer surface with a periodic step/terrace structure is expected to be highly useful as a well-defined substrate for nanostructure fabrication and high-quality film deposition, and to be useful in many other research fields. © 2001 American Institute of Physics. [DOI: 10.1063/1.1339993]

The hydrofluoric acid (HF)-etched Si surface has been examined in various works. The earliest work in the field was carried out by Yablonovitch. 1 He detected the existence of Si–H on the surface using Fourier transfer infrared spectroscopy (FTIR) in attenuated total reflection mode (ATR), but he was not able to clarify the overall elemental composition on the surface. Following this work, Takahagi 2,3 and Burrows 4 confirmed the hydrogen-termination and hydrogen-passivation phenomenon on a HF-etched Si surface based on precision analysis techniques such as FTIR ATR and x-ray photoelectron spectroscopy (XPS) methods. These findings have become essential to the development of new preparation techniques in Si device-production processes. Moreover, Higashi 5 and Jakob 6 have developed a novel preparation technique for obtaining an atomically smooth Si (111) surface with monohydride termination by treatment in a buffered HF or ammonium fluoride (NH4F) aqueous solution. Unfortunately, scanning tunneling microscopy (STM) atomic images of a surface prepared by NH4F treatment show many defects such as etch pits on a terrace and kinks in a step edge. 7,8

Until now, there has little success in preparing a defect-free hydrogen-terminated Si surface. The development of a preparation method for a defect-free Si surface is greatly anticipated. In this work, we have improved a wet process for the preparation of an atomic-scale defect-free wafer-sized Si surface. The Si wafer surface, which has an ordered terrace-and-step surface structure, may be a useful substrate for nanofabrication and many other processes. 9,10

We used an n-type Si (111) wafer specially polished for the present work. The samples were cut at various miscut angles off the (111) plane in (112) direction. Organic contamination was removed by treatment in boiling mixed solution of sulfuric acid and hydrogen peroxide (H2SO4:H2O2 = 3:1) after washing in acetone. The native oxide layer on the Si surface was removed by immersion in a 5% HF solution after the removal of organic contamination.

Finally, the Si wafer was immersed in a 40% NH4F solution.

In this study, both the complete removal of organic contamination and the prevention of its reabsorption on the Si surface during the wet treatment were very important, as residual organic contamination acts as an etching mask, creates inhomogeneous etchings, and finally leads to irregular morphology on the wafer surface. We therefore used ultra-pure water with total organic carbon levels of less than 4 ppb, and vessels and tweezers were used immediately after being cleaned in a boiling 1% sodium peroxodisulfate (Na2S2O8) aqueous solution, then followed by rinsing with ultra-pure water. Boiling Na2S2O8 aqueous solution is a strong oxidant and decomposes organic contamination on the surfaces of vessels and instruments into carbon dioxide and water. The surface morphology was observed by ultrahigh vacuum STM and atmosphere atomic force microscopy (AFM), and the chemical structure of the surface was also measured using polarized FTIR ATR. The surface elemental composition was monitored using XPS.

Figure 1 shows STM images of the Si (111) surfaces prepared by NH4F treatment. The Si surfaces cut off at 1° in the (112) direction have an atomically smooth surface. The treatment times at 20 and 72 °C were 6 min and 30 s, respectively. These times were optimized values at both solution temperatures. The surface prepared using a conventional treatment in NH4F at 20 °C shows step/terrace atomic scale smoothness but also has many atomic-scale irregular structures such as etch pits and kinks. The existence of many kinks on step-edges results in nonlinear step edges.

In contrast, the surface treated at 72 °C has very few crystallographic defects such as etch pits or kinks, and also has straight step-edge lines and a homogeneous periodic step/terrace structure. The step height is 0.31 nm, corresponding to a silicon bilayer. Terminal-hydrogen atoms can be clearly seen in an enlarged STM atomic image as shown in Fig. 1(c). Hydrogen atoms in step edges are ordered in a straight line in the (110) direction. We found that the treatment using hot NH4F aqueous solution dramatically improved the regularity of the Si (111) surface structure.

Figure 2 shows FTIR-ATR spectra of the surfaces...
treated by NH₄F solution. IR measurements were performed by sticking the sample surface to a prism at a resolution of 1.0 cm⁻¹. The prism was made by 1×20×50 mm³ of Ge° and 60° bevel edges on both short sides. The sample size for the IR measurement was 15×35 mm². The off direction of the sample surfaces was oriented perpendicular to an optical path of IR light as shown in Fig. 2. Background reference spectra were obtained by measuring only the Ge prism. The p-polarized spectrum of the surface treated in hot NH₄F solution is dominated by one very sharp vibrational line at 2084 cm⁻¹. This peak was assigned to the monohydride on the terrace. Slight shoulder peaks assigned to the monohydride at 2071, 2087 cm⁻¹ and the dihydride at around 2100 cm⁻¹ on the step edge were observed. The dihydride peak was likely due to a defect structure, as an ideal step has a monohydride structure. Higashi has estimated the defect density from the peak under the s-polarized spectrum because only H modes at defects have vibrational components parallel to the surface. After correction for misalignment of 1°, resulting in an apparent contribution at 2084 cm⁻¹ in the s-polarized spectrum shown in Fig. 2(b), the defect density was found to be 0.11%. This value is the same or lower than Higashi’s value of <0.5%. However, even the defect density of the surface treated at 20 °C, on which many defects were observed by STM as shown in Fig. 1, was estimated at a similar value of 0.12%. Most of the defects observed by STM are considered to be etch pits and steps in the [110] direction. Because these defects are terminated by monohydride, they cannot be detected by IR measurement of the dihydride structure. The STM observation is necessary to make a close evaluation of the defect density.

We tried in the present study to determine a clear procedure for the reduction of crystallographic defects such as kinks and etch pits on the surface by hot NH₄F treatment. At first, the dissolved oxygen concentration (DOC) in the NH₄F solution at 72 °C was measured to be 1.8 ppm, which was lower than the 5.0 ppm concentration found at 20 °C. In order to confirm the effects of the dissolved oxygen, we tried a treatment using NH₄F solution with low DOC prepared by nitrogen gas bubbling. Despite a treatment temperature of 20 °C, the wafer surface treated with NH₄F solution with a low DOC of 0.1 ppm had a morphology similar to that of the surface prepared with hot NH₄F solution, as shown in Fig. 3. Oxygen dissolved in NH₄F solution proved to result in an irregular structure on Si surfaces. Wada and Chidsey have reported a similar result regarding the use of dissolved oxygen in NH₄F solution. In their study, the removal of oxygen from the fluoride solution by sparging with argon substantially reduced the formation of etch pits. However, many kink structures in the step edge remained, and the step/terrace period was not uniform.

Dissolved oxygen is thought to result in the formation of a partially oxidized structure. The etching rate of the oxidized portion in NH₄F solution is presumed to be higher than that of a Si metal part by an etching rate measurement. The
etch pits and kinks are generated on the Si surface as the partial oxidation of the Si surface randomly occurs on the terrace and step edge. An irregular structure spreads from etch pits and kinks formed on traces of etched parts. Therefore, NH$_4$F treatment is able to remove crystallographic defects, but dissolved oxygen in the treatment solution induces new defects. The production process involving the creation of surface defects by dissolved oxygen is considered to antagonize the process of reducing defects by NH$_4$F etching.

We attempted to create a periodic step/terrace wafer-sized structure. Figure 4 shows the AFM images obtained at nine points on the surface of a 4 in. wafer treated by hot NH$_4$F solution with an off-angle of 1° in the (112) direction. The same regular morphologies were observed at all points, thereby confirming that the periodical structure at a wafer size. It is, however, surprising that an extremely large number of step lines (5 \times 10^6) at regular intervals of \sim 20 nm exist on the Si wafer surface. We believe that the wafer specially polished for the present work has a uniform miscut angle on the whole surface. In the AFM observation, the completed periodic step/terrace Si surface structure appeared to be in a steady state; in addition, the etching process was completely stopped. To determine the reason why an extremely ordered surface structures is self-organized across the entire wafer surface, we have simulated an etching reaction using the Monte Carlo method. The simulated results suggest that the native-ordered surface crystal structure appears after removal of the irregular structure on the top surface. Detailed simulation results will be reported in our next letter.

We developed a wafer-size wet-treatment technique for preparation of a periodic clean Si (111) surface with a very small amount of atomic-scale defect. This wafer is expected to be highly useful as a well-defined substrate for nanostructure fabrication, high-quality film deposition, and many other research fields. The hydrogen-terminated surface will be used as a hydrophobic substrate. In addition, after oxidation, the hydrogen-terminated surface also changes to an oxide surface, but the periodic atomically smooth surface has been confirmed to be retained. We can use the wafer as a hydrophilic atomically smooth substrate with periodic morphology.

In summary, we have achieved the preparation of an atomic-scale defect-free hydrogen-terminated Si (111) surface with a periodic step/terrace structure using a low oxygen and organic-contamination-free NH$_4$F treatment procedure on a laboratory scale. It was revealed that the dissolved oxygen forms a partially oxidized structure on the Si surface, and that defects arise from the oxidized portion. It was confirmed that an ordered structure was created at wafer size.

The authors would like to thank Dr. Habuka of Shin-Etsu Handotai Co., Ltd., for the special Si wafer polishing. The work was partially supported by the Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Corporation (JST).