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# Atomic scale flattening and hydrogen termination of the Si(001) surface by wet-chemical treatment

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An ultrahigh vacuum scanning tunneling microscopy has been applied to analyze wet-chemically prepared Si(001) surfaces in an atomic scale. The surface treated by 2.5% HF is atomically rough and is covered by featureless corrugations resulting from an etching by OH ions in the solution. The surface treated by HF:HCl=1:19 mixed solution without controlling an oxide-removal direction is also atomically rough, but is characterized by a kinkful morphology, which reflects the crystallographic nature of the Si(001) surface. On the other hand, the surface treated by the same mixed solution but by controlling the oxide-removal direction is covered by regular monatomic steps and the ordered dihydride phase on the terrace. From these facts, we have confirmed that these factors, the concentration of the OH ions and the way of the oxide-removal, play roles in the preparation of the atomically flat Si(001) surface. (© 1996 American Vacuum Society.)

### I. INTRODUCTION

An atomic scale flattening of the Si surfaces by wetchemical processes is now becoming an important key factor for the Si ultralarge scale integration (ULSI) technology. Among many processes, the treatment using HF-containing solutions has been attractive for the purpose to control the surface flatness.<sup>1,2</sup> Dipping into the HF-containing solution, the surface oxide is removed from the surface and surface bonds are terminated by hydrogen (H) atoms which prevents the surface from oxidation. At the same time, the OH ions in the HF-containing solutions etch the Si surfaces, whose rate is mainly controlled by changing their concentration. In the case of Si(111) surfaces, an atomically flat Si(111) surface has been prepared reproducibly by using solutions with  $pH\sim 8.^{3-6}$ 

However, in the case of Si(001) surfaces, it has been pointed out that the surface flattening by the wet-chemical method is quite difficult due to the following two reasons.<sup>7–11</sup> The first one originates from the effect of the anisotropic etching by OH ions on the Si surface, resulting in the formation of (111) facets. When the (111) microfacets appear on the (001) surface during the treatment, the surface becomes rough. The second one is directly related to the atomic structure on the H-terminated Si(001) surface. Infrared (IR) spectroscopy<sup>7</sup> has revealed that dihydrides are the main species on the Si(001) terraces treated by the HFcontaining solutions. When the Si(001) surface is covered by the dihydrides uniformly, two H atoms belonging to the neighboring Si atoms are very close, causing a strong static repulsion force between them [Fig. 1(a)]. Then, this effect makes the terrace energy high. In order to reduce the surface energy, each dihydride tends to tilt slightly from its symmetric position to enlarge the separation between the neighboring H atoms as shown in Fig. 1(b).<sup>12</sup> Generally, this relax-

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ation occurs randomly on the Si(001) surface and the domain structure is formed.<sup>9,13</sup> Then, the domain boundaries could be easily attacked by the etchant molecules and the surface could become rough.<sup>12</sup>

Recently, we have confirmed that these two factors mentioned above should be taken into account at the same time in the preparation of the ideal H-Si(001) surface.<sup>9,11</sup> (1) To suppress the anisotropic etching by the OH ions, extremely low pH solution should be used to remove the pre-formed oxide layer from the surface. (2) To reduce the surface energy originating from the static repulsion between the closest H atoms. Ordered step structure should be introduced to the surface by using vicinal sample since no neighboring H atoms exist just at the step edge. Moreover, to prevent the inhomogeneous relaxation of the dihydride radicals on the surface, the sample was dipped into the solution from one end to another with a constant speed as schematically shown in Fig. 2. Then the oxide layer on the surface was removed moderately so as to form uniform structure. In this article, we shall show how these factors play important roles in the preparation of the atomically flat Si(001) surface by measuring ultrahigh vacuum scanning tunneling microscopy (UHV-STM).

#### **II. EXPERIMENT**

The samples used in this experiment were cut from a boron-doped *p*-Si(001) wafer misoriented by 1° from the [001] axis toward the [110] direction into the  $3 \times 13$  mm<sup>2</sup> rectangular shapes, while its long side is parallel to the [110] direction. After precleaning by the RCA method, about 1100-Å-thick oxide layers were formed by annealing samples at 1000 °C in a dry oxygen atmosphere using an open-air furnace. Then the sample surfaces were treated by following three ways. The first sample (No. 1) was dipped into a

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(a) Symmetric phase



FIG. 1. Schematic drawings of the dihydride phases on Si(001) surface (side views). (a) the symmetric dihydride phase; (b) the canted dihydride phase. Closed and open circles represent H and Si atoms, respectively.

2.5%-HF (pH=2) solution for 5 min without controlling the dipping direction. This is the standard procedure for removing the oxide layer. Then, the resulting surface was terminated by the H atoms, which was confirmed by the fact that the surface became hydrophobic. The second sample (No. 2) was dipped into a mixed solution of HF:HCl=1:19 (pH<1) for 2 min without controlling the dipping direction, whose solution contains less OH ions than that for sample No. 1. The treated surface became hydrophobic after about 2 min dipping, indicating the hydrogen termination. Then, the etching rate of the SiO<sub>2</sub> by the mixed solution is roughly estimated as 550 Å/min. The third sample (No. 3) was dipped into the mixed solution of HF:HCl=1:19 (pH<1) for 2 min from one end to another as shown in Fig. 2.<sup>11</sup> The dipping direction was along the [110] direction, and its speed was



FIG. 2. Schematic drawing for the dipping procedure of Si(001) sample (No. 3) into the solution. The sample was dipped into the solution at a constant speed from the  $[\overline{110}]$  direction to the [110] direction.



FIG. 3. Typical ( $480 \times 345 \text{ Å}^2$ ) STM image of as-prepared Si(001) surface (No. 1). The tip was biased at -2.0 V (the empty states) and the tunneling current was maintained at 0.02 nA.

about 1 mm/s. During this dipping process, the oxide layer was removed moderately along one direction with leaving the Si/SiO<sub>2</sub> interface. The prepared surface was also hydrophobic, indicating H termination. It should be mentioned that these three samples were not rinsed by a deionized water after treatment by HF containing solutions prior to STM measurement. This is because that the water contains OH ions and acts as the strong etchant for the Si(001) surface. Therefore certain amounts of fluorine (F) atoms exist on these unrinsed surfaces in addition to the H atoms. In present case, however, most (about 90%) of the surfaces are covered by the H atoms and only 10% by the F atoms, since total amount of the HF molecules in the solutions is about 2.5%.<sup>2</sup>

After treatment, samples No. 1, No. 2 and No. 3 were introduced into a vacuum chamber within 10 min and the STM measurement was carried out in an UHV  $(10^{-10} \text{ Torr})$  without any further treatment.

#### **III. RESULTS**

Figure 3 shows a typical,  $480 \times 345$  Å<sup>2</sup>, STM image of sample No. 1. The corrugation amplitude of this image is about 4.5 Å. The surface is atomically rough and no specific structures reflecting the crystallographic nature of the Si(001) surface are seen. This type of image was reproducibly obtained for over a few weeks in UHV, indicating that the surface should be quite stable due to the H termination even after carrying the sample through the air. However, a small amount of the F atoms on the surface would result in the noisy feature of the STM image of sample No. 1, but we were unable to identify the adsorption sites of the surface F atoms from the STM image.

Figure 4 shows a typical,  $480 \times 330$  Å<sup>2</sup>, STM image of sample No. 2. The corrugation amplitude is about 4.5 Å and the image is quite noisy. However, we can recognize the surface structure is quite kinkful and is characterized by rectangular-shaped morphologies running along [110] and [110] directions, reflecting the crystallographic nature of the Si(001) surface.



FIG. 4. Typical ( $480 \times 330$  Å<sup>2</sup>) STM image of as-prepared Si(001) surface (No. 2). The tip was biased at -2.2 V (the empty states) and the tunneling current was maintained at 0.05 nA. The crystallographic direction is shown in the inset. Rectangular feature is clearly seen at the bottom half of the image.

Figure 5(a) shows a typical,  $420 \times 350$  Å<sup>2</sup>, STM image of sample No. 3. In this image, there is regular step structure with a height of 1.4 Å oriented roughly toward the [010] direction, which corresponds to a monolayer step on the Si(001) surface. Figure 5(b) shows a high resolution,  $37 \times 25$ 



FIG. 5. Typical [(a)  $420 \times 350$  Å<sup>2</sup>; (b)  $37 \times 25$  Å<sup>2</sup>] STM images of asprepared Si(001) surface (No. 3). The tip was biased at -2.2 V (the empty states) and the tunneling current was maintained at 0.05 nA. The crystallographic direction is shown in the inset. In the high resolution image (b), the unit cell for the regular atomlike dots is superimposed.

 $Å^2$ , STM image of a terrace shown in Fig. 5(a). In this image, we can recognize regular atomlike dots which form a rectangular lattice. The size of the unit cell of the lattice is about 3.8 Å in the [110] direction and about 2 Å in the  $\overline{[110]}$ direction. Here we should recall that the unit cell of the Si(001)-1×1 surface is a rectangular shape of  $3.8 \times 3.8$  Å<sup>2</sup> in the [110] and [110] directions, respectively. Therefore, the observed lattice parameter of the cell along the [110] direction is nearly half of Si(001)-1 $\times$ 1 cell. Since, as mentioned previously, almost all the surface is covered by the H atoms, we can expect that this atomic structure originates from the ordered dihydride phase on the Si(001) surface.<sup>11</sup> These images are completely different from those of samples No. 1 and No. 2, and are observed only in the limited area of sample No. 3. The other area of the surface shows noisy image like Fig. 4.

#### **IV. DISCUSSION**

First we shall discuss the origin of the morphology difference among samples No. 1, No. 2 and No. 3. It is well known that Si/SiO<sub>2</sub> interface formed by the thermal oxidation is atomically flat.<sup>14</sup> Then, if only the oxide layer is removed by the HF-containing solutions moderately from the surface, atomically flat H-terminated Si surface should appear. In fact, on the sample No. 3 surface there are regular step structure and symmetric dihydride phase as shown in Fig. 5. This means that the present pre-formed Si/SiO<sub>2</sub> interface is really atomically flat and the etching effect of the OH ions is effectively reduced in the novel preparation method for sample No. 3. On the other hand, in the cases of samples No. 1 and No. 2, there are no clear features of ordered steps, which clearly indicates that the etching for samples No. 1 and No. 2 occurs during the oxide removal and H-termination processes.

The oxide layers on both samples No. 1 and No. 2 were removed without controlling the oxide-removal direction with different solutions. Then we could expect that the different surface morphology is related to the different concentration of the OH ions in the solutions. The concentration of OH ions in the solution for sample No. 1 is higher than that for sample No. 2. Hence the etching effect by the OH ions for sample No. 1 would be stronger than that for sample No. 2, and more Si atoms would be removed from the sample No. 1 surface than from sample No. 2. For the etching by the OH ions, it is also pointed out that the Si atoms in the step edge, kink or defects, etc. are more easily etched than those on the terrace.<sup>7</sup> From this point of view, the step edges or kinks on the surface preferentially etched by the OH ions from sample No. 1 surface, and then surface is changed to less-kinked and featureless structures. On the other hand, in the case of sample No. 2, the etching by the OH ions is weak and the kinkful feature is kept during the etching. However in the case of samples No. 2 and No. 3, treated by the same solution, there exists large morphology difference, which means that there are other factors affecting the surface morphology. As mentioned in the previous paper, the way of the oxide removal can affect the formation of the atomic



FIG. 6. Schematic drawings of the multidomain surface of possible dihydride phases on the same terrace: Side view (a) and top view (b). Closed and open circles represent H and Si atoms, respectively. In (b), different domains of the dihydride phases are indicated by different patterns.

structure on the Si(001) surface.<sup>11</sup> In the normal process of the oxide removal, the etching of surface oxide layer does not proceed uniformly over the surface, and hence the multidomain should be formed. Figure 6 shows a schematic drawing of multidomain structure, where the symmetric phase and two canted phases with opposite tilting directions coexist on the same terrace. These domain boundaries are easily attacked and etched by the etchant molecules by the effect of the steric hindrance as shown in Fig. 7.9,15 On the initial surface [Fig. 7(a)] covered by the multidomain, the domain boundaries and step edges would be removed preferentially by the OH ions. Since these domain boundaries tend to align toward [110] and [110] directions as shown in Fig. 6, the resulting structure would reflect the (001) crystallographic nature [Fig. 7(b)]. This kind of surface structure is seen in Fig. 4 for sample No. 2. On the other hand, as for sample No. 3, where the oxide removal direction was controlled, the dihydride phase expands continuously from one end to another and forms a single domain, and therefore no domain boundaries appear on the terraces. Then, we can expect the etching mainly from the step edges, not from the terrace, while keeping the mutual step structure during the etching process, which is clearly seen in the case of the Fig. 5(a). However, it is noted that, on sample No. 3 misoriented toward the [110] direction, we observed [010] directed steps in the STM image. This may be due to the macroscopic fluctuation of the interface flatness on the Si/SiO<sub>2</sub>.<sup>11</sup> In this case, the shape of the step should not be straight and must become wavy in macroscopic scale. There occasionally appear the steps directed toward [010] direction in microscopic scale. Then, the [010] directed steps on sample No. 3 surface is stable during the treatment process because of the reason as discussed in previous paper.<sup>11</sup> On the other hand, in the case of the [110] directed steps, the surface energy originat-



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FIG. 7. Schematic drawings of the etching for the multidomain surfaces. Before etching (a), terraces are covered by three kinds of dihydride phases, symmetric phases and two canted phases. After the etching (b), the domain boundaries and step edges are selectively etched and form the rectangular-shaped structures with edges along to the [110] and [110] directions.

ing from the repulsion force between two H atoms cannot be released from the step edge, since the dihydride row on the terrace is parallel to the [110] direction. Then, surface energy becomes high and the surface is etched to become rough.

Finally we shall discuss the origin of the well-ordered atomlike dots in Fig. 5(b) relating to the dihydride states on the Si(001) surface. As mentioned previously, there are two possible ordered dihydride phases on Si(001) surface as shown in Fig. 1. In addition it has been pointed out that the canted phase is more energetically favorable than the symmetric phase.<sup>7,12</sup> However, in the present experiment, the arrangement of the atomlike dots in Fig. 5(b) is likely to fit to the symmetric phase.<sup>11</sup>

Figure 8 shows a schematic drawing for the Si(001) surface stepping down toward the [010] direction, where terraces are separated by monolayer steps as shown by terraces A and B. The step structure and the terrace width (about 20 Å) of this drawing correspond to those shown in Fig. 5(a). On each terrace, two H atoms belonging to a single dihydride align toward either the [110] direction on terrace A or the [110] direction on terrace B, and the directions of both dihydrides deviate by  $\pm 45^{\circ}$  from the [010] step direction. In this particular case, there are eight dihydride species along the single dihydride row. Then, the Si atoms just below the step edge (marked by an arrow  $\alpha$ ) form monohydride, where there are three Si–Si bonds. Therefore the H–Si bond of this



FIG. 8. Schematic drawings of the top and side views of Si(001) surface stepped down toward the [010] direction. Terraces are covered by symmetric dihydride phase, where closed and open circles represent H and Si atoms, respectively. The crystallographic direction is shown in the inset. Labels A and B denote two types of terraces separated by the monolayer steps. The arrow  $\alpha$  points a monohydride species on the terrace.

monohydride can hardly change tilting angle. In this case, the tilting angle of each dihydride in the associated row may be small comparing with that of the dihydride in the calculated canted phase. In other words, the height difference of the H atoms belonging to the same Si atom is small compared with the calculated of value for canted phase (about 1.4 Å). In addition, we must keep in mind that, STM gives us the spatial distribution of the local density of state (LDOS), not the position of the atoms. In the present case, the Si–H bond is polarized and the maximum of the LDOS shifts toward the H-atom side from the center of the bond, because of the difference in the electronegativity between Si and H atoms. Then, the height difference between the maximum position of the LDOS for two Si–H bonds becomes smaller than the real H–H height difference. As a result, the height difference of the STM-observed maximum for two Si–H bonds in weakly tilted dihydride should be very small and could not be observed by the present STM measurement. Therefore we can conclude that the each dihydride species should tilt toward the outside of the step but its tilting angle should small, which would be the reason why the surface structure seems "symmetric" dihydride.

#### V. SUMMARY

The UHV-STM was applied to analyze wet-chemically prepared H–Si(001) surface on an atomic scale. Then, we elucidated how the factors such as the concentration of the OH ions in the treatment solutions, way of the oxide-removal and the step direction affect to the formation of the surface flattening. However, the STM observation was done only in small area. In order to examine the surface structure over wide area, the experimental methods such as IR measurements are highly required.

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- <sup>1</sup>V. A. Burrows, Y. J. Chabal, G. S. Higashi, K. Raghavachari, and S. B. Christman, Appl. Phys. Lett. **53**, 998 (1988).
- <sup>2</sup>T. Takahagi, I. Nagai, A. Ishitani, H. Kuroda, and Y. Nagasawa, J. Appl. Phys. **64**, 3516 (1988).
- <sup>3</sup>G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, Appl. Phys. Lett. **56**, 656 (1990).
- <sup>4</sup>S. Watanabe, N. Nakayama, and T. Ito, Appl. Phys. Lett. **59**, 1458 (1991).
- <sup>5</sup>Y. Morita, K. Miki, and H. Tokumoto, Jpn. J. Appl. Phys. **30**, 3570 (1991).
- <sup>6</sup>H. Tokumoto, Y. Morita, and K. Miki, Mater. Res. Soc. Symp. Proc. **259**, 409 (1992).
- <sup>7</sup>Y. J. Chabal, Mater. Res. Soc. Symp. Proc. 259, 349 (1992).
- <sup>8</sup>U. Neuwald, H. E. Hessel, A. Feltz, U. Memmert, and R. J. Behm, Surf. Sci. Lett. **296**, 8 (1993).
- <sup>9</sup>Y. Morita, and H. Tokumoto, Mater. Res. Soc. Symp. Proc. **318**, 293 (1994).
- <sup>10</sup>S.-L. Yau, K. Kaji, and K. Itaya, Appl. Phys. Lett. 66, 766 (1995).
- <sup>11</sup>Y. Morita, and H. Tokumoto, Appl. Phys. Lett. 67, 2654 (1995).
- <sup>12</sup>J. E. Northrup, Phys. Rev. B 44, 1419 (1991).
- <sup>13</sup>J. J. Boland, Surf. Sci. 261, 17 (1992).
- <sup>14</sup>J. M. Gibson, M. Y. Lanzerotti, and V. Elser, Appl. Phys. Lett. 55, 1394 (1989).
- <sup>15</sup>Y. Morita, and H. Tokumoto, Mater. Res. Soc. Symp. Proc. **315**, 491 (1993).