Water wettability of Si(111) and (001) surfaces prepared to be reconstructed,
atomic-hydrogen terminated and thinly oxidized in an ultrahigh vacuum chamber

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Abstract

Water contact angles on three types of Si(111) and (001) surfaces were measured in nitrogen gas atmosphere without exposing them to air; the surfaces were prepared to be (I) cleaned and reconstructed, subsequently (II) atomic hydrogen (H) terminated, or (III) thinly oxidized in an ultrahigh vacuum (UHV) chamber. The surfaces were characterized by Auger electron spectroscopy and atomic force microscopy. The H-terminated Si surfaces showed as less hydrophilic with a water contact angle of about 37° on the (111) and about 60° on the (001) surface, respectively. The clean and oxidized surfaces showed as super-hydrophilic with the angles less than 6°. To quantitatively evaluate the contact angles on the super-hydrophilic surfaces, an optical interference fringe method was used under an optical microscope in air. The most

super-hydrophilic surface was the oxidized Si(111) surface. The reactivity of the Si surfaces and their degree of hydroxyl group termination to the Si surfaces responsible for water wettability were discussed.

Keywords

Silicon, Water contact angle, Super-hydrophilicity, Optical interference fringe method, Atomic hydrogen termination, Oxidation

1. Introduction

Today silicon (Si) is the most widely used semiconducting material for electronic devices. The rapid evolution of large-scale integrated (LSI) circuits using silicon has crucially demanded super-fine and super-clean technologies to control the structures and properties of silicon surfaces to improve their device performance [1-3]. Silicon devices have been mostly fabricated by a combination of wet and dry processes. To briefly confirm the achievement levels in the processes, the water wettability of silicon can be a useful indicator to discern the surface chemical reactivity, since the wettability is sensitive to the surface chemical termination; the silicon surfaces covered with hydroxyl (OH) group or atomic hydrogen (H) usually exhibit water hydrophilicity or hydrophobicity, respectively. As an application of the termination in device fabrications, intensely related to the water wettability, OH- or H-terminated silicon surfaces in well-controlled manners have been utilized to form strong bonds between two silicon wafers, i.e., silicon wafer bonding, leading to fabrication of three-dimensional Si devices [4].

In order to evaluate the water wettability, the water contact angle (WCA) has been frequently measured, which can concisely examine the degree of cleanliness, H-termination or oxidation of a silicon surface in the wet processes [5,6]. The WCA is a measure involving free energies at interfaces through the Young equation as below [7],

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (1)$$

where γ_{SV} is the interfacial free energy between a solid and a vapor, γ_{SL} is the interfacial free energy between the solid and a liquid, γ_{LV} is the interfacial free energy between the liquid and the vapor, and θ is the WCA of a water droplet on the solid. The surface reactivity, such as hydrogenation or hydroxylation, responsible for

achievements in the processes can be estimated from the WCA.

Meanwhile, a large number of studies have been reported on individual water molecules adsorbed on well-defined silicon surfaces using cutting-edge analytical methods in surface science [8-10]. To our knowledge, however, the WCA measurement has not been applied to the well-defined silicon surfaces prepared by ultrahigh vacuum (UHV) techniques, possibly because of incompatibility between water droplets and UHV environments. From a viewpoint of basic science, it is interesting to reveal behaviors of water droplets on the well-defined silicon surfaces prepared in UHV. This possibly leads us to building a bridge between basic surface science and applied surface science aiming at characterization and control of atmospheric-conditioned surfaces [11].

In the present study we prepare three types of Si(111) and (001) surfaces in a UHV chamber and measure WCAs on the surfaces in nitrogen (N_2) gas atmosphere without exposing them to air. The surfaces are cleaned and reconstructed, and subsequently H-terminated or oxidized in well-controlled manners in the UHV chamber; the surfaces are characterized by Auger electron spectroscopy (AES) and atomic force microscopy (AFM). To quantitatively evaluate low values of WCAs on super-hydrophilic silicon surfaces, an optical interference fringe method is used. The reactivity of these Si surfaces is discussed in terms of chemical group termination responsible for water wettability.

2. Experimental

Rectangular pieces cut from Si(111) and (001) wafers (P doped with a resistivity of 0.4-0.9 Ω cm and 8-12 Ω cm, respectively, Shin-Etsu Chemical Co., Ltd.) were used for

samples, cleaned in an ultrasonic bath with acetone and in an ozone cleaner (NL-UV253, Nippon Laser & Electronics Lab) to remove particles and organic contaminants on their surfaces. Subsequently, the sample was set onto a tantalum sample holder and quickly transferred to a UHV chamber with a base pressure of the order of 10^{-11} Torr and heated at about 500 °C for degassing by passing a current into the sample. When the pressure of the chamber recovered to 10^{-11} Torr, the sample was flashed at 1200 °C while keeping the pressure better than a low of 10^{-9} Torr. Afterwards the sample was gradually cooled down to room temperature, resulting in a clean Si surface with the reconstruction of 7×7 for the (111) surface or of 2×1 for the (001) surface. The UHV chamber was combined through a gate valve with a scanning Auger electron microscope (SAM670, ULVAC-PHI) with a Schottky thermal-field emission gun with an electron beam diameter less than 45 nm at 10 kV and 10 nA, which was used to analyze the surface elemental conditions of samples. The surface topography of each sample was observed by frequency modulation atomic force microscopy (FM-AFM) (proto-type of SPM-8000FM, Shimadzu Corp.) operated in a conventional vacuum or in air.

Each cleaned Si sample was treated in three ways as follows: first, the clean sample was brought to the next examination as it was; second, the surface was terminated with atomic hydrogen (H), generated with a thermal cracker (TC50, Oxford Applied Research) with an iridium tube heated by electron bombardment at 30 W, where hydrogen gas (H_2) was admitted at a H_2 pressure of 1×10^{-8} Torr measured in the chamber, at a substrate temperature of 300 °C for 3 min; third, a clean thin oxide overlayer was formed on the cleaned surface by admitting oxygen gas (O_2) at 1×10^{-8} Torr while the sample was being heated at 600 °C for 10 min. This process forms a uniform silicon oxide layer with a thickness less than 1 nm according to refs. 12-14.

Afterwards the samples were cooled to room temperature in the UHV chamber.

After the above treatments, the sample was taken out from the UHV chamber into a plastic bag, which covered the load lock chamber connected to the UHV chamber system and was filled with pure N₂ gas to protect the surface from quick formation of contamination layers. In the N₂ gas-filled plastic bag a Milli-Q water droplet of 5 μ l purged with N₂ gas was placed on the sample surface with a micropipette, and the photos of the droplet were taken with a compact camera in the plastic bag from top and side views (static sessile drop method). The contact angles were measured on the photos by the classical $\theta/2$ method [15].

When the WCA is close to zero degrees, the measurement on the photos in the static sessile drop method is not very precise in critically assessing the super-hydrophilicity of the surface. Thus, a method utilizing optical interference fringes to evaluate the WCA close to zero degrees was examined under an optical microscope. We took the photo of the water droplet boundary on the surface using a differential interference contrast microscope (Optiphot-2, Nikon Corp.) with a digital camera. As a monochromated light source to make the interference fringes clear, we used a sodium discharge lamp of yellow light at wavelengths of the D lines (589.6 and 589.0 nm). The lamp was placed at the light entrance of the microscope instead of a conventional halogen illumination lamp. The light of the lamp entered almost perpendicularly to the light entrance of the microscope. Before the sample was transferred from the load lock to the optical microscope stage, it was immersed in Milli-Q water in a reservoir inside the N₂ gas-filled plastic bag to protect the surfaces against contaminants from laboratory air. Subsequently, the sample was retracted from the water near the optical microscope, and quickly placed on the optical microscope stage to observe the interference fringes

around a slowly drying recessive water boundary.

The water contact angle θ is calculated from the interval of interference fringes Δx using the following equation [16],

$$\theta = \tan^{-1} \frac{\lambda}{2n\Delta x} \quad (2)$$

where λ is the wavelength of the lamp (about 590 nm as a significant figure) and n is the refractive index of water (1.33).

3. Results and discussion

First, AES compositional analysis was carried out on the sample surfaces. Fig. 1 shows the AES spectra of the Si(111) and Si(001) surfaces after each sample was prepared in the UHV chamber. We found the AES peaks of Si KLL around 89 eV with small shoulders at 73 eV and at 105 eV, but no C KLL peaks around 263 eV for all samples. The AES peaks of O KLL around 503 eV were found for only the clean oxidized samples, which exhibited the change in the Si peak due to the chemical shift by the oxidation. The AES analysis indicated that the surfaces were prepared as we had expected within the detection limit of our AES analysis.

In order to examine the effectiveness of the N₂ gas-filled plastic bag to suppress the contamination and oxidation of the surfaces, we conducted the AES analysis for the samples kept in the bag; we simply transferred the samples from the UHV chamber into the N₂ gas-filled plastic bag without exposing them to air, kept them in the bag for 10 min, and returned them to the UHV chamber through the load lock. Figs. 2(a) and (b) show the AES spectra of the cleaned samples indicating no additional peak appearance after they were kept in the bag in comparison with the spectra taken just after being

cleaned. For the H-terminated and the oxidized samples, similarly we did not detect additional peaks in Figs. 2(c)-(f). This means that the surface states did not change in the procedure of only locating the sample into the N₂ gas-filled plastic bag within the detection limit of our AES analysis, that is, less than a few surface-atomic percentages.

After placing the water droplets on the surfaces in the N₂ gas-filled plastic bag, we found that the carbon and oxygen AES peaks, accompanied by the chemical shift of Si main peak from 89 eV to 73 eV, for all samples though to varying degrees, as shown in Fig. 2. In general, the water can promote the oxidation of Si through water dissociation into OH groups and H atoms on the Si surfaces as well as complicated reactions involved in Si back bonds [17,18]. In particular, the clean Si surfaces were oxidized after water droplets were placed (Figs. 2(c) and (d)). On the other hand, it is notable that, when water was dropped on the H-terminated Si surfaces, the Si peaks were not depressed much. This demonstrates the inertness of the H-terminated Si surfaces, but weak O peaks were found to be about one-third and one-seventh peak intensities of those found in the cleaned surfaces after water droplets for Si(111) and Si(001), respectively. The hydrogen atoms remained at the dangling bonds, which prevented the additional oxygen atoms from covering the surfaces. Meanwhile, the appearance of the C peaks indicated that hydrocarbons or CO₂ gas might be in the water droplets. The sensitivity of O atoms in AES analysis is about 4.7 times lower than that of C atoms and 3.9 times lower than Si atoms [19]. Thus, from the surface sensitive AES analysis, the surfaces were estimated to be about 50% covered with C atoms rather than O atoms in surface atomic percent after the water droplets were evaporated, as coffee stains condensed after water evaporation.

Figs. 3 and 4 show the photographs of water droplets on the samples taken in the N₂

gas-filled plastic bag for Si(111) and Si(001), respectively. For samples flashed to be clean, the WCA measured less than 10° for Si(111) and less than 5° for Si(001); the water droplets quickly spread out over the surfaces. For the H-terminated samples, the water droplets looked hemispherical; the contact angle measured 37° for Si(111) and 60° for Si(001). For samples thinly oxidized in O_2 gas, the water droplets spread out with the WCAs less than 5° . Although it was not easy to precisely measure the WCAs less than 5° and to compare their hydrophilicity, since the water droplets on the oxidized surfaces spread faster than those on the clean samples, the oxidized surfaces seemed to be the most hydrophilic. Meanwhile, the droplets on the H-terminated surfaces evaporated quickly compared with those on the other sample surfaces.

Fig. 5 shows the optical microscope photographs of optical interference fringes on water droplets at their boundaries between the droplets and the bare Si surfaces. The boundaries gradually retreated from right to left in Fig. 5 owing to water evaporation in air. For clean and oxidized surfaces of Si(111) and Si(001), in Figs. 5(a), (d) and in Figs. 5(c), (f), respectively, optical interference fringes were observed on the edges of water droplets. The fringe contrasts were weakened from the right to the left, and subsequently looked unclear on the left side, because the left region of droplet was out of focus in the microscope. For the H-terminated surfaces, their WCAs were so large that the droplets looked only dark with no distinct optical inference fringes (Figs. 5(b) and (e)) at the contact angle of about 37° and 60° measured from the photos in Figs. 3 and 4, respectively.

The measured intervals of fringes around their boundaries are plotted in Fig. 6. The intervals for the clean surfaces and the oxidized surfaces were almost constant, indicating that the respective slopes of water droplets were linear at their boundaries.

According to eq. (2), the WCAs were calculated to be 5.6° , 2.7° , 1.9° and 2.2° from the intervals for the clean Si(111), the clean Si(001), the oxidized Si(111), and the oxidized Si(001) surfaces, respectively. The edge line of the droplet in Fig. 5(c) was not straight, which seemed to be pinned by small protrusions on the surface. From the fluctuating interval of the fringe closest to the boundary in Fig. 5(c), the WCA was evaluated to be 1° at minimum. The interval possibly changed owing to a local surface inhomogeneity with variations of the surface free energy. This method detected the inhomogeneity on a micrometer size. Table 1 summarizes typical WCA values measured on the samples. We found that the H-terminated surfaces exhibited less hydrophilicity and the oxidized surfaces exhibited more hydrophilicity than the clean surfaces for both (111) and (001) surfaces.

Figs. 7 and 8 show FM-AFM images of the Si(111) and (001) surfaces after WCA measurements, which were exposed to air during transfer into the FM-AFM setup as well as exposed to the Milli-Q water on WCA measurements. The clean Si(111) and Si(001) surfaces appeared rough with protrusions of ~ 30 nm in height on flat areas with pits (Figs. 7(a) and 8(a)). The AES analysis showed the oxygen and carbon atoms on the surfaces after placing a water droplet on the surfaces, even before exposure to air. Since the clean Si surfaces are reactive due to the dangling bonds of Si atoms and easily reacted with covering materials, it is likely that the surface features were formed with the water. Although some protrusions possibly involved carbon atoms out of hydrocarbons or CO_2 dissolved into the water, the water molecules on the clean Si surfaces were dissociated into hydroxyl groups and hydrogen atoms, resulting in the Si and hydroxyl related aggregation with water-etched Si pits [20]. It is worth mentioning that the nanoscale roughness of the surfaces can change the water wettability with a low

WCA according to Wenzel law [21], because of the increase in apparent contact area involving hydroxyl-related protrusion with high water wettability. We computed the effective surface area from the AFM images, which was larger than its apparent area by 50-60% for the clean surface, by 10-40% for the H-terminated surfaces, and by 20-30% for the thinly oxidized surfaces, respectively. It was difficult to precisely evaluate the effective surface areas on the WCA measurements, because we observed the surfaces with the FM-AFM after the WCAs were measured; the surfaces had been covered with residual stains after the water evaporation. Even if the calculated area values were used to correct the WCA for the respective virtual flat areas using the Wenzel law, the order of hydrophilicity for the surface treatments did not change. In addition, the correction did not change much the evaluated contribution from the chemical termination per dangling bond, which will be shown later, because the surface density of dangling bond also increased with larger effective surface area.

The FM-AFM images of the H-terminated Si(111) surface exhibited bunched-step terrace structures with step heights of ~ 5 nm with smooth terraces on a nanoscale (Fig. 7(b)). While the step bunching was attributed to the miscut of the Si wafer from the (111) plane, the smooth terraces signified that the H-terminated Si surface was inert to water and air. The H-terminated Si(001) exhibited smooth flat terraces on a nanoscale without the step bunching (Fig. 8(b)), indicating the inertness to water and air [22,23]. The FM-AFM images of the oxidized Si(111) surface (Fig. 7(c)) also showed bunched-steps with terraces with slightly wandering step lines and with an increase in terrace roughness compared with the image of the H-terminated surface (Fig. 7(b)). Meanwhile, the FM-AFM image of the oxidized Si(001) surface exhibited a flat but slightly wrinkled surface (Fig. 8(c)). The roughening of their terraces was attributed to

the disordered oxide layer by inserting oxygen atoms into the Si back bonds [24].

As summarized in Table 1, the H-terminated Si surfaces showed less hydrophilicity. This tendency was also reported for Si surfaces terminated with atomic hydrogen in wet chemical processes using hydrofluoric acid with typical WCAs of about 79° on Si(111) and about 75° on Si(001) [5]. We also measured the WCAs of our Si wafers after the wet processes; the WCAs were about 80° for Si(111) and Si(001). Since the WCAs for various H-terminated Si surfaces measured about 80°, the number of hydrogen atoms terminating the surfaces was not so sensitive to the WCA. It is deduced that the interaction of H-terminated Si atoms with water molecules does not contribute to lowering the WCA, whereas the hydrogen bonding interaction of the silanol group of -Si-O-H at the surface with water molecules greatly contributes to lowering it [24]. It is likely that the WCAs on the H-terminated Si surfaces are chiefly dominated by only the dispersive van der Waals force between water droplets and the Si bulk, irrespective of the chemical interaction at the interfaces between the water and the Si surfaces.

We discuss the interfacial free energy between the water droplet and the H-terminated Si surfaces by the wet process on the basis of the number of H-terminated dangling bonds. The number of the H-terminated dangling bonds on a Si(001) surface treated in the wet processes (about 13.6 dangling bonds/nm²) is 1.7 times larger than that of a Si(111) surface on the basis of 1×1 surface structure [25]. According to eq. (1), since γ_{LV} of water is about 73 mJ/m² = 0.46 eV/nm² at 20 °C [26], the difference in the interfacial free energy between solid-water vapor and solid-water liquid of the H-terminated Si(001) surface in wet processes is given as

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta = 0.46 \times \cos 80^\circ \approx 0.08 \text{ [eV/nm}^2\text{]} \quad (3)$$

As the number of the H atoms for the Si(001)-1×1 surface structure is 13.6 /nm², the

contribution per hydrogen atom terminating the dangling bond is evaluated to be so weak as 5 meV to draw the water droplet to be wet on the H-terminated surface, even if the contribution of the dispersive interaction as the van der Waals force is ignored. The magnitude of the energy of 5 meV seems much less than that of hydrogen bonding between a water molecule and a silanol group; the typical value of hydrogen bonding in water is ~ 0.2 eV for OH^+-O^- .

Next, we turn to the H-terminated Si(001)- 2×1 surface prepared in the UHV chamber with a WCA of 60° ; this value was obviously less than 80° of the surface prepared by the wet process. It is most likely that silanol groups partially terminated the surface after placing water and contributed greatly to determining the WCA, because the contribution of the hydrogen atoms terminating the dangling bonds was negligible in regard to lowering the WCAs from the discussion in the previous paragraph. The surface was widely known to be inert with the H-termination, but it was partially reacted with water molecules by placing a water droplet [23], probably resulting in the silanol termination of the Si dangling bonds at the defect sites, including the replacement with the H-termination. Meanwhile, the oxidized Si(001) surface was estimated to be fully covered with silanol groups, and exhibited $\text{WCA} \sim 2^\circ$, in Table I. Similarly using eq. (3), we obtain $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos 2^\circ \approx 0.46 [\text{eV}/\text{nm}^2]$. If the surface density of silanol groups terminating Si dangling bonds for the oxidized surface is $13.6/\text{nm}^2$, the contribution per silanol termination is evaluated as ~ 0.034 eV in order to draw the water droplet to be wet on the surface. Accordingly, assuming that the contribution of the silanol group termination to the interfacial free energy is additive per group, since $\cos 60^\circ = 0.5$ for the WCA measured for the Si(001)- 2×1 -H surface, half of total Si dangling bonds over the surface were estimated to be terminated with the silanol

groups, in comparison to that for the oxidized Si surface fully terminated with silanol groups. Since the Si(001)-2×1-H surface has Si dimers bounded with Si-Si bonds on the surface, it is likely that the water molecules attacked the Si dimer to break their bonds, resulting in the OH-termination to the Si atoms through water dissociation as well as H-termination. After the OH-termination likely replaced the H-termination under the balance of their formation energy, followed by H₂ release through the reaction, half of the whole surface was possibly terminated with silanol groups, leading to the WCA of 60°. This is contrasted to the case of Si(001)-1×1-H by the wet process. It is noted that the siloxane structure of -Si-O-Si- where the oxygen atom looks to be inserted between the Si dimer does not contribute much to lowering the WCA [26].

Concerning the difference in the WCA between the Si(111) and (001) surfaces, the differences in the density and angle of dangling bonds to the surfaces may be essentially responsible. For instance, the dangling bond density of a Si(111)-7×7 surface and a Si(111)-1×1 surface is $\sim 1/4.5$ and $\sim 1/1.7$ of that for the Si(001)-1×1 surface, respectively, and their angle on the (111) surface is vertical, whereas the dangling bond angle on the (001) surface is slant to the surface. The angle difference may change the hydration structure of water molecules on the surface owing to steric effects, leading to the different contribution to the interfacial free energy. The WCAs of the oxidized Si(111) and (001) surfaces exhibited the similar WCA $\sim 2^\circ$, i.e., $\cos 2^\circ \sim 1$. Consequently we speculate that the energetic contribution per silanol group to lower the WCA for the (111) surface is estimated to be 1.7 times larger than that for the (001), by taking into account the difference in the dangling bond density. The difference in the energetic contribution per silanol group between the (111) and the (001) surfaces can be ascribed to the difference in the angle of their dangling bonds. **Namely, the contribution per**

silanol group terminating Si(111) is evaluated as ~ 0.059 eV by contrast with ~ 0.034 eV for Si(001). For the cleaned Si(111) and Si(001) surfaces, the difference in cosine of the WCAs was small, $\cos 5.6^\circ = 0.995$ and $\cos 2.7^\circ = 0.998$, respectively. Thus, the difference in the density of silanol groups for the cleaned Si surfaces seemed unchanged in regard to the dangling bond number per unit area of 1×1 surface structure, if the difference in the energetic contribution per silanol group persisted.

On the other hand, for the H-terminated surfaces, there was a difference, that is, $\cos 37^\circ \sim 0.8$ and $\cos 60^\circ = 0.5$, for the (111) surface and the (001) surface, respectively. We assume that the energetic contribution per silanol group is different by a factor of about 1.7, due to the difference in the angle of the dangling bonds. From equation (3) to evaluate the difference free energy, we obtain $0.46 \times \cos 37^\circ \approx 0.367$ [eV/nm²] for the H-terminated Si(111). Assuming that the contribution per silanol terminating Si(111) is evaluated as ~ 0.059 eV, we estimate the surface density of silanol groups as 6.2 [/nm²]. Since the surface density of the dangling bonds on the Si(111)- 1×1 is 7.6 [/nm²], the density ratio of the silanol groups on the H-terminated (111) surface is evaluated as ~ 0.8 . This value directly corresponds to $\cos 37^\circ \sim 0.8$, because we assume that the surface fully covered with the silanol groups shows $\cos 0^\circ = 1$ and the energetic contribution of each silanol group is additive. For the H-terminated Si(001), since $0.46 \times \cos 60^\circ / 0.034 = 6.8$ [/nm²], the coverage of silanol groups was calculated as 50% ($= 6.8 / 13.6$ (the dangling bond number per unit area)). The other dangling bonds were assumed to be terminated with H atoms, i.e., 20% (1.6 nm^{-2}) and 50% (6.8 nm^{-2}) for (111) and (001) surface, respectively. This indicates that, after placing a water droplet on them, the H-terminated Si(111)- 7×7 surface (transformed to 80% coverage of silanol groups) and the H-terminated Si(001)- 2×1 surface (to 50%, i.e., $\cos 60^\circ = 0.5$) exhibit different behaviors

of the termination with the OH groups in water. This also indicates that the water-resistive inertness of the Si surfaces terminated with atomic hydrogen and prepared for the UHV chamber is different from those prepared by wet processes. Perhaps the atomic hydrogen generated in the dry process is a rather soft scavenger compared to the H and OH ions in the wet process using a HF solution or even just water, simply terminating the dangling bonds exposed to the vacuum.

4. Summary

We prepared three types of Si(111) and (001) surfaces in the ultrahigh vacuum chamber to be cleaned and reconstructed. We subsequently H-terminated or thinly oxidized in the UHV chamber, and measured the water contact angles on their surfaces in the N₂ gas-filled plastic bag, which covered the UHV load-lock chamber without exposing the surfaces to air. The effectiveness of the bag in avoiding serious damage to the surfaces was evidenced by AES analysis. The clean and oxidized surfaces showed super-hydrophilicity with the angles less than 6°, which were precisely evaluated by the optical interference fringe method. The most super-hydrophilic surface was the oxidized Si(111) surface. The H-terminated (111) and (001) surfaces exhibited different WCAs. Based on the Young equation on the interfacial free energies, the energetic contribution of silanol group termination responsible for water wettability was estimated. We roughly explained the change in the WCA using a simplified concept on the differences of the density and angle of Si dangling bonds between the (111) and (001) surfaces. However, further study is needed to make them more evident. It is worth mentioning that measurements of WCAs on solid surfaces are simple but can provide valuable

information on chemical surface states by combining the cutting-edge methods in surface science. Consequently, we can concisely evaluate the chemical termination on the surfaces through the WCA measurements and confirm the achievement of industrial surface treatments step by step on the basis of modern surface science.

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Table 1

Summary of typical water contact angles of Si surfaces prepared in the UHV chamber.

	Clean	H-terminated	Thinly oxidized
Si(111)	5.6°	37°	1.9°
Si(001)	2.7°	60°	2.2°

Fig. 1. AES spectra of (a) a clean, an H-terminated and an oxidized Si(111) surface, and (b) a clean, an H-terminated and an oxidized Si(001) surface prepared in the UHV chamber.

Fig. 2. AES spectra of (a) a clean Si(111) surface, (b) a clean Si(001) surface, (c) an H-terminated Si(111) surface, (d) an H-terminated Si(001) surface, (e) a **thinly** oxidized Si(111) surface, and (f) a **thinly** oxidized Si(001) surface. The AES spectra after locating respective surfaces in the N₂ gas-filled plastic bag, and after placing a water droplet on respective surfaces are also shown.

Fig. 3. Photographs of water droplets on Si(111) surfaces. (a) side view and (b) top view of a clean Si(111) surface. (c) side view and (d) top view of an H-terminated Si(111) surface. (e) side view and (f) top view of a **thinly** oxidized Si(111) surface.

Fig. 4. Photographs of water droplets on Si(001) surfaces. (a) side view and (b) top view of a clean Si(001) surface. (c) side view and (d) top view of an H-terminated Si(001) surface. (e) side view and (f) top view of a **thinly** oxidized Si(001) surface.

Fig. 5. Photographs of water droplet edges with optical interference fringes under the irradiation of a Na lamp, taken by a differential interference contract microscope. Top row for Si(111): (a) a clean surface, (b) an H-terminated surface, and (c) a **thinly** oxidized surface. Bottom row for Si(001): (d) a clean, (e) an H-terminated, and (f) a **thinly** oxidized surface. The areas of respective photographs are $200 \times 300 \mu\text{m}^2$.

Fig. 6. Interval variations of optical interference fringes as a function of the order of the fringe from the boundaries between a water droplet and a bare Si surface for clean Si(111) (▲), clean Si(001) (◆), thinly oxidized Si(001) (■), and thinly oxidized Si(111) (●).

Fig. 7. FM-AFM images of Si(111) surfaces after WCA measurements on (a) a clean surface, (b) an H-terminated surface, and (c) a **thinly** oxidized surface. The images were taken after dropping water in the N₂ gas-filled plastic bag. The AFM scan areas are 200×200 nm².

Fig. 8. FM-AFM images of Si(001) surfaces after WCA measurements on (a) a clean surface, (b) an H-terminated surface, and (c) a **thinly** oxidized surface. The images were taken after dropping water in the N₂ gas-filled plastic bag. The AFM scan areas are 200×200 nm².