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Description	

Frequency modulation atomic force microscope observation of $TiO_2(110)$ surfaces in water

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Rutile titanium dioxide (TiO_2) (110) surfaces were examined in water using a frequency modulation atomic force microscope. On the surfaces cleaned by Ar^+ sputtering and annealing in ultrahigh vacuum, step-terrace structure was observed. The inlets at the steps and the pits on the terraces indicated erosion of the surface in water. Strings extended to the [001] direction were occasionally observed in the topography images and assigned to the clusters of the H_2O molecules. The tip experienced a repulsive force when the vertical tip position of z was less than 6 nm from the surface, and the force oscillated at z at less than 2 nm. The repulsive force originated from the disruption of the hydrogen bonding network of H_2O molecules formed on the hydrophilic sputter-annealed surface. The oscillatory force arose from structural alternate order-disorder transitions of the H_2O molecules at the gap between the tip and the TiO_2 surfaces. On the TiO_2 surface annealed in air, no strings were observed in the topography images. The tip experienced an attractive force before experiencing a repulsive force in its approach to the surface. Oscillatory behavior was not observed in the force curve. The air-annealed TiO_2 and tip surfaces were both hydrophobic and attracted to each other to expel the H_2O molecules from their gap. Ordering the H_2O molecules at the gap between the two hydrophobic surfaces was entropically unfavorable. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3294707]

I. INTRODUCTION

Titanium dioxide (TiO_2) has a variety of industrial applications including gas sensors,[1] photocatalysts,[2] catalyst supports,[3] photoelectrodes,[4] and biocompatible materials.[5] Clarifying the origins of such industrially important properties has been the motivation for the extensive studies of TiO_2. Surface science studies in ultrahigh vacuum (UHV) employing well-defined single crystal surfaces have provided a great deal of nanoscale information on the TiO_2 surfaces.[6]

Analysis in liquid would further develop the understanding of the useful surface properties of TiO_2. Under ambient reaction conditions, the surfaces of TiO_2-based catalyst are covered by H_2O, and therefore the catalysts are essential in an aqueous medium.[7,8] The aggregation process of dye molecules in a solution is expected to be key in governing the performance of the dye-sensitized TiO_2 photoelectrode and is under investigation.[9,10] The electric double layer, which affects reaction kinetics at the solid-liquid interface, would be sensitive to the adsorbates from the liquid.[11]

In the present study, rutile $TiO_2(110)$ surfaces were examined in water using an atomic force microscope with a frequency modulation detection method (FM-AFM). Hiasa *et al.*[12] reported a pioneering FM-AFM study of the $TiO_2(110)$ surface in liquid, in which the surface was annealed in air and examined in a KCl solution. We employed the $TiO_2(110)$ surfaces cleaned in UHV by Ar^+ sputtering and annealing as well as the surfaces annealed in air, and we attempted FM-AFM analysis in pure water for the future research of water photolysis. The results indicated that a network of H_2O molecules by hydrogen bonding was present on the sputter-annealed surface.

The $TiO_2(110)$ surface is a prototypical system for the UHV surface science studies of TiO_2. Scanning tunneling microscope (STM) observation in UHV revealed that the sputter-annealed (110) surface consists of atomically flat terraces separated by steps with a height of 0.32 nm (single height steps), and that the terraces exhibit a nonreconstructed (1×1) structure.[13] A model of the $TiO_2(110)$-(1×1) surface is shown in Fig. 1. The topmost O atoms are bound to two sixfold-coordinated Ti atoms in a bridging coordination (bridge O atoms) and form rows along the [001] direction. Between the bridge O atom rows, Ti atoms coordinated to five O atoms (fivefold-coordinated Ti atoms) are exposed. A recent STM study showed that the (1×1) structure was retained after 10 min exposure to laboratory air.[14]

The FM-AFM employs a cantilever with a tip at its one end as a probe and detects interaction force between the tip and the sample as a change in the resonant frequency of the cantilever (Δf).[15] In UHV studies, the FM-AFM has proven to be a powerful analytical tool with an atomic scale resolution through surface imaging, atom manipulation, and force analysis. Several groups extended its application to solid-liquid interfaces and reported atomic scale surface topography using a homemade microscope with a low noise optical deflection system.[16–18] In this experiment, a commercial intermittent contact mode AFM was operated as the FM-AFM using a phase locked loop (PLL) system.

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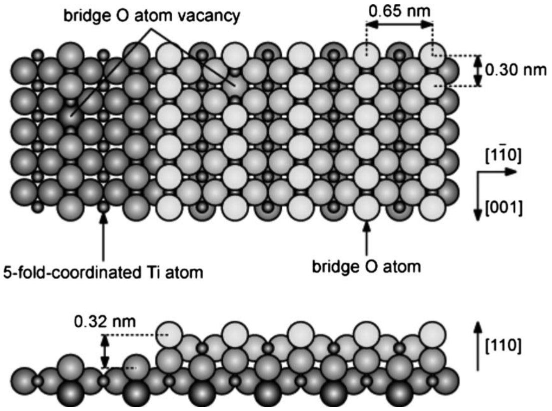

FIG. 1. Ball model of the $TiO_2(110)$-(1×1) surface including a single height step. Small and large spheres represent Ti and O atoms, respectively. The O atoms are shaded according to their depth.

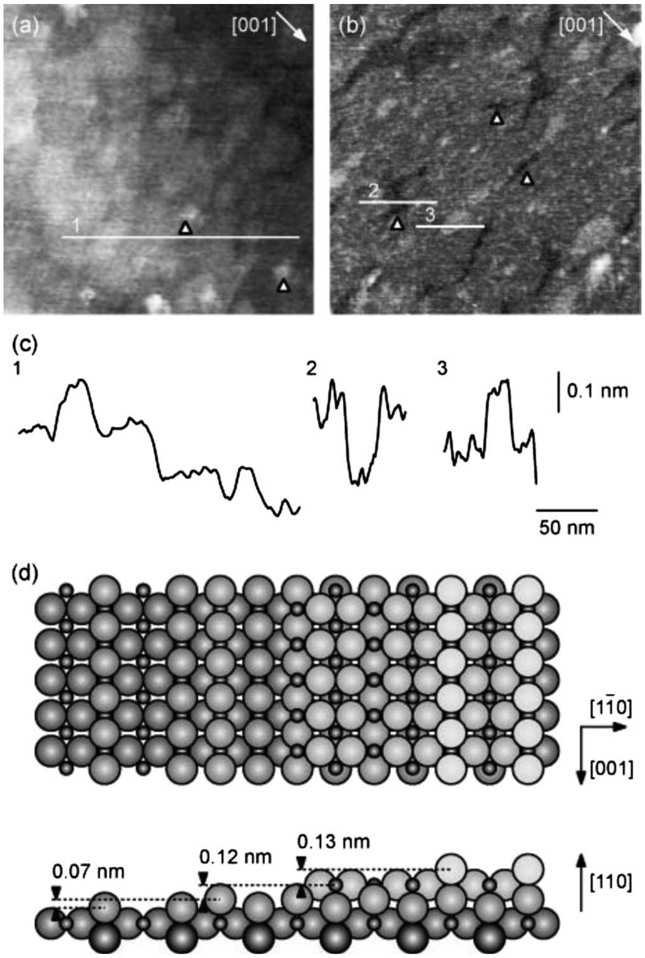

FIG. 2. [(a) and (b)] Constant frequency shift topography of the sputter-annealed $TiO_2(110)$ surfaces in water (300×300 nm^2). Peak-to-peak amplitude of cantilever oscillation ($A_{\text{p-p}}$)=4 nm. (a) Frequency shift (Δf)=+440 Hz. (b) Δf=+192 Hz. (c) Cross sections along the solid lines in the images. (d) A ball model of the $TiO_2(110)$ surface including different surface termination layers. Small and large spheres represent Ti and O atoms, respectively.

II. EXPERIMENT

The experiments were performed using a multipurpose scanning probe microscope (5500 AFM/SPM, Agilent Technologies) with no modification in the optical deflection system. The microscope stage was placed in a glass chamber filled with an Ar gas at room temperature, and the entire microscope setup was in a shaded vibration-isolation box. The microscope was operated with the software in an intermittent contact mode with a magnetic amplitude control (MAC). Silicon cantilevers with their back side coated with a paramagnetic film (MAC-lever type I, Agilent Technologies) were used as a probe with no additional treatment. The resonant frequency of the cantilever was ~150 kHz in air and was reduced to ~70 kHz in water. The Q-factor in water was ~70. The factory-determined calibration of the piezoscanner was verified by observing a highly oriented pyrolytic graphite and a Ga_2O_3.[19] The cantilever oscillation was controlled by a PLL system (easy PLL plus, Nanosurf AG). The frequency shift signal from the PLL system was fed into the input of the microscope controller in place of an amplitude signal for the intermittent contact mode. The topography was obtained with the feedback control of a constant frequency shift under constant amplitude of the cantilever oscillation. The oscillation amplitude was estimated from the dependence of the tip-sample separation on the voltage applied to the piezoelectric oscillator. The image contrast did not depend on the sample bias voltage between −2.0 and +2.0 V, and the sample bias voltage was set to 0 V. The images were presented without filtering, and the cross sections were measured on the images smoothed by a nine-point median filter.

The $TiO_2(110)$ surface (Shinko-sha) was cleaned in an UHV chamber with a base pressure of 10^{-7} Pa by repeated cycles of Ar^+ sputtering and annealing at 1100 K. A tungsten wire mesh placed behind the TiO_2 wafer was used as a resistive heater. After being cooled to room temperature, the wafer was transported in laboratory air to the liquid cell of the microscope, and the cell was filled with Ar-purged Milli-Q water. The pollution of the liquid cell stored in Milli-Q water was checked by the cyclic voltammetry of a flame-annealed Au film in 0.1M sulfuric acid. No peak attributed to the redox reactions of the adsorbates was observed in the voltage range between −0.5 and +1.0 V versus in the quasireference electrode of Au wire. In order to anneal the TiO_2 surface in air, a PID-controlled electric furnace was used. The TiO_2 wafer was placed in a quartz case and was heated at 1273 K for 24 h.

Water was spread over the sputter-annealed surface set in the liquid cell, while a dome-shaped droplet formed on the air-annealed surface. The sputter-annealed surface was hydrophilic, and the air-annealed surface was more hydrophobic than the sputter-annealed surface.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the constant frequency shift topography of different areas of the sputter-annealed TiO_2 surface. The surface consisted of terraces separated by steps with many inlets, as shown in Fig. 2(a). The steps had a height of ~0.1 nm, as shown in cross section 1 in Fig. 2(c), and were lower than the single height step of the (1×1) surface. The bright particles with heights of 0.2–0.3 nm, which are indicated by the arrowheads in Fig. 2(a), would be either TiO_x species or unidentified contaminants. The arrowheads in Fig. 2(b) indicate the pits on the terraces. The depth of the pits was ~0.1 nm, as shown in cross section 2 in Fig. 2(c).

The inlets and the pits indicated that the surface was eroded in water. Unfortunately, time-lapse imaging of the creation of the inlets and the pits in the identical region was not attained. Uetsuka *et al.*[20] reported in their UHV-STM study that the number density of the pits and the inlets increased on the $TiO_2(110)$-(1×1) surface 5 min after immersion in distilled water and concluded that the surface was eroded. The resurfacing promoted by diffusion of hydroxylated Ti atoms and the stabilization of crystallographic planes which were different from those of the (110) plane by adsorbed H_2O molecules were proposed as the source for the erosion process. The heights of the steps and the depths of the inlets in our FM-AFM study were inconsistent with those of the UHV-STM study where the heights of the steps were ~0.3 nm and the depths of the pits were integral multiples of 0.3 nm.[20] The images shown in Figs. 2(a) and 2(b) were obtained 3 h after immersion in water, and the surface erosion should have been more advanced. The step height of ~0.1 nm suggested that the surface was terminated by layers different from those of the (1×1) surface. The model of the surface including geometrically possible termination layers is shown in Fig. 2(d), where Ti atoms and O atoms were simply removed layer-by-layer from the (1×1) surface. A part of the bridge O atoms should have been removed to maintain the surface stoichiometry. The height differences between the terminations were approximately 0.1 nm. Such termination layers might have been stabilized by adsorbates such as H_2O molecules, hydroxyl groups, and hydroxylated Ti atoms.

Figure 3(a) shows the constant frequency shift topography in which strings extending to the [001] direction were observed with the step-terrace structure. Such strings were occasionally observed on the sputter-annealed surface. Figures 3(b) and 3(c) are a close up view of the surface and the cross sections obtained in the image, respectively. Strings with lengths of 20–50 nm were aligned with a separation of ~9 nm to the $[1\bar{1}0]$ direction. The strings were composed of particles which protruded 0.2–0.4 nm from the surface. The particles were partially arranged with a period of 5.9 nm to the [001] direction. The morphological change in the strings was not confirmed during imaging. Figure 3(d) shows the strings observed in a narrower scan area on another sputter-annealed surface. The strings were directed to the [001] direction, and the string-to-string distance in the $[1\bar{1}0]$ direction was ~2 nm, as shown in cross section 1 in Fig. 3(e). In a part of the image, dimmed rows directed to the [001] direction with an interval of 0.6 nm were observed as indicated by the arrowheads in the image. The cross section 2 in Fig. 3(e) shows that the string was partially corrugated with a periodicity of 1.5 nm to the [001] direction.

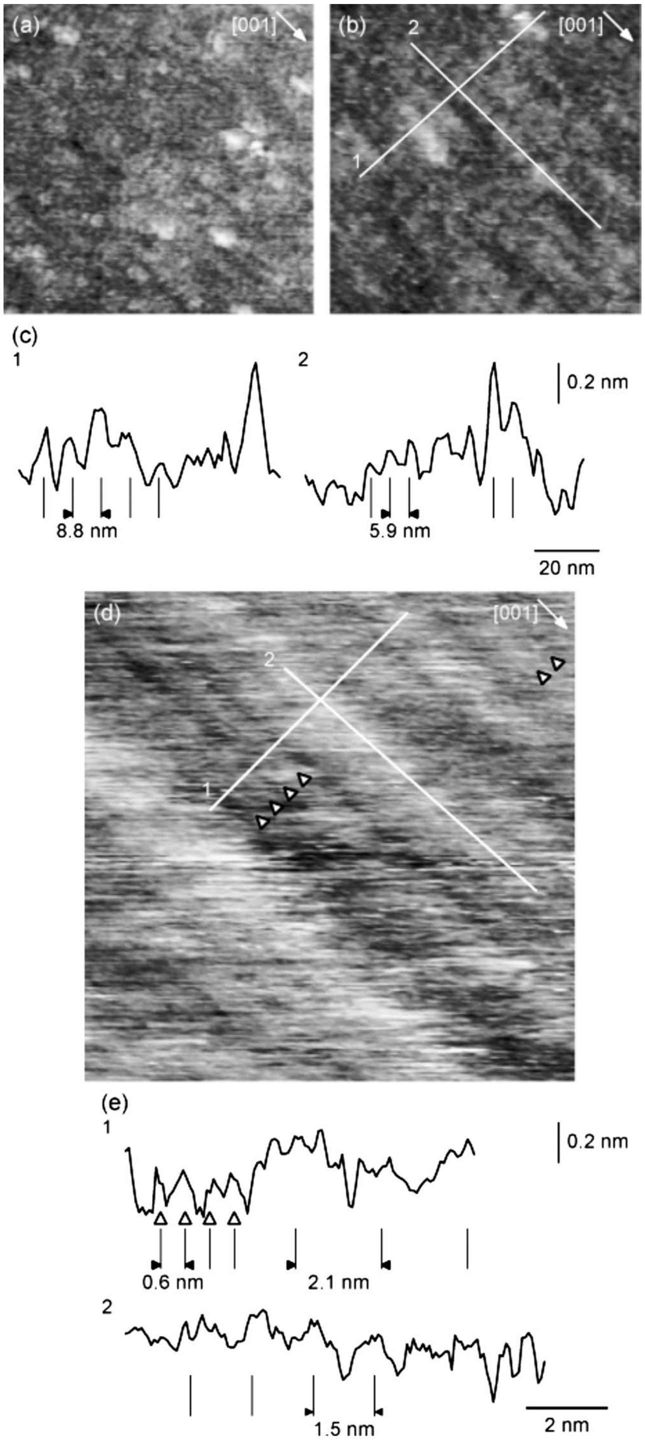

FIG. 3. Constant frequency shift topography of the sputter-annealed $TiO_2(110)$ surfaces in water and cross sections in the images. (a) Scan area=300×300 nm^2, Δf=+264 Hz, and $A_{p\text{-}p}$=4 nm. (b) Scan area=100 $\times$100 nm^2, Δf=+264 Hz, and $A_{p\text{-}p}$=4 nm. (c) Cross sections along the solid lines in Fig. 2(b). (d) Scan area=15×15 nm^2, Δf=+150 Hz, and $A_{p\text{-}p}$=2 nm. (e) Cross sections along the solid lines in Fig. 2(d).

A possible assignment of the strings is composed of clusters of H_2O molecules formed around the H_2O molecules bound to the TiO_2 surface. H_2O molecules bond to the top of the fivefold-coordinated Ti atoms through the O atom with the O–H bonds pointing away from the surface.[21] The H_2O

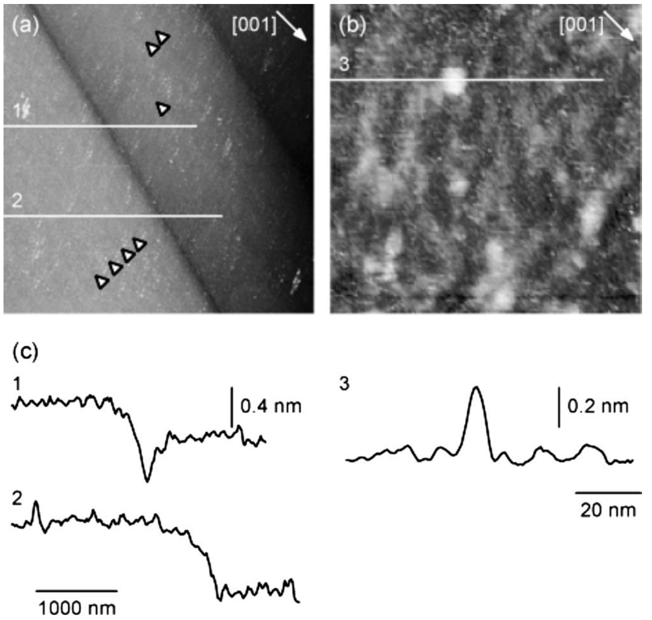

FIG. 4. Constant frequency shift topography of the air-annealed $TiO_2(110)$ surface in water. (a) $5000 \times 5000\ nm^2$, $\Delta f = +354$ Hz, $V_s = 0$ V, and $A_{p-p} = 4$ nm. (b) $200 \times 200\ nm^2$, $\Delta f = +354$ Hz, $V_s = 0$ V, and $A_{p-p} = 4$ nm.

molecules adsorbed on the Ti atoms were observed as strings directed to the [001] direction in low-temperature STM images.[22] Surface hydroxyl groups formed on the bridge O atoms[23] might have contributed to the formation of the clusters. Unidentified products in the erosion such as Ti hydroxide are also candidates forming the strings. Quantitative analysis of the number density of the strings in relation to the growth of the inlets and pits is a future subject for examination of the contribution of the erosion products. The rows aligned with the separation of 0.6 nm are possibly the bridge O atom rows which are observed as bright rows in the UHV-FM-AFM images.[24]

Figure 4 shows the constant frequency shift topography of the $TiO_2(110)$ surface annealed in air. The surface shows a step-terrace structure. The direction of the steps was shifted from the [001] direction by 13.1° and was almost along the $[1\bar{1}9]$ direction, and the step-to-step distance was more than 2000 nm, as shown in Fig. 4(a). The height of the step fluctuated between 0.3 and 0.6 nm, depending on the measurement point, as shown in the cross sections in Fig. 4(c). On some terraces, fringes with a height of less than 0.1 nm directed to the [001] direction were observed as indicated by the arrowheads. As shown in Fig. 4(b), the terrace showed a corrugation with a height of ~ 0.1 nm with the unidentified particles with a height of ~ 0.3 nm. No inlets at the steps nor pits on the terraces were observed, and the surface topography did not change during imaging for 2 h. There were no strings observed on the sputter-annealed surface.

When annealed in oxidative atmosphere, the stoichiometry of the TiO_2 surface is maintained, and the surface would be terminated mostly by O atoms. The insolubility of the air-annealed surface is possibly due to the limited number of surface Ti atoms which form hydroxides in water. The uniform surface stoichiometry is expected to result in the site-independent interaction between the tip and the surface. Therefore, the topography image is likely to reflect the true morphology of the surface. As far as we know, the formation of the multiheight steps on the $TiO_2(110)$ surface has not been reported. Hiasa *et al.*[12] found that the height of the step on the air-annealed surface was equivalent to that of single height step. The direction of the steps in Fig. 4(a) differed from the preferential direction of the steps on the (1×1) surface in the $\langle 001 \rangle$ and $\langle 1\bar{1}1 \rangle$ directions.[25] No fringes on the terraces were identified based on the analogy of other research results. The unreported features of the air-annealed surface might be related to the surface segregation and oxidation of Ti interstitials.[26]

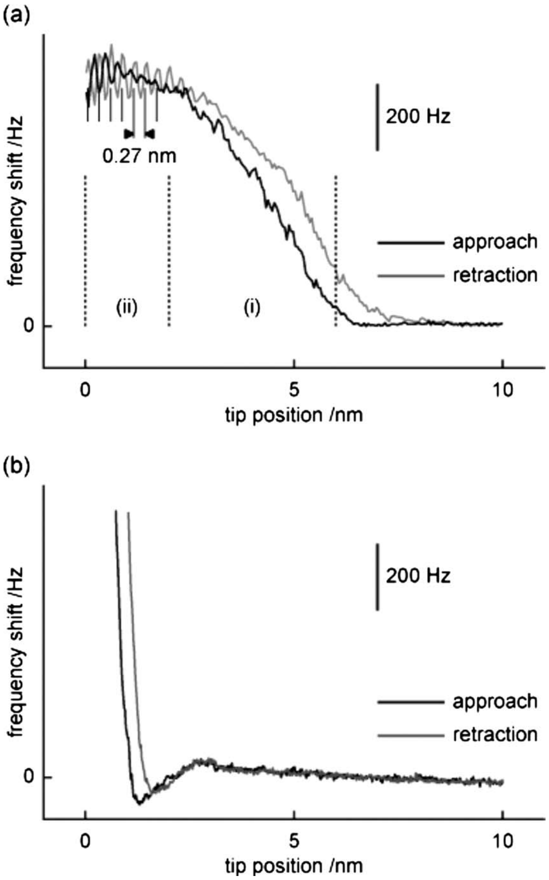

FIG. 5. Frequency shift as a function of the vertical position of the tip on (a) the sputter-annealed and (b) the air-annealed $TiO_2(110)$ surfaces. The separation values of the sampling position were 0.05 and 0.02 nm for (a) and (b), respectively, with a sampling time of 5×10^{-4} s.

Figure 5 shows the Δf curves with respect to the vertical tip position of z. The zero of z was set at the position where the amplitude of the cantilever oscillation started to decrease. At $z = 0$, the tip end possibly touches the TiO_2 surfaces at the oscillation peak. The positive shift of the Δf is caused by a repulsive force between the tip and the sample, and the negative shift of the Δf is caused by an attractive force. As shown in Fig. 5(a), the tip started to experience a repulsive force at $z = 6$ nm when approaching the sputter-annealed surface. The repulsive force increased with the reduction in z in region (i), and the increment in the repulsive force became gradual. Several peaks irregularly appeared in the curve. When z was reduced to 2 nm, the force started to oscillate with respect to z, as shown in region (ii). The force oscillation peaks appeared with an interval of 0.27 nm. In the tip retraction process, the force oscillation continued up to $z=3$ nm. The repulsive force was diminished with an increase in z and was not detected at z larger than 7 nm. When the tip approached the air-annealed surface, it experienced a repulsive force which gently increased with the tip approaching, as shown in Fig. 5(b). The repulsive force started to decrease at $z=2$ nm, and the tip experienced an attractive force at $z=1$ nm. An additional approach of the tip resulted in a steep increase in the repulsive force. No irregular peaks nor force oscillation was detected in the curve.

The repulsive force in region (i) on the sputter-annealed surface is attributed to the disruption of the network of the H_2O molecules by hydrogen bonding. The H_2O molecules bound to the surface Ti atoms are expected to promote the hydrogen bonding network of the H_2O molecules. On the mica surface, the effective range of the repulsive force due to the disruption of the network of the H_2O molecules reached 5 nm from the surface.[27] The reduced increment in the repulsive force with z might have been due to an extension of the tip-sample distance caused by the structural deformation of the tip and TiO_2 surfaces by the increased repulsive force. The irregularly appeared peaks indicated partially rigid bonding of the H_2O molecules. The force oscillation in region (ii) originated from structural alternate order-disorder transitions of the H_2O molecules at the gap between the tip and TiO_2 surfaces. When liquid molecules are condensed at a molecular-size gap between two surfaces which are approaching each other in liquid, the surfaces experience an oscillatory force with a periodicity of the diameter of the molecule with respect to the gap distance.[27] The surfaces experience the strongest repulsive force when the liquid molecules are most closely packed at the gaps of the integral multiples of the molecular size. The repulsive force is reduced when the density of the molecules is decreased at the gaps of the nonintegral multiples of the molecular size. The peak-to-peak interval of 0.27 nm shown in Fig. 5(a) was comparable to that of the size of the H_2O molecule. Disagreement of the retraction curve with the approach curve was due to the nonlinearity of the piezoscanner. In our measurements, the retraction curve was shifted to a larger z region by 0.3–1.0 nm, depending on the sweep distance and the sweep speed. When the retraction curve shown in Fig. 5(a) was shifted to a smaller z region by 0.7 nm, the slope of the curve and the phase of the oscillation agreed with those in the approach curve. The cause of the increment in the oscillation amplitude in the tip retraction process was unclear.

The long-range repulsive force that the tip experienced on the air-annealed surface seemed to have originated from the overlapping of the electrostatic double layers on the tip and air-annealed surface. The attractive force arose from the hydrophobicity of the air-annealed surface. The tip surface is expected to be hydrophobic due to organic contaminants from laboratory air. When two hydrophobic surfaces approach each other at a distance of several nanometers in water, they receive an attractive force.[27] Forming the hydrogen bonding network of H_2O molecules at the gap between two hydrophobic surfaces is entropically unfavorable, and therefore the two surfaces are attracted, and thus the H_2O molecules are expelled from the gap. The expelling of the H_2O molecules would have reduced the order-disorder transitions at the gap and resulted in the absence of the oscillatory behavior in the force curve.

IV. CONCLUSION

The FM-AFM observation in water showed that the sputter-annealed $TiO_2(110)$ surface was eroded and that the air-annealed $TiO_2(110)$ surface was not. On the sputter-annealed surface, particles that were arranged reflecting the anisotropy of the atomistic surface structures were observed. The Δf versus vertical tip position curve indicated the existence of the hydrogen bonding network of H_2O molecules on the sputter-annealed surface. The oscillatory behavior in the curve was attributed to structural alternate order-disorder transitions of the H_2O molecules at the gap between the tip and the TiO_2 surfaces. The results suggest that the sputter-annealed $TiO_2(110)$ surface exhibited atomically well-defined structures in water and has a potential to be a good platform for FM-AFM studies.

ACKNOWLEDGMENT

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