

Photoinduced surface roughness variation in polycrystalline TiO₂ thin films under different atmospheres

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Abstract

For this study, we evaluated photoinduced surface roughness variation of polycrystalline anatase thin films under different atmospheres using atomic force microscopy (AFM). A TiO₂ thin film with large grains was prepared using the sol–gel process and vacuum ultraviolet (VUV) irradiation before firing. Upon UV illumination, the surface image became blurred with an apparent surface roughness increase in ambient air. The appearance of this image change was delayed in dry air, and was not observed in dry nitrogen. These results imply that this photoinduced surface change is related to water adsorption from the atmosphere.

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1. Introduction

Titanium dioxide (TiO₂) is a well-known photocatalyst material. Electron and hole pairs are generated when ultraviolet (UV) is illuminated onto TiO₂. They reduce and oxidize adsorbates on the surface, respectively, thereby producing radical species. These radicals can decompose most organic compounds. Many studies have examined application of TiO₂ to water and air purification [1–3]. Aside from these conventional applications, the photoinduced hydrophilicity of a TiO₂ photocatalyst was discovered in 1995 [4,5]. A highly hydrophilic surface is generated when UV is irradiated onto the surface of TiO₂. This surface exhibits both antifogging and self-cleaning properties. A polycrystalline TiO₂ film coating has been applied on various industrial items such as automobile side mirrors and exterior tiles using this property [6–8].

Very recently, we reported photoinduced surface roughness variation in transparent anatase polycrystalline thin films with large grains (–200 nm) using tapping mode atomic force

microscopy (AFM) with a Si cantilever [9]. Films were subjected to a vacuum ultraviolet (VUV) pretreatment before heating at 500 °C. After recording the initial surface structure and roughness, UV illumination (0.7 mW/cm²) was performed for 150 s using a Hg–Xe lamp with an optical-fiber coupler. Then, the surface structure and roughness were recorded 13 times successively, without additional UV illumination. Upon UV illumination, the surface image became blurred with an apparent increased surface roughness. This structural change gradually terminated and the scanning image returned to its initial state after stopping UV illumination. The microstructural change corresponded mainly to hydrophilic to hydrophobic conversion, and was remarkable at the grain boundary. Because the change was recorded mainly after stopping UV illumination, the effect of electron transfer from excited Si to TiO₂ by the initial UV illumination on this phenomenon was negligible; this behavior is attributable to continuous change of the distance between the film surface and cantilever.

For this study, we measured this behavior with illuminating UV under various atmospheres (ambient air, dry air and dry nitrogen) to investigate whether the change appears in the photoinduced hydrophilicizing process and to clarify the influence of water concentration in this structural change.

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2. Experimental

Film processing procedure followed the process used in previous works [9–11]. Reagent-grade titanium isopropoxide ($\text{Ti}(\text{OCH}_2\text{CH}_2)_4$; Kanto Chemical Co. Inc., Tokyo, Japan) was mixed with a commercial titanium isopropoxide solution (NDH-510C; Nippon Soda Co. Ltd., Tokyo, Japan) (mixing ratio = 6.1:40 ml). After stirring for 15 min in air, the mixed solution was hydrolyzed by adding a drop of nitric acid solution (1.44 ml, pH 1; Wako Pure Chemical Industries Ltd., Tokyo, Japan) while stirring at room temperature to form a coating solution. The amount of water for hydrolysis was a four-fold molar excess of the titanium concentration in the mixed alkoxide. The hydrolyzed solution was then coated onto a Si(100) wafer (Aki Corp., Miyagi, Japan) using dip-coating at a fixed pulling rate of 0.5 mm/s in dry air. After coating, the film was exposed to dry ozone for 1 h to remove organic compounds in the coated film. Then, the film was illuminated by vacuum ultraviolet light using a Xe excimer lamp (wavelength 172 nm; Ushio Inc., Tokyo, Japan) for 30 min at room temperature in N_2 atmosphere. The illumination intensity of the VUV light in N_2 was 18 mW/cm^2 . The film was fired at 500°C for 1 h in air after VUV illumination.

Water wettability conversion of the film by UV illumination was examined in air using the sessile drop method with a commercial contact angle meter (CA-X, Kyowa Interface Science Co. Ltd., Saitama, Japan). The droplet size used for the measurements was $1 \mu\text{l}$. The experimental accuracy of the measurement of one point was 1° . The standard deviation values of the contact angle in the film are within $3\text{--}4^\circ$. Using a fluorescent black-light bulb with UV intensity of 0.7 mW/cm^2 , UV illumination was carried out. The remaining carbon concentration in the film was evaluated using X-ray photoelectron spectroscopy (XPS, 5500MC; Perkin-Elmer Physical Electronics, Eden Prairie, MN) with Ar^+ etching. For that purpose, $\text{Mg K}\alpha$ radiation was used; the photoelectrons were collected at a takeoff angle of 45° with respect to the film-surface-fixed molybdenum holder.

The film was then set on the stage of the AFM (JSPM-5200; JEOL, Tokyo, Japan). A BK7 glass cover was set on the film to control the sample chamber atmosphere (volume ca. 1.4 l). The initial surface structure and roughness were evaluated with tapping mode AFM using a Si cantilever in the $500 \text{ nm} \times 500 \text{ nm}$ region. The AFM measurement was performed in ambient air, dry air and dry nitrogen. Under the ambient air condition, AFM measurement was carried out without introducing any gas while illuminating UV on the film surface over the glass cover, as shown in Fig. 1. Then, UV (0.7 mW/cm^2) was illuminated using a Hg–Xe lamp with an optical-fiber coupler. The surface structure and roughness were recorded 9 to 10 times sequentially during UV illumination. Each measurement required about 7 min for recording. Consequently, the overall measurement period was about 65 min. Alternatively, under the dry gas condition, dry air (H_2O content about 0.5 ppm; Taiyo Nippon Sanso Corp., Tokyo, Japan) or dry nitrogen (H_2O content about 7 ppm; Toho Sanso Co. Ltd., Kanagawa, Japan) was flowed into the sample chamber for 60 min (the flow rate; 4.8 l/min) after evacuating the sample chamber for 40 min. Then, AFM measurement was

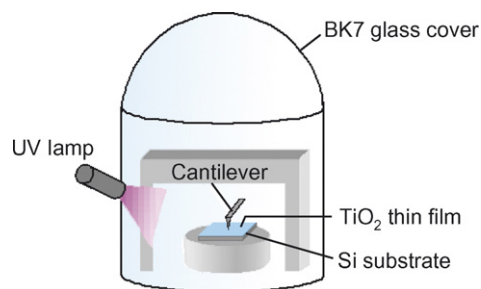


Fig. 1. Schematic illustration of the AFM measurement during UV illumination.

carried out with flowing dry gas in the same way as that in ambient air. The contact angles of water on the film before and after the AFM measurement were also measured. Because the contact angle was measured in ambient air, the surface state of the dry air sample and dry nitrogen sample might have been altered by the adsorption of atmospheric water and organic compounds. Therefore, we measured the contact angle of these samples only before and after UV illumination.

3. Results and discussion

The polycrystalline TiO_2 thin film prepared using the process described above was composed solely of anatase with random crystallite orientation. The grain size and average surface roughness were, respectively, around 200 and 0.40 nm; XPS analysis with Ar^+ etching revealed that the remaining carbon concentration in the film was negligible. Fig. 2 shows the time-dependence of the water contact angle on the film under 0.7 mW/cm^2 UV illumination. The film exhibited photoinduced hydrophilicity, and its water contact angle became about 10° after 30 min UV illumination.

Fig. 3 shows the average surface roughness measured for each AFM image during 0.7 mW/cm^2 UV illumination in ambient air. Some sequentially recorded AFM images are also shown; the upper x -axis of the figure indicates the UV illumination time. The surface roughness was maintained at about 0.40 nm for the first 15 min. Then the image was blurred with a sudden increase of apparent surface roughness. The apparent surface roughness

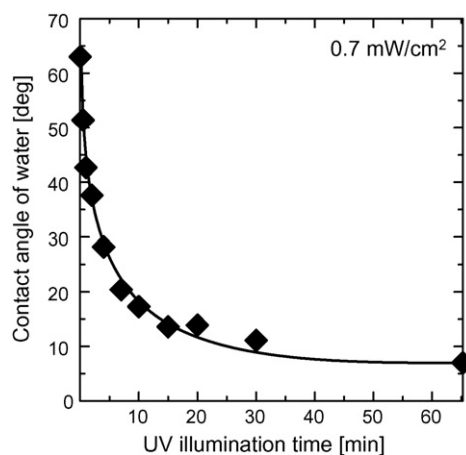


Fig. 2. Contact angle change of water on the film under UV illumination.

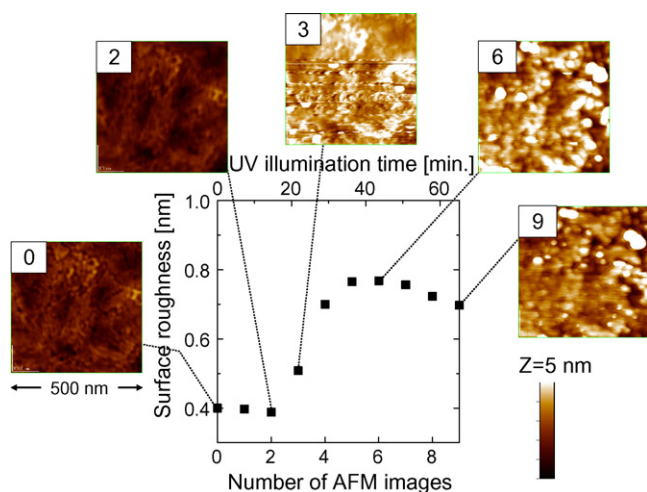


Fig. 3. Average surface roughness measured for each AFM image under 0.7 mW/cm^2 UV illumination in ambient air, and some recorded AFM images.

reached 0.77 nm after it was recorded six times. Then it began to decrease gradually. These changes were not observed when the same experiment was carried out on a Si substrate. These results indicate that the photoinduced surface roughness variation occurs even in the photoinduced hydrophilicizing process. The initial 15 min will be the time required for decomposition of organic substances that are adsorbed on the film surface. We believe that surface roughness values obtained from these experiments are apparent and not absolute ones because a proper distance between cantilever and sample surface are not attained. The change of surface roughness in this study merely indicates a trend.

Fig. 4 shows the result of the same experiment carried out in dry air. The surface roughness was almost constant from the initial image to the eighth one in dry air. Then, the image began to blur with increasing apparent surface roughness as in ambient air. Various studies have suggested that the adsorption of water molecules is enhanced on the surface of TiO_2 under UV illumination [5,12–16]. The result obtained in the present study suggests that the surface roughness change is related to water

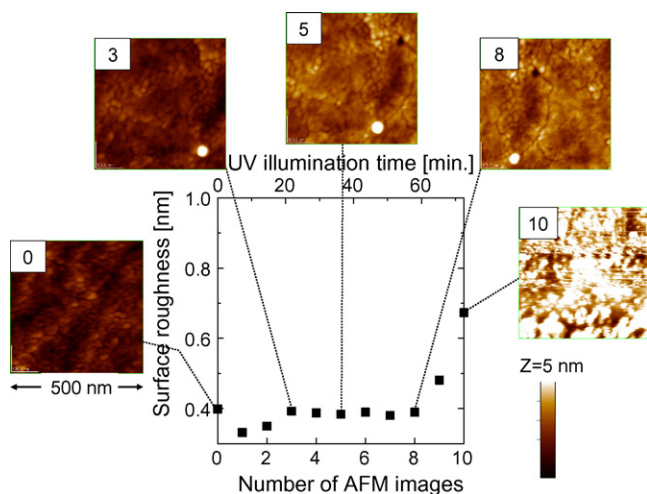


Fig. 4. Average surface roughness measured for each AFM image during 0.7 mW/cm^2 UV illumination in dry air, and some recorded AFM images.

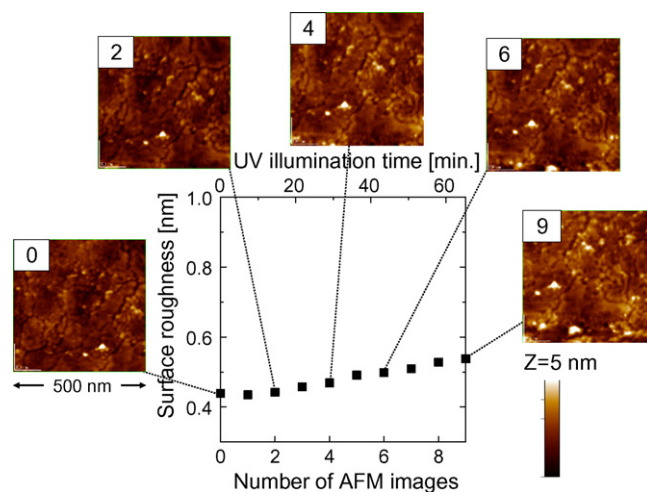


Fig. 5. Average surface roughness measured for each AFM image during 0.7 mW/cm^2 UV illumination in dry nitrogen, and some recorded AFM images.

adsorption from air atmosphere. This change occurs even in the existence of parts-per-million-order water content.

Fig. 5 shows the result of the same experiment carried out in dry nitrogen. The surface roughness was almost constant in dry nitrogen and the image was clear even after recording nine times, although the water concentration was about 10 times higher than that of dry air. This result implies that oxygen in air is also related to surface roughness variation. The slight roughness change will occur because of the drift of the image for each measurement.

The reproducibility of these phenomena was confirmed more than five times, but the degree of these phenomena depends on the observation point at each experiment. Figs. 3–5 show representative results. The contact angles of water on the film before and after the AFM measurement in ambient air, dry air and dry nitrogen are listed in Table 1. The contact angle change was different, even though the total UV illumination time was identical. After AFM measurements in ambient air and dry air, the contact angle decreased, respectively, to less than 10° and to about 20° . Under the dry nitrogen condition, the contact angle did not decrease after the AFM measurement. Photocatalytic oxidation is caused by radical species such as OH radicals and O_2^- . They are produced by the reduction and oxidation of adsorbed oxygen and water on the TiO_2 surface by the photo-generated electrons and hole pairs. Under the dry nitrogen condition, the photo-generated electrons have difficulty reducing nitrogen because of the high reduction potential of nitrogen [17], resulting in the suppression of the oxidation because of the recombination between electrons and holes. In contrast, under the ambient air and dry air conditions, oxidation will occur because electrons can transfer

Table 1

Contact angles of water on the film before and after the AFM measurements in ambient air, dry air and dry nitrogen

Atmosphere	Contact angle ($^\circ$)	
	Before AFM measurement	After AFM measurement
Ambient air	68	7
Dry air	66	20
Dry nitrogen	64	68

to oxygen. Therefore, photocatalytic oxidation of the hydrocarbons adsorbed on the surface and subsequent adsorption of water molecules on the surface advances.

The AFM image in dry air (Fig. 4) was blurred when its contact angle was about 20°. In contrast, that in ambient air (Fig. 3) was not blurred even though its contact angle was about 20° (after 7–14 min UV illumination, Fig. 2). Although both surfaces exhibit almost equal water contact angles, it does not mean that the surface state of TiO₂ under UV illumination is the same for these two. The amount of water adsorption is small on the TiO₂ surface in ambient air under UV illumination at the initial two images (14 min) because the AFM image (Fig. 3) was clear. Consequently, it is deduced that a contact angle of about 20° in ambient air is mainly attributable to the decomposition of surface organic compounds [18,19]. In contrast, the surface roughness increases with the blurred AFM image (Fig. 4) under UV illumination after 70 min implies that a certain amount of water adsorbed onto the TiO₂ surface in dry air in this condition. However, adsorption of organic compounds on the surface is unavoidable for the dry air sample during the period for removing it from the dry air-filled vessel, and for subsequent procedures of contact angle measurement in ambient air. Consequently, the contact angle in the dry air sample will be affected by contamination of surface organic compounds that occurs during that period.

Results obtained in this study can be explained by inferring the removal of hydrocarbons and subsequent water adsorption. However, this study provides no information about the adsorption behavior of water to TiO₂ surface. Detailed analysis of this fact is left as a subject for future work.

As described in a previous work [9], surface roughness variation was difficult to attribute to thermal expansion. Because of the existence of symmetry center in the space group (*I4₁/amd*) of anatase, the piezoelectric effect is negligible. This phenomenon continues even after stopping UV illumination. Therefore, the possibility of the photoplastic effect reported on some inorganic semiconductors such as ZnO [20,21] or GaAs [22] is also negligible. The most plausible explanation is continuous change of the distance between the film surface and cantilever by water adsorption. Two possibilities exist as causes of this distance change. One is continuous actual roughness change by the adsorption of water molecules. Yoshida et al. investigated the dynamic hydrophobicity of ultrasMOOTH hydrophobic surfaces coated with heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane (CF₃(CF₂)₇CH₂CH₂Si(OCH₃)₃) and octadecyltrimethoxysilane (CH₃(CH₂)₁₇Si(OCH₃)₃) [23]. They evaluated coating time-dependence of the water contact angle, surface roughness and dynamic hydrophobicity, and reported that surface roughness reaches its maximum when about the half of the surface is covered by these silanes' monolayer. Once the coverage ratio becomes greater than the half, surface roughness gradually decreases with the increasing coverage ratio. A similar phenomenon might occur if the surface height increases slightly in a region where water molecules are adsorbed. A second possibility is continuous interaction change through adsorption of water molecules. This change also affects the distance

between the cantilever and film surface. Several recent reports have implied that the photoinduced volume increases on TiO₂ [24–26]. Although evidence remains insufficient, the former seems more likely. Further investigation is necessary to identify the mechanism of the distance change between the film surface and cantilever.

4. Conclusion

In this work, photoinduced surface roughness variation of polycrystalline anatase thin films under different atmospheres was evaluated using AFM. A TiO₂ thin film with large grains was obtained using the sol–gel process and VUV irradiation before firing. Once UV light was illuminated, the surface image became blurred with increasing apparent surface roughness in ambient air. The appearance of this image change was delayed in dry air, and was not observed in dry nitrogen. These results suggest that this photoinduced surface change is related to the adsorption of atmospheric water.

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