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Preparation of a Superhydrophilic Thin Film on Glass Substrate Surfaces with Titanium Alkoxide Solution

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Thin films of anatase titanium dioxide (TiO_2) were prepared on slide glass substrate surfaces by a titanium alkoxide hydrolysis operation, and the hydrophilicity and the transparency of their films were examined. The contact angles of water and the transmittances of visible light for their substrates changed with the duration of tetraethyl orthotitanate (TEOT) hydrolysis operations. They were influenced by the thickness of the films and the size of the deposited particles on the silicon dioxide-coated slide glass substrate surfaces. The contact angles also changed with the irradiating duration of ultraviolet light. When acetylacetone was added to a TEOT solution, the contact angles on the thin films became larger and the transparency was better during the same duration of TEOT hydrolysis operations. On addition of acetylacetone, nucleation of TiO_2 particles at the initial stages of TEOT hydrolysis operations was restrained and, subsequently, the supersaturations of TiO_2 in the solution became comparatively higher in the later stages of TEOT hydrolysis ones.

Nomenclature

S	specific surface energy (J/m^2)
γ	roughness factor (dimensionless)
θ	contact angle of water (°)
Subscript	
SG	solid–gas
SL	solid–liquid
GL	gas–liquid

I. Introduction

Photocatalysts have been widely used in the fields of building materials, glass, electrical appliances, automobiles, and medicine, and are characterized by two properties: strong oxidation[1] and superhydrophilicity.[2] When exterior walls, windows of buildings, or mirrors of automobiles are coated with photocatalysts and then sunlight or artificial light is irradiated, the glass does not fog and dust and dirt are removed from the walls and glasses because of the self-cleaning effects of the photocatalysts.

Crystals and thin films of anatase titanium dioxide (TiO_2), which is a representative photocatalyst, are produced by dry processes such as sputtering[3,4] and chemical vapor deposition methods,[5] or wet processes such as dip-coating,[6,7] sol–gel,[8,9] spray–coating,[10,11] and spin-coating methods.[12] Although wet-processing operations are relatively easy and require no specialized equipment, it is difficult to control the size of the crystalline particles or the thickness of the thin films of anatase TiO_2.

Instead of the conventional wet processes, a method in which anatase TiO_2 crystals are directly deposited onto the substrate surfaces using a hydrolysis operation of titanium alkoxide has been proposed.[13] This technique is useful for anatase TiO_2 coating on small and special-shaped substrate surfaces.[14] In the sol–gel methods, the sol particles of TiO_2 are formed by the hydrolysis of titanium alkoxide and by the subsequent polycondensation of TiO_2 particles. And the hydrolysis reaction of titanium alkoxide is decelerated by addition of acetylacetone in the solution.[15] Therefore, it is expected that the hydrolysis reaction rates of titanium alkoxide would be suppressed by addition of acetylacetone and, consequently, the size of crystalline particles and the thickness of thin films of anatase TiO_2 can be controlled.

The final goal of our investigations is to establish the production methods of anatase TiO_2 thin films, which are excellent in terms of both photocatalytic characteristics and transparencies. In this paper, we prepared anatase TiO_2 thin films on slide glass substrate surfaces using a hydrolysis operation of titanium alkoxide, and examined the influence of the duration of titanium alkoxide hydrolysis operations and effects on the addition of acetylacetone, which is the hydrolysis reaction-decelerating reagent, of the hydrophilicity and the transparency of their slide glass substrates.

II. Experimental Procedure

(1) Formation of Silicon Dioxide (SiO_2) Thin Films on Slide Glass Substrates

As a slide glass substrate consists of soda lime glass, sodium ions are diffused into anatase TiO_2 thin films when they are formed using annealing operations.[16] In order to avoid the diffusion of sodium ions, the slide glass substrate surfaces were coated with SiO_2 in advance, and then the anatase TiO_2 thin films were formed on their SiO_2-coated slide glass substrate surfaces.

63.9 mL of dehydrated ethanol (EtOH, Wako Pure Chemicals Industries Ltd., Osaka, Japan) and 5.50 g of tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS, Wako Pure Chemicals Industries Ltd.) were mixed in a poly vinyl chloride (PVC) vessel, and slide glass substrates (Matsunami Glass Ind. Ltd., Osaka, Japan) were immersed in the TEOS solution. 14.57 g of 28% ammonia aqueous solution (Wako Pure Chemicals Industries Ltd.) and 2.47 g of distilled water were mixed in a 50 mL volumetric flask and its solution was diluted with dehydrated EtOH. The water-containing EtOH solution was then added rapidly to the TEOS solution and it was shaken at 100 rpm at 20°C. After 2 h, the slide glass substrates were removed from the solution and were washed in EtOH solution containing 1.50×10^{-1} mol/L of distilled water. They were then dried at 20°C and 70°C for 2 h to avoid breakages of the SiO_2 thin films on the slide glass substrate surfaces when the EtOH entrained among or in the SiO_2 particles was evaporated.

(2) Formation of TiO_2 Thin Films on Glass Substrates

In the present study, we used tetraethyl orthotitanate ($Ti(OC_2H_5)_4$, TEOT) as the titanium alkoxide. One hundred

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milliliters of a dehydrated EtOH sample containing 1.37 g of TEOT (Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan) and a certain amount of acetylacetone (Wako Pure Chemicals Industries Ltd.), were mixed in a PVC vessel and the slide glass substrates coated with SiO_2 previously were immersed in the solution, after which 20.7 mL of EtOH solution containing 3.60×10^{-2} mol of distilled water was added to the TEOT solution rapidly, and the solution was shaken at 100 rpm at 20°C. After a given period of time, the slide glass substrates were removed from the solution and were washed with an EtOH solution containing 2.89×10^{-1} mol/L of distilled water. The slide glass substrates were then dried at 20°C and 70°C for 2 h, and were annealed at 500°C for a further 2 h.

In the present study, the durations of TEOT hydrolysis operations (15–420 min) and the amount of added acetylacetone ($0\text{–}6.0 \times 10^{-4}$ mol) were changed.

(3) Evaluation of TiO_2 Thin Films

The types of TiO_2 thin films deposited on the SiO_2-coated slide glass substrate surfaces were identified using a thin-film X-ray diffraction (XRD; RAD-2C, Rigaku Co. Ltd., Tokyo, Japan). An ultraviolet (UV) light (9700 $\mu W/cm^2$) was irradiated onto the slide glass surfaces coated with TiO_2 for 1 h and, then, the contact angles of water on the substrate surfaces were measured by a contact angle meter (CA-DT; Kyowa Interface Science Co. Ltd., Saitama, Japan). The slide glass substrates were cut into pieces of 3 cm × 1 cm and they were placed in a quartz cell. The cells were set in a UV-visible spectrophotometer (UV-2450; Shimadzu Corporation, Kyoto, Japan), and the intensities of the reflected light of their substrates for visible light, whose wavelengths were 400–800 nm, were measured. In contrast, the substrates were set in a UV-visible spectrophotometer and the intensities of the transmitted light on their substrates were measured. The appearance of the TiO_2 thin film surfaces was observed by a field emission scanning electron microscope (FE-SEM; S-4300; Hitachi High-Technologies Co., Tokyo, Japan), and size of the crystalline particles and thickness of the thin films of TiO_2 were measured using an atomic force microscope (AFM; Nanoscope IIIa, Digital Instruments, Woodbury, NY).

III. Results and Discussion

(1) Correlations between Hydrophilicity or Transparency of Slide Glass Substrates and Durations of TEOT Hydrolysis Operations

From thin-film X-ray diffraction (XRD) analysis, all the TiO_2 thin films deposited on the SiO_2-coated slide glass substrate surfaces were identified with anatase TiO_2. The hydrophilicity and the transparency of the anatase TiO_2 thin films were evaluated by the contact angles of water and by the transmittances or the reflectances of visible light, respectively. The contact angles of water on the substrate surfaces decreased with increasing durations of TEOT hydrolysis operations, as shown in Fig. 1. The experimental scatters of the contact angles of water were about ±0.7°. In general, if the contact angle of water is less than 10°, the substrate surfaces are thought to show hydrophilicity.[16] When the hydrolysis experiments of TEOT were carried out for 10 min, the contact angle became lower than 4°, as can be seen in Fig. 1. Therefore, the SiO_2-coated slide glass substrates showed hydrophilicity by the hydrolysis operations of TEOT. As the durations of TEOT hydrolysis operations were, however, longer than 60 min, the contact angles on the anatase TiO_2-deposited slide glass substrate surfaces fell below 1°, and the differences of contact angles in the reaction durations of TEOT hydrolysis were experimentally scattered.

In the blank tests, slide glass substrates coated with SiO_2 were immersed in an EtOH solution containing 4.53×10^{-2} mol/L of TEOT and the solution was shaken at 100 rpm for 5 and 30 min. Their slide glass substrates were removed from the solution and were washed with EtOH solution containing 2.89×10^{-1} mol/L of distilled water. They were then dried at 20°C and 70°C for 2 h and were annealed at 500°C for a further 2 h. No deposit of TiO_2 was observed in their EtOH solution containing TEOT with the naked eye, and the contact angles of the slide glass surfaces were 2.4° and 3.1° (average: 2.8°). Therefore, the slide glass substrate surfaces coated with anatase TiO_2 thin films showed superhydrophilicity when the TEOT hydrolysis was carried out for 60 min.

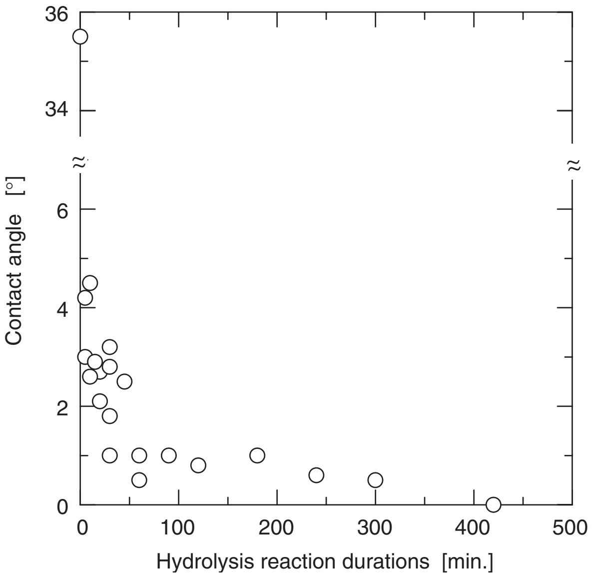

Fig. 1. Changes in contact angles of water with hydrolysis reaction duration.

Changes in the transmittances of visible light (400–800 nm) of their substrates with the reaction durations of TEOT hydrolysis operations measured by a UV-visible spectrophotometer are illustrated in Fig. 2, in which the dotted line indicates the transmittance through a slide glass substrate when no hydrolysis operation was carried out. The transmittances of visible light decreased with increasing durations of TEOT hydrolysis operations. However, the differences of the substrate transmittances between blank and the TEOT hydrolysis operations for 15 min-coated ones would be the experimental scatters. The declines in transmittance in the durations of TEOT hydrolysis operations were notable in the shorter wavelength range (400–500 nm).

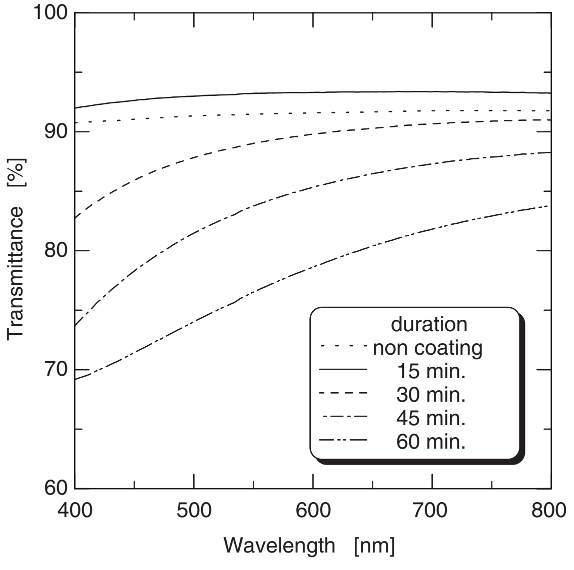

Fig. 2. Transmittances of visible light for variable hydrolysis reaction durations.

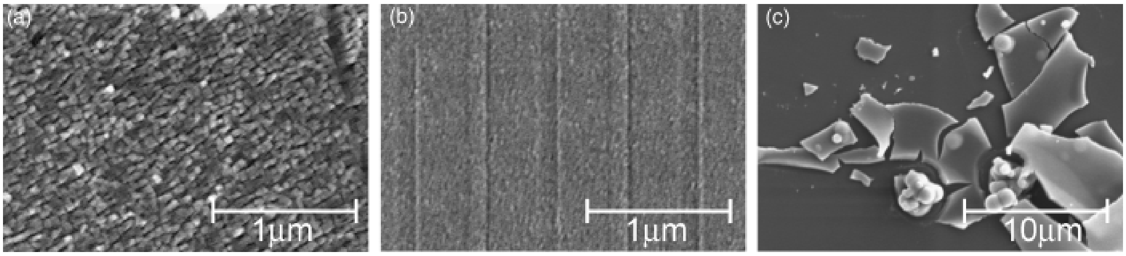

Fig. 3. Appearances of slide glass surfaces (a) 15 min, (b) 90 min, and (c) 420 min.

Figure 3 shows the appearances of the slide glass substrate surfaces observed using an FE-SEM. Although the anatase TiO_2-deposited slide glass substrate surfaces were almost similar to the non-coated ones observed with the naked eyes, their surfaces were full of particles whose size were about 30 nm (Fig. 3(a)), when the duration of TEOT hydrolysis operations was 15 min. At 90 min, the slide glass substrate surfaces appeared to be opaque and it was difficult to distinguish the grain boundaries of the anatase TiO_2 particles (Fig. 3(b)). White deposits were observed on the surfaces for 420 min and some of the anatase TiO_2 thin films peeled off from the slide glass surfaces (Fig. 3(c)).

The properties of the anatase TiO_2 thin films prepared by a TEOT hydrolysis operation were investigated in terms of the changes in the thickness of the anatase TiO_2 thin films with the duration of TEOT hydrolysis operations. Silicone rubber was painted onto a part of the SiO_2-coated slide glass substrate surfaces, and anatase TiO_2 particles were then deposited on them by TEOT hydrolysis. After the hydrolysis reactions, the silicone rubber was peeled off by immersion in toluene and the thickness of the anatase TiO_2 thin films was measured using an atomic force microscopy (AFM). Figure 4 shows the relations between the thickness of the anatase TiO_2 thin films and the reaction duration of TEOT hydrolysis. Although the anatase TiO_2 thin films were thicker for the longer reaction durations of TEOT hydrolysis, the changes in thickness with the duration decreased with increasing durations. As nucleation of TiO_2 particles occurred rapidly at the initial stages of TEOT hydrolysis, the supersaturation of TiO_2 in the solution became low in the later stages of TEOT hydrolysis operations and, consequently, suspended TiO_2 particles in the solution grew slowly.

The contact angles of water on the substrate surfaces were smaller for the thicker anatase TiO_2 thin films, as can be seen in Figs. 1 and 4, but the contact angles then became constant ($\approx 1°$) when the thickness of their films was larger than about 60 nm. As UV light irradiated on the anatase TiO_2 thin films, electrons and holes were generated on their surfaces and, consequently, the hydrophilicity on the substrate surfaces was caused by their holes. When the durations of the TEOT hydrolysis operations were 60 min, the substrate surfaces were completely covered with anatase TiO_2. Therefore, although the TEOT hydrolysis experiments were carried out for longer than 60 min, the contact angles of water did not improve any more.

Although the contact angles of water on the substrate surfaces were reduced by the longer durations of UV light irradiation, the contact angles became almost constant when the durations were longer than 60 min, as shown in Fig. 5. Changes in the contact angles with the duration of UV light irradiation were smaller for the thicker anatase TiO_2 thin films.[17] The thickness of the anatase TiO_2 thin films increased with the duration of the TEOT hydrolysis operations, as can be seen in Fig. 4. As the anatase TiO_2 thin films or their surfaces would be saturated with the holes generated by irradiation of UV light, photocatalytic properties such as superhydrophilicity do not improve any more. The hydrophilicity on the slide glass surfaces was, therefore, influenced by the thickness and/or the surface areas of the anatase TiO_2 thin films, rather than the duration of UV light irradiation.

(2) Effects of Addition of Acetylacetone on Hydrophilicity and Transparency

As the TiO_2-deposited slide glass substrates were annealed at 500°C for 2 h after the TEOT hydrolysis operation, no acetylacetone would be remaining in their thin films. The effects of the addition of acetylacetone on the contact angles of water on the

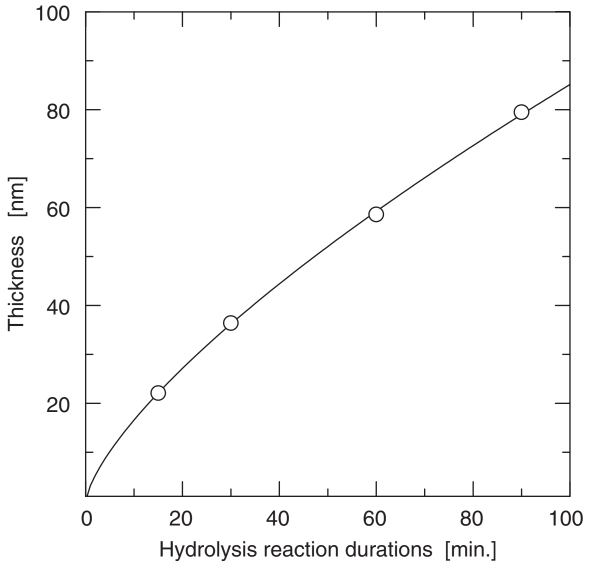

Fig. 4. Thickness of anatase titanium dioxide thin films on slide glass surfaces.

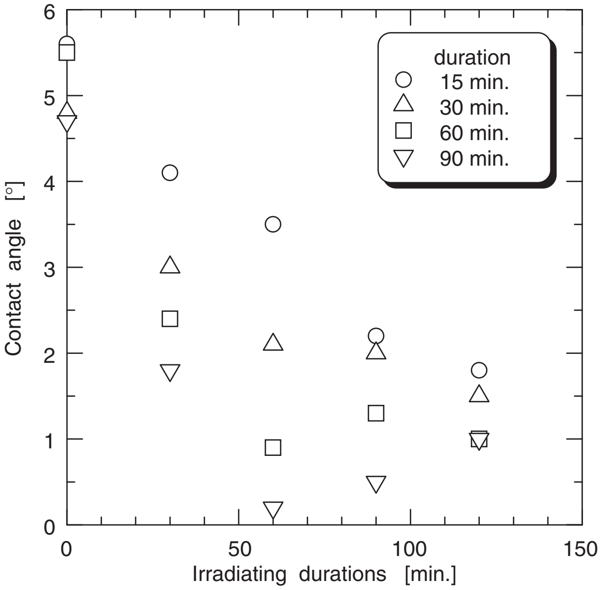

Fig. 5. Changes in contact angles of water with the duration of ultraviolet (UV) irradiation.

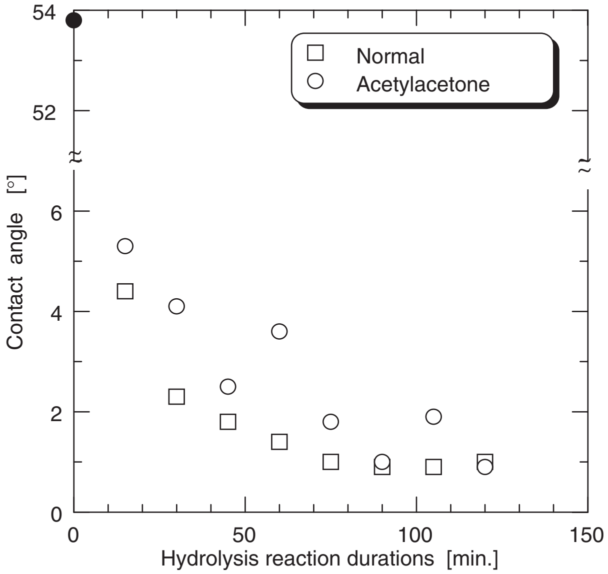

Fig. 6. Influence of addition of acetylacetone on contact angles of water.

anatase TiO_2-deposited slide glass surfaces are shown in Fig. 6, in which □ represents the changes in the mean contact angles with the hydrolysis reaction durations of TEOT when no acetylacetone is added to the TEOT solution, as shown in Fig. 1. When acetylacetone was added to the TEOT solution, the contact angles were less than 1° during TEOT hydrolysis durations of about 90 min, and these durations were longer than those for the case without acetylacetone.

Figure 7 shows the changes in the reflectances of visible light on the anatase TiO_2-deposited slide glass substrate surfaces when acetylacetone was added to the solution during TEOT hydrolysis. When the durations of TEOT hydrolysis operations were the same, the reflectances on the slide glass substrate surfaces obtained by the addition of acetylacetone were lower than those for the case without acetylacetone. Therefore, the transparencies of the slide glass substrates were improved by the addition of acetylacetone in the case of the same durations of TEOT hydrolysis operations.

When the slide glass substrate surfaces were observed using an AFM instead of an FE-SEM and the mean size of the deposited anatase TiO_2 particles was determined by the image analysis, the anatase TiO_2 particles deposited on the SiO_2-coated slide glass substrate surfaces were larger for the longer durations of TEOT hydrolysis operations. Similarly, the particles were larger when acetylacetone was added, compared with the cases without acetylacetone, as shown in Fig. 8. The contact angles of water on the rough surfaces of a certain substrates, θ, are shown in the following equation[18];

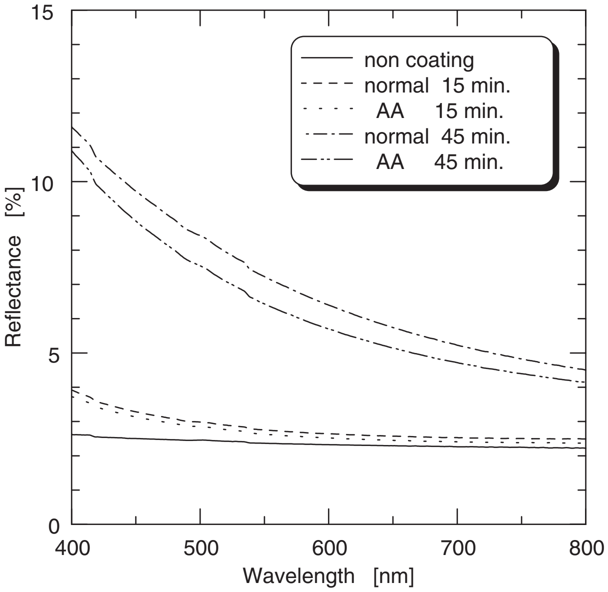

Fig. 7. Reflectances of visible light in the case with acetylacetone (AA).

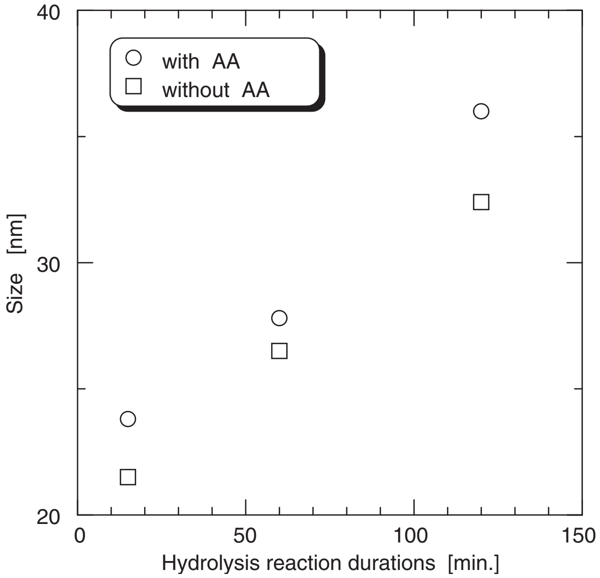

Fig. 8. Differences of particle size deposited on slide glass surface on addition of acetylacetone (AA).

$$\gamma(S_{SG} - S_{SL}) = S_{GL}\cos\theta \quad (1)$$

where S_{SG}, S_{SL} and S_{GL} are the specific interface energies between solid–gas, solid–liquid, and gas–liquid, respectively. The roughness factors of the substrate surfaces, γ, are shown by the following equation:

$$\gamma = \frac{\text{actual surfaces}}{\text{geometric surfaces}} \quad (2)$$

Therefore, the contact angles of water on the anatase TiO_2 thin films for the rough surfaces were smaller than those for the smooth ones. In sol–gel methods, acetylacetone is added in order to decelerate the reaction rates of titanium alkoxide hydrolysis.[15] When the aqueous solution was added to the TEOT solution, the supersaturations of TiO_2 in the solution increased rapidly because of TEOT hydrolysis. Consequently, a large number of amorphous TiO_2, which is metastable compared with anatase TiO_2, were nucleated in the solution in the initial stages of TEOT hydrolysis operations. Then, as the amorphous TiO_2 suspended in the solution grew, the supersaturation of TiO_2 in the solution decreased. Therefore, the supersaturations of TiO_2 in the later stages of TEOT hydrolysis operations were low.[19] In the present study, very small amorphous TiO_2 suspended in the solution were deposited on the SiO_2-coated slide glass substrate surfaces. The amorphous TiO_2 suspended in the solution would adhere onto the surfaces and would grow in the solution during the experiments. Therefore, the size of the anatase TiO_2 particles deposited on the SiO_2-coated slide glass substrate surfaces became small in the case without acetylacetone.

By contrast, when acetylacetone was added to the TEOT solution, the rapid increase in the supersaturations of TiO_2 by the TEOT hydrolysis was restrained. Consequently, nucleation of amorphous TiO_2 in the initial stages of TEOT hydrolysis operations was controlled and the supersaturations of TiO_2 were comparatively higher in the later stages of TEOT hydrolysis. Therefore, the size of TiO_2 particles deposited on the SiO_2-coated slide glass substrate surfaces was larger and, subsequently, the surface area became smaller than those for the case without acetylacetone, even if the durations of TEOT hydrolysis operations were the same. The contact angles of water for the rough surfaces, θ, were re-arranged from Eq. (2) into the following equation;

$$\cos\theta = \frac{\gamma(S_{SG} - S_{SL})}{S_{GL}} \tag{3}$$

The specific surface energies between solid–gas and solid–liquid, S_{SG} and S_{SL}, are influenced by the kinds of materials composing the substrate surfaces and the "solid" is anatase TiO_2 in the present study. As the particle size was smaller the surface area was larger and, consequently, the substrate surfaces became rough. Therefore, as the roughness factor, γ, was larger for the rough surfaces, the contact angles for rough surfaces, θ, became smaller. When the reaction durations of TEOT hydrolysis were the same, the contact angles became larger and the transparency was higher, as can be seen in Fig. 7, for the case with acetylacetone.

We, therefore, concluded that it is better to add acetylacetone in the titanium alkoxide solution to produce anatase TiO_2 thin films that have both excellent photocatalytic characteristics and excellent transparencies because it is easy to control the duration of the titanium alkoxide hydrolysis operations.

IV. Conclusions

Thin films of anatase TiO_2 were prepared on SiO_2-coated slide glass substrate surfaces by TEOT hydrolysis operations, and the hydrophilicity and the transparency of the substrate surfaces were examined. The contact angles of water on their surfaces were smaller for the longer durations of TEOT hydrolysis operations and fell below 1° when the duration was longer than 60 min. As the durations of TEOT hydrolysis operations were longer, the transmittances of visible light through their substrates were lower. The anatase TiO_2 thin films on the slide glass substrate surfaces were thicker but the changes in the thickness of the films with the reaction duration of TEOT hydrolysis were smaller for the longer duration of TEOT hydrolysis operations. The contact angles of water decreased with increasing duration of UV irradiation. The hydrophilicity and transparency of the slide glass substrates were, therefore, influenced by the thickness and/or the surface areas of the anatase TiO_2 thin films, rather than the duration of UV irradiation.

The durations of TEOT hydrolysis operations, at which the contact angles on the slide glass surfaces were lower than 1°, were longer when acetylacetone was added to the TEOT solution. In the same duration of TEOT hydrolysis operations, the reflectances of visible light on the slide glass substrate surfaces resulting from the addition of acetylacetone were close to those of slide glass substrates without an anatase TiO_2 coating. The addition of acetylacetone caused the nucleation rates of amorphous TiO_2 to be reduced in the initial stages of TEOT hydrolysis operations and, subsequently, the supersaturations of TiO_2 remained higher in the later stages of TEOT hydrolysis. Therefore, the addition of acetylacetone is an effective method for controlling both the thickness of the thin films and the size of the crystalline particles of anatase TiO_2 when TEOT hydrolysis operations are carried out.

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