

# Correlation between Surface Morphology and Hydrophilic/Hydrophobic Conversion of MOCVD–TiO<sub>2</sub> Films

Ha Yong Lee, Yong Hwan Park, and Kyung Hyun Ko\*

Department of Materials Science & Engineering, Ajou University, Suwon 442-749, Korea

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The relationship between hydrophilicity and surface morphology of TiO<sub>2</sub> film was investigated. TiO<sub>2</sub> films were deposited by MOCVD, and anatase films were crystallized. The rougher the surface of anatase film, the slower the conversion from hydrophilic to hydrophobic state. Also in some films, even the sonication could not accelerate the kinetics. However, the recovery rate to hydrophilicity under UV illumination had a reverse dependency on the surface roughness. It was assumed that the rougher TiO<sub>2</sub> films could have a large concentration of Ti<sup>3+</sup> generated by UV illumination on the surface, which plays a major role as adsorption sites of –OH in the water as well as in the air. Therefore, the healing kinetics of Ti<sup>3+</sup> by oxygen in the air of a dark room could have been different among films with various surface roughnesses. Conclusively, the sustaining tendency of hydrophilic or hydrophobic properties could mainly depend on the concentration of Ti<sup>3+</sup> by UV light, and in turn on the processing conditions of film deposition.

## I. Introduction

Recently TiO<sub>2</sub>, usually known as a typical dielectric material, has been studied actively in the area of environmental technologies, such as a photocatalyst for decomposing organic compounds when TiO<sub>2</sub> films are illuminated by UV light.<sup>1–9</sup> Furthermore, the hydrophilic coating (0° water contact angle) has emerged as a new and very attractive application of TiO<sub>2</sub>.

TiO<sub>2</sub> films have amphiphilic properties under UV illumination so that they can be utilized for many kinds of applications such as anti-fogging and self-cleaning coatings of glasses and ceramics.<sup>10</sup> According to R. Wang<sup>11</sup> and A. Fujishima,<sup>12</sup> Ti<sup>4+</sup> ions on TiO<sub>2</sub> surfaces are converted into Ti<sup>3+</sup> ions by UV light, and the characteristics of charge transfer between Ti ions and adsorbents such as hydroxyl ion and/or oxygen can be altered by UV radiation. Consequently, the hydrophilicity of TiO<sub>2</sub> films would be established. Also, it was conceivable that the existence and quantity of Ti<sup>3+</sup>/Ti<sup>4+</sup> on the surfaces could be reset by the cyclic use of UV radiation and (ultrasonic + dark room) treatment in which ·OH and O<sub>2</sub> healing of surface occurred, resulting in restoration of hydrophobic state.

Because amphiphilicity also depends on adsorption properties of the film surface, another factor, which affects

the characteristics of hydrophilic/hydrophobic conversion of TiO<sub>2</sub> films, would be suggested. As reported in Machida,<sup>13</sup> hydrophilicity was affected by the amount of SiO<sub>2</sub> addition, because surface morphology on TiO<sub>2</sub> films has been changed with SiO<sub>2</sub> addition. Therefore, it can be assumed that certain factors affecting the surface morphology of films such as the film preparation technique could play a significant role in the hydrophilic/hydrophobic conversion cycle. Regarding surface morphology related to hydrophilicity of TiO<sub>2</sub> film, the preparation method of many research studies has usually been sol–gel or sputtering. In this work, the relationship between hydrophilic/hydrophobic conversions of TiO<sub>2</sub> films deposited by MOCVD has been investigated in terms of surface morphology.

## II. Experimental Section

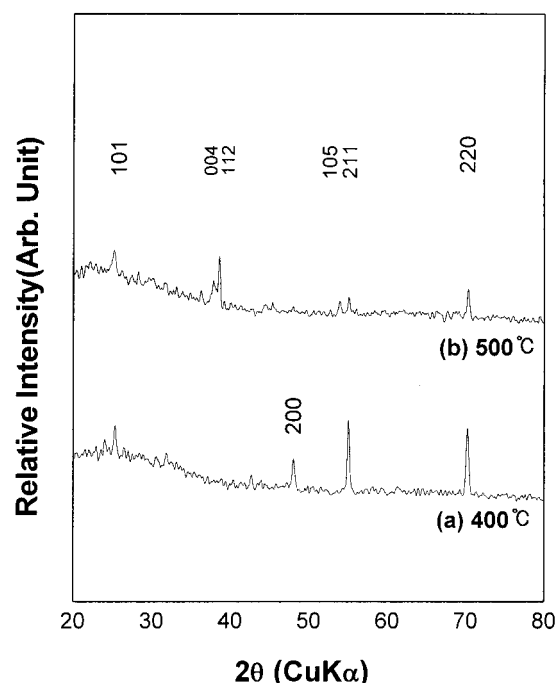
**II.1. Preparation of TiO<sub>2</sub> Films.** TiO<sub>2</sub> films were deposited by MOCVD on bare and rutile-presputtered glass substrate. As starting materials, TTIP (titanium tetrakis(isopropoxide), Aldrich Ltd.) was loaded in the bubbler. The substrate temperatures were 400 and 500 °C, while the bubbler temperature was kept at 60 °C and the flow rates of carried gas were 50 and 110 sccm, respectively. The reactant gases were carried by nitrogen gas and sprayed from the nozzle to the substrate. The deposition pressure was 1 Torr. Film thickness and deposition rate were measured by a-step.

Crystalline phases of TiO<sub>2</sub> films were measured by X-ray powder diffraction (XRD; M18XHF-SRA, McScience, Japan), and surface morphologies of films were investigated using scanning electron microscope (SEM; S-2400, Hitachi, Japan) and atomic force microscope (AFM; Ls, Park instrument). The Ti atom state on film surface was analyzed by X-ray photoelectron spectroscopy (XPS; Ariesarsc 16MCD150, Vacuum Science Workshop, United Kingdom). The stoichiometries of films were analyzed by RBS using a 2 MeV tangem type ion accelerator.

**II.2. Test of TiO<sub>2</sub> Films Hydrophilic/Hydrophobic Conversion.** To make as-deposited TiO<sub>2</sub> films into the hydrophilic state, films were illuminated by Hg lamp (10 W, Philips). Then, TiO<sub>2</sub> films with hydrophilic state were sonicated for 1 h by the ultrasonic source with a 60 Hz generator followed by storage in a dark room for up to 7 days considering the kinetics of the conversion of hydrophilic to hydrophobic state. Thereafter, films

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**Figure 1.** XRD patterns of  $\text{TiO}_2$  films deposited at (a) 400 °C, (b) 500 °C on the glass (flow rate, 50 sccm; bubbler temperature, 60 °C).

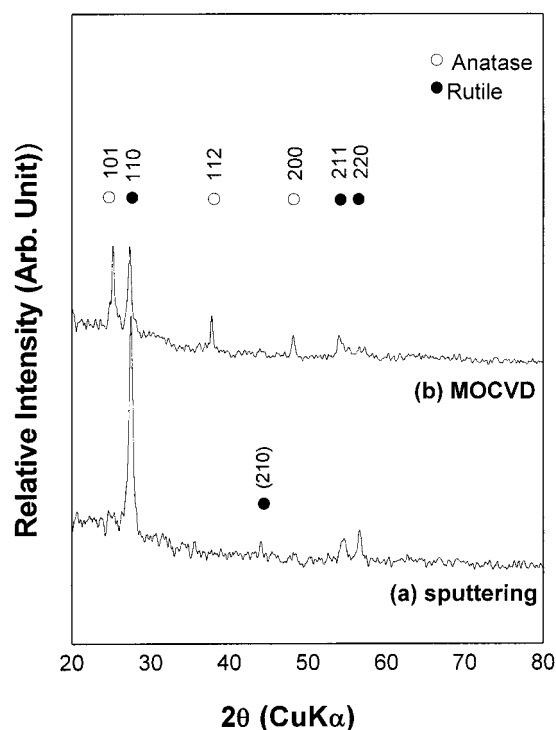
were reilluminated for 120 min by the same UV light. In the respective process, the contact angle of water droplet on  $\text{TiO}_2$  surfaces, and thus the surface wettability, was evaluated as a measure of hydrophilicity.

### III. Results and Discussion

**III.1. Phase of  $\text{TiO}_2$  Films.** Figure 1 shows X-ray diffraction patterns of  $\text{TiO}_2$  films deposited at 400 and 500 °C on glass substrates. All as-deposited films were crystallized as anatase phases. Four peaks of  $\text{TiO}_2$  films deposited at 400 °C are corresponding to (101), (200), (211), and (220) planes, while it seemed that films deposited at 500 °C had a different set of peaks such as (101), (004), (112), (105), (211), and (220), presumably textured.<sup>15</sup> As shown in Figure 2, the phase of films deposited by sputtering on fresh glass was only rutile and then that of film by MOCVD on rutile-predeposited substrate was anatase. It was found that all films have a stoichiometry by measuring RBS.

**III.2. Surface Morphologies of  $\text{TiO}_2$  Films.** It was observed that the surface roughnesses of anatase films are considerably different depending on preparation conditions such as substrate temperature, flow rate, and substrate. Figure 3 shows SEM photographs of the surfaces of anatase films deposited with various deposition parameters. The surface of Figure 3d was the smoothest of all, and the surface became rougher in the order of (a) → (c) → (b). For quantitative measurements of surface morphologies of anatase films deposited at each condition, films were analyzed by AFM (Figure 4.) resulting in the same trend of surface morphologies observed by SEM. The RMS of roughnesses of these films were (a) 129, (b) 274, (c) 217, and (d) 85 Å, respectively.

The reason for different surface morphology with substrate temperature (Figure 3a,b and Figure 4a,b) is due to the change of deposition rate. Figure 5 shows the deposition rate of  $\text{TiO}_2$  with substrate temperature with



**Figure 2.** XRD patterns of  $\text{TiO}_2$  films (a) deposited by sputtering on the glass substrate, (b) deposited at 500 °C by MOCVD on rutile film deposited by sputtering (flow rate, 50 sccm; bubbler temperature, 60 °C).

50 sccm on the glass. In the case of 400 and 500 °C, rate-limiting steps are surface-reaction controlled and diffusion-controlled kinetics with the deposition rate of 3200 and 2000 Å/min, respectively. It is, therefore, interfered that surface morphology of  $\text{TiO}_2$  film deposited at 500 °C is more rough than that at 400 °C owing to the limited time of position adjustment for incident molecules with higher velocity.

By the same token, the flow rate could also affect surface morphology via altering deposition rate. In the surface reaction controlled kinetics regime such as 400 °C, the deposition rate is increased with flow rate. For example, the deposition rate of 50 and 110 sccm at 400 °C are 2000 and 3300 Å/min, respectively. Meanwhile, those of the diffusion-controlled regime such as 500 °C showed saturated behavior (Figure 6).

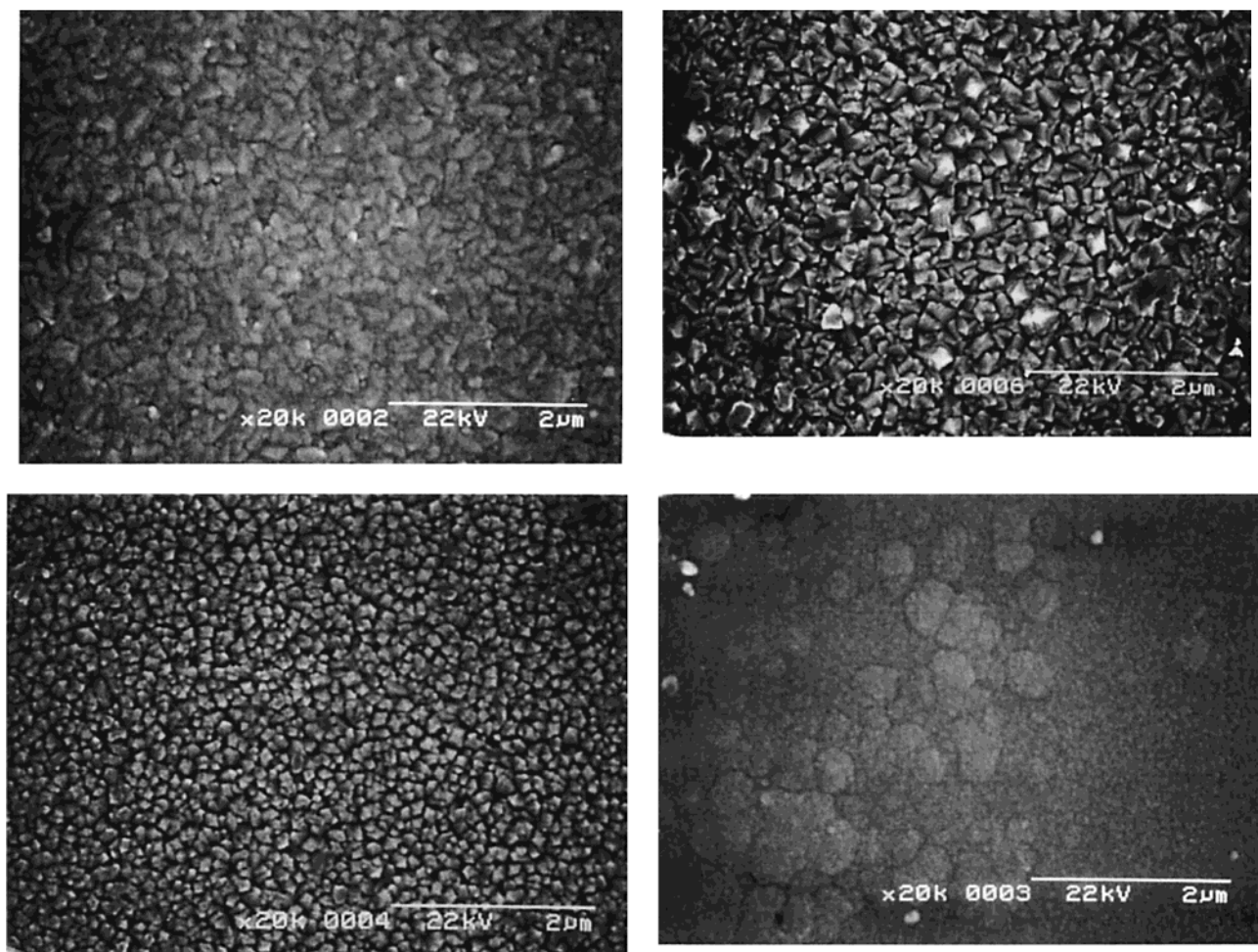
Rutile-predeposited substrate seemed to provide surface features different from polished glass substrate: that is, predeposited film was deposited by sputtering and crystalline phase with (110) texture. So, it could be assumed that the differences in surface atomic mobility and/or ability of lattice matching can affect the final roughness of anatase film on this substrate resulting, in very smooth surface feature.

**III.3. The Contact Angle Changes of Water on  $\text{TiO}_2$  Surface.** Figure 7 shows the cyclic change of contact angles of water dropped on the UV-illuminated anatase films that appeared in Figure 3 after 60 min of sonication and then storage in the dark room for 7 days followed by reillumination of UV light. All as-deposited anatase films by MOCVD showed hydrophobic properties and immediately changed into the hydrophilic state after UV illumination. When hydrophilic anatase films were stored in the dark room, the degree of hydrophobicity tended to increase up to certain saturation values and sonication seemed to accelerate this process. For example, the contact angle of anatase film showed in Figure 3a increased up

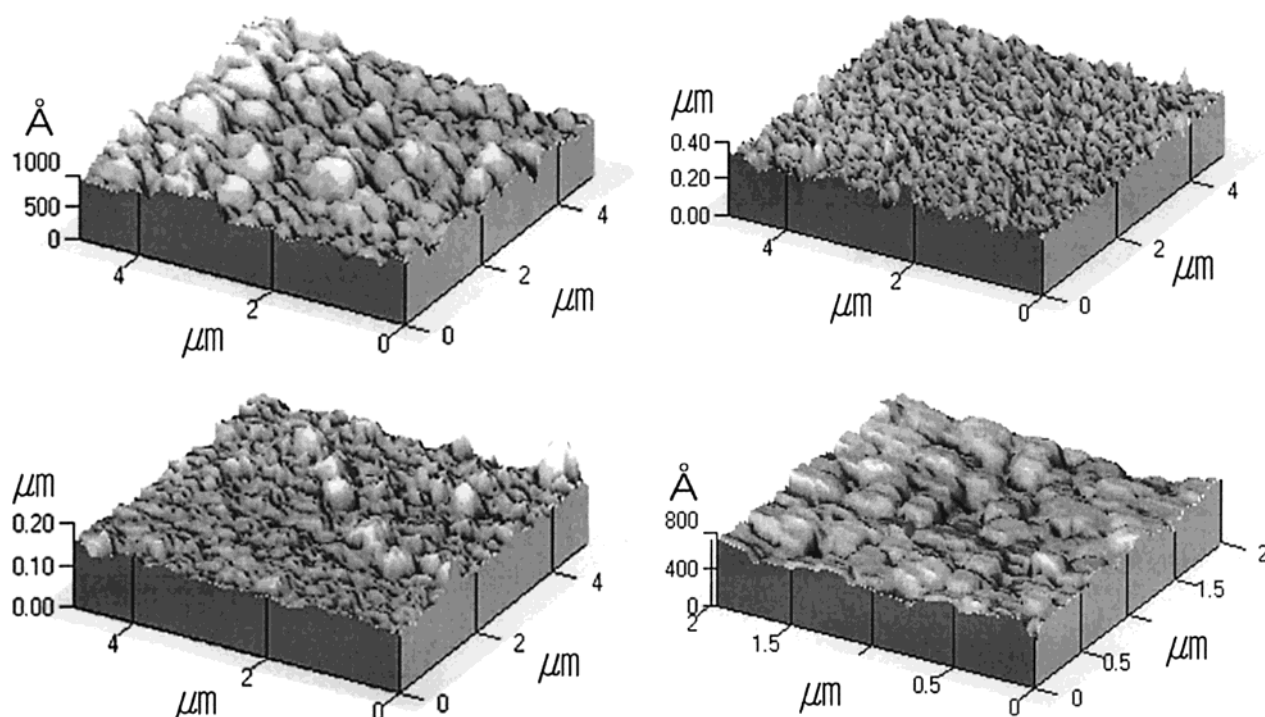
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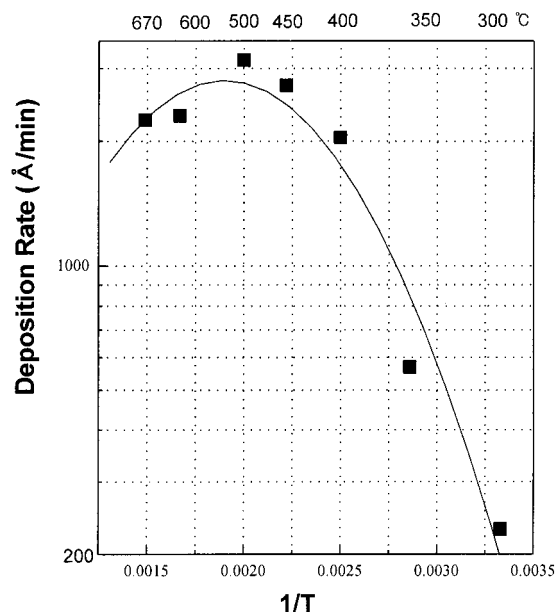
**Figure 3.** Surface morphology of anatase films by scanning electron microscope deposited at (a, top left) 400 °C, (b, top right) 400 °C with 110 sccm of flow rate, (c, bottom left) 500 °C, (d, bottom right) 500 °C with 50 sccm on predeposited rutile substrate (substrate of (a), (b), and (c): glass; flow rate of (a), (c), and (d): 50 sccm).



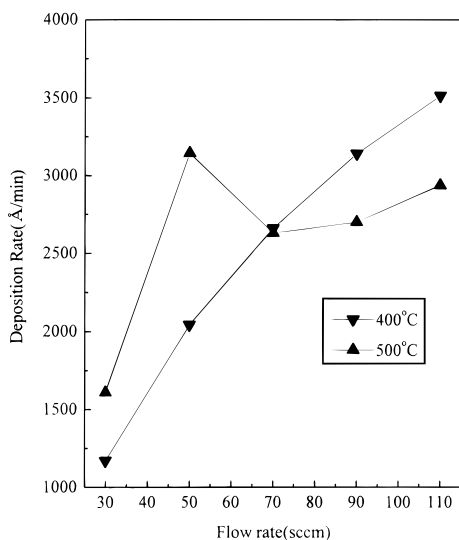
**Figure 4.** Surface morphology of anatase films by atomic force microscope deposited; (a)–(d) are as in Figure 3.

to about 75° of saturation angle in the dark room for 7 days. After those films were illuminated by UV light, the

hydrophilicity could be fully recovered to the original state and complete cycle.

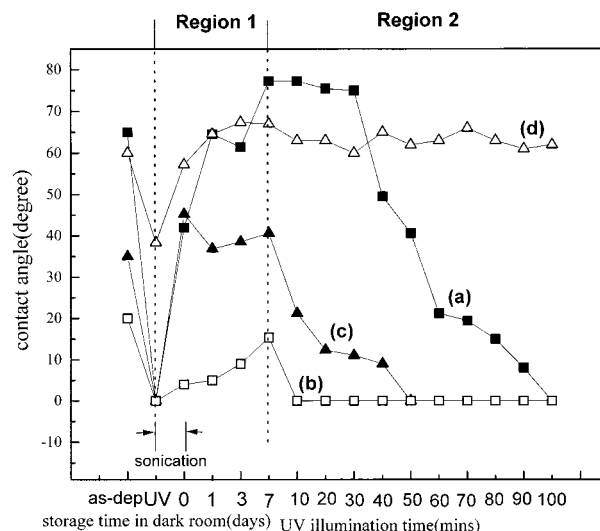


**Figure 5.** Substrate temperature dependence of deposition rate of  $\text{TiO}_2$  film; (bubbler temperature, 60 °C, flow rate, 50 sccm).



**Figure 6.** Effects of precursor flow rate on the deposition rate of MOCVD  $\text{TiO}_2$ .

As depicted in Figure 7, the characteristics of cyclic change of contact angle, and so the hydrophilic  $\leftrightarrow$  hydrophobic state, were different from specimen to specimen. For the film denoted by (b) in Figures 3 and 7, the saturation contact angle of the specimen was as low as 15° and the conversion kinetics from hydrophilic to hydrophobic state was the slowest of all. Furthermore, there seemed to be minimal effect of sonication for this film. On the contrary, other films showed fast conversion kinetics after sonication so that the contact angle increased up to 60–100% of the saturation values, demonstrating large acceleration efficiency of sonication for surface state conversion. In the recovering stage to the original hydrophilic state, the kinetics was reversed. The contact angle of film b which has the lowest hydrophobic property of all, returned to 0° right after 10 min of UV illumination. However, films c and a required 50–100 min to be fully recovered. Most significantly, in the case of film d, the hydrophilic surface state did not return at all, showing virtually no change from the saturation value even after 2 h of UV illumination.



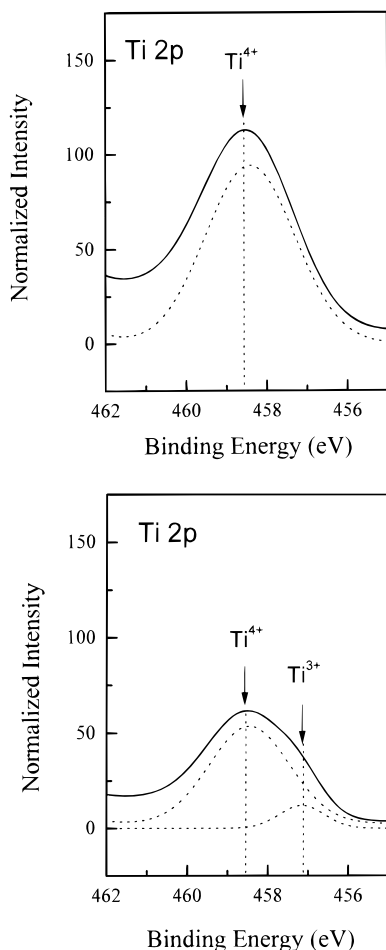
**Figure 7.** Changes of contact angle after 1 h of sonication and subsequent storage in the dark room for 7 days followed by UV illumination; (a)–(d) are as in Figure 3. Region 1, storage time in dark room; region 2, UV illumination time.

From the results mentioned in sections III.2 and III.3, it was found that changes in hydrophilicity of  $\text{TiO}_2$  films have been very closely related to surface morphology.  $\text{TiO}_2$  films with high roughness, such as anatase films deposited at 400 °C with 110 sccm of flow rate (film b), had the slowest conversion to hydrophobic state, resulting in the smallest contact angle after 7 days of dark room storage. This film also showed the fastest recovery of hydrophilicity under UV illumination. The recovery rate to hydrophilicity increased in the order of (d)  $\rightarrow$  (a)  $\rightarrow$  (c)  $\rightarrow$  (b), which coincided with the order of roughness.

According to R. Wang,<sup>10</sup> from the investigation of water-wetted surface of hydrophilic film by Fourier transform infrared spectroscopy (FT-IR), it was claimed that IR bands could be assigned to the stretching of OH groups supposedly chemisorbed on  $\text{Ti}^{3+}$  on the surfaces. From XPS data, Ti 2p spectra of two samples (parts a and c of Figure 3, respectively) are shown in Figure 8. While the peak of sample with rougher surface shows a shoulder around 457 eV, there is no such trace in the peak corresponding to the smoother one. This overlap is consistent with the creation of  $\text{Ti}^{3+}$  on the surface by UV illumination,<sup>16</sup> and the contribution of  $\text{Ti}^{3+}/\text{Ti}^{4+}$  on the surface is about 15%. It was also found that for both samples in Figure 8, adsorbed OH groups on  $\text{TiO}_2$  film with rough surface were detected<sup>12,16</sup> but OH groups on smooth surface film were not detected from XPS measurement. (Figure 9) Therefore, it is conceivable that anatase films with high roughness such as Figure 3c would have more  $\text{Ti}^{3+}$  by generated UV light, and thus more adsorption sites of OH groups on the  $\text{TiO}_2$  surface than those on smooth films (Figure 3a). Because both smooth and rough surface showed superhydrophilicity after UV illumination (Figure 7), it can be assumed that  $\text{Ti}^{3+}$  and OH groups concentration of two samples were similar and that the differences in concentration of both films were generated during dark room storage.

According to N. Skai,<sup>12</sup> the oxygen in the air was responsible for oxidizing of hydrophilic surface via  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  state during storage in the dark room. Therefore, it was seemed that during the dark storage period, so-called “oxygen healing”, could be a candidate for hydrophilic/

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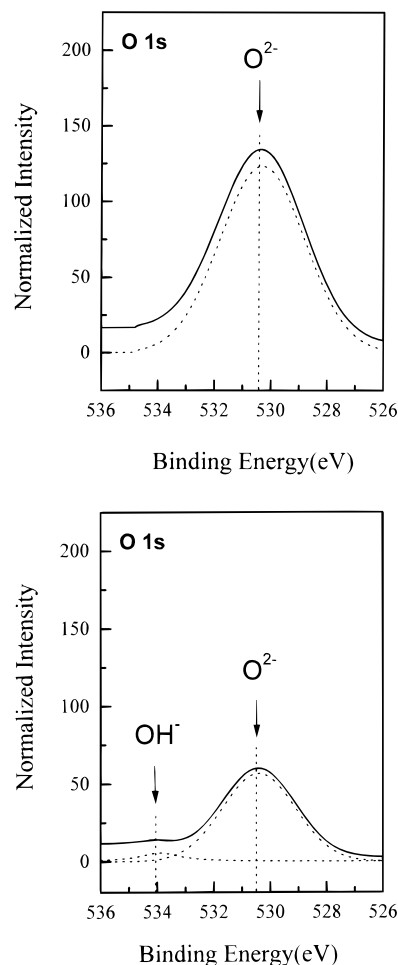


**Figure 8.** Ti 2p XPS spectra of TiO<sub>2</sub> thin films at (a, top) 400 °C and (b, bottom) 500 °C on glass (flow rate: 50 sccm). The samples are illuminated by UV light for 2 h and then stored in the dark room for 1 day.

hydrophobic conversion mechanism. In light of this hypothesis, it is likely that the smoother surface can be more susceptible to oxidation of Ti<sup>3+</sup> during dark room storage and, therefore, that the regeneration of hydrophilic state by UV illumination would take more time than the rough surface.

#### IV. Conclusions

It was suggested that the characteristics of hydrophilic/hydrophobic conversion of MOCVD-TiO<sub>2</sub> films are very closely related to their surface morphologies. While the water contact angle of anatase film with the largest roughness, which was deposited at 400 °C with 110 sccm of flow rate, was about 15° after 1 h of sonication followed by subsequent dark room treatment for 7 days and restored



**Figure 9.** O 1s XPS spectra of TiO<sub>2</sub> thin films at (a, top) 400 °C and (b, bottom) 500 °C on glass (flow rate: 50 sccm). The samples are illuminated by UV light for 2 h and then stored in the dark room for 1 day.

hydrophilicity within as short as 10 min of UV illumination, the smoother films such as anatase film deposited at 500 °C on rutile predeposited substrate had 70° of contact after the same treatment but sustained the hydrophobic state even after 2 h of illumination. Assuming the kinetics of surface conversion depends on the concentration of so-called unhealed Ti<sup>3+</sup> generated by UV illumination, the rougher the surface, the slower conversion to hydrophobicity and the faster recovery to hydrophilic state because more Ti<sup>3+</sup> on the surfaces could exist. Therefore, deposition conditions such as substrate temperature and flow rate of precursor can alter the surface conversion of TiO<sub>2</sub> films.

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