Article

Thermoinduced and Photoinduced Sustainable Hydrophilic Surface of Sputtered-TiO₂ Thin Film

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Abstract: To achieve self-cleaning at a low maintenance cost, we investigated the possibility of obtaining a sustainable hydrophilic surface of TiO₂ thin film. As the hydrophilicity of TiO₂ films fabricated by FTS has not yet been studied, we deposited TiO_x using FTS, and then TiO₂ was formed through additional treatment. Hydrophilic surfaces were obtained by thermoinduced and photoinduced methods. UV irradiation led to the conversion of Ti⁴⁺ to Ti³⁺ in the lattice structure and an increase in the number of OH groups on the surface, and annealing induced the formation of Ti³⁺ defect sites, as well as organic degradation and changes in the crystal structure. Through the annealing process, the water contact angle of as-deposited film was decreased from 78.7° to 35.7°, and crystallinity changed from amorphous to anatase. These changes contributed to the formation of a hydrophilic surface and reduced the water contact angle by up to 10.8°. After the formation of a hydrophilic surface through annealing and UV irradiation, the sample returned to its original state. We confirmed that the water contact angle of the returned sample was decreased through exposure to sunlight; it reduced the water contact angle of the returned sample by 15.2°. Thus, the results revealed that the crystallinity influences the hydrophilicity and its sustainability for TiO₂ films under sunlight.

Keywords: TiO₂; hydrophilicity; thermoinduced; photoinduced; thin film

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1. Introduction

Photocatalysts are promising for use in environment- and energy-related applications owing to their sustainability and environmental friendliness. They utilize light energy to cause a chemical reaction such as degradation of organic compounds [1]. In photocatalysis, an electron is excited from the valence band to the conduction band; this leads to the generation of positive electron holes in the valence band when the photon energy of the light source is higher than the bandgap energy. The atmospheric oxygen is reduced to superoxide ions by the excited electrons, and the electron holes oxidize the water or OH[−] to OH radicals on the surface. The reaction equation for photocatalysis is as follows [2]:

Through these reactions, TiO₂ can clean the surface by decomposing organic matter and pollutants into CO₂ and H₂O, as well as produce hydrogen [2–5]. Since the first report on photocatalysis by Fujishima and Honda in 1972 [6], it has been employed to remove pollutants (e.g., through air and water purification) and convert optical energy into chemical energy, as well as in self-cleaning applications and for hydrogen production [1–3,5]. Self-cleaning is an important property for various products, such as wide window glasses,

furnishing materials, and solar panels [7–9]. There are two types of self-cleaning surfaces, hydrophilic and hydrophobic [10,11]. Water spreads easily on hydrophilic surfaces, and water droplets rapidly flow along the surface to remove impurities. Therefore, films with a hydrophilic surface can be cleaned with flowing water from natural sources, such as rainfall; this considerably reduces the maintenance cost. Consequently, numerous materials have been studied to obtain self-cleaning films. Among them, TiO_2 has been extensively investigated owing to its photocatalytic properties, such as a high oxidizing power and hydrophilic surface [12].

TiO_2 thin films have been fabricated by various methods, including solution process such as spin coating, spray pyrolysis, dip coating [13–16], chemical vapor deposition (CVD) [17], and sputtering [18]. Compared with other methods, DC and RF magnetron sputtering can deposit thin films at a low temperature; further, by adjusting the sputtering conditions, it is easy to control the composition, structure, and thickness of the thin films [15]. However, because the substrate is located within plasma areas, the surface of the films is damaged owing to high-energy-particle collisions in typical sputtering systems. Therefore, in this study, a facing-target sputtering (FTS) system was used for deposition. In an FTS system, the targets face each other within the chamber, plasma is formed between them, and the substrate is separated from the chamber, resulting in less surface damage compared with typical sputtering [19,20]. The high-speed accelerating particles moving between the targets form a magnetic field with a high ionization rate, enabling the fabrication of high-quality thin films [21,22]. Figure 1 shows a schematic diagram of the FTS.

Figure 1. Schematic of the FTS system.

2. Experimental Section

In this study, using an FTS system, we fabricated TiO_2 thin films with a hydrophilic surface that are sustainable under sunlight. To investigate the influence of UV irradiation on the formation of a hydrophilic surface, we compared the X-ray photoelectron spectroscopy (XPS) profiles of the films before and after irradiation. The TiO_2 films were formed with an anatase or amorphous structure depending on the sputtering conditions. The correlation between the hydrophilicity of the surface and the crystal structure was studied with X-ray diffraction (XRD). Finally, to confirm whether the hydrophilicity of the surface was sustainable under sunlight, the TiO_2 films were placed in a dark room and then irradiated with sunlight, following which the sessile drop method was performed for contact angle measurements.

2.1. Fabrication of TiO₂ Thin Films

TiO₂ thin films were fabricated using a 4-inch FTS system. Soda lime glass substrate with dimensions of 76 × 26 × 1 mm³ (Microspore glass, Marienfeld, Lauda-Königshofen, Germany) was used as the substrates. Ultrasonic cleaning was successively performed with ethyl alcohol (C₂H₅OH, 94%, extra pure, DUKSAN Pure Chemicals, Ansan, Korea) and acetone (CH₃COCH₃, ≥99.5%, SAMCHUN Pure Chemicals, Pyeongtaek, Korea) for 10 min; each cleaning procedure was followed by rinsing with distilled water for 5 min. Finally, the substrates were dried using N₂ gas and an oven. For sputtering, 4-inch Ti targets were used, the base pressure was 3 × 10^{−5} Torr, and the working pressure was set to 2 mTorr. The input power and sputtering time were varied to adjust the crystal structure and thickness. Table 1 lists the specific sputtering conditions, while Table 2 shows the sample parameters.

Table 1. Sputtering conditions.

Parameters	Conditions
Targets	Ti, 4 inches
Substrate	Glass microscope slides
Base pressure	3 × 10 ^{−5} Torr
Working pressure	2 mTorr
Gas flow	Ar, 10 sccm; O ₂ , 1 sccm
Input power	100 W, 150 W

Table 2. Sample parameters.

Samples	A	B	C	D	E	F	G	H
Input power (W)	100	150	150	150	100	150	150	150
Deposition time (min)	60	20	40	60	60	20	40	60
Annealing (500 °C)	X	X	X	X	O	O	O	O

2.2. Formation of a Sustainable Hydrophilic Surface

Figure 2 illustrates the method of fabrication of the hydrophilic TiO₂ films. The water contact angle was reduced by ultraviolet (UV) irradiation and annealing. After deposition, the samples were cut into two equal parts. One half was placed in an electric muffle furnace and annealed in an air atmosphere and at 500 °C for 3 h to form anatase TiO₂. Then, samples were cooled naturally in the furnace to room temperature. Sample H was used to confirm the sustainable hydrophilic properties of the TiO₂ film. After 12 h of UV irradiation, the sample was stored in a dark room for a few days, and then exposed to sunlight for 2, 4, 6, and 8 h. The sessile drop method was repeated every 2 h.

2.3. Evaluation of TiO₂ Thin Films

A UV-C lamp (G15T8, peak: 253.7 nm, intensity: 1.36 mW/cm², SANKYO DENKI, Hiratsuka, Japan) was used to irradiate the TiO₂ films. The intensity of the UV-C lamp was measured using a UVC light meter (UV C-254SD, Lutron, Coopersburg, PA, USA). The degree of hydrophilicity of the surface was evaluated using a contact angle meter (DSA100, KRÜSS, Hamburg, Germany). The thickness of the TiO₂ thin films was measured by the Alpha-Step profilometer (Alpha-Step-500 profilers, KLA-Tencor, Milpitas, CA, USA). A UV/Vis spectrometer (Lambda 750 UV/vis/NIR, Perkin Elmer, Waltham, MA, USA) was used to analyze the optical properties. The crystal and surface structures of the films were analyzed by XRD using a high resolution X-ray diffractometer (SmartLab, Rigaku, Tokyo, Japan) in the scanning range of 10°–90° and scanning electron microscopy (SEM, S-4700, Hitachi, Tokyo, Japan), respectively. XPS (K-alpha+, Thermo Fisher Scientific, Waltham, MA, USA) was employed to investigate the difference in the binding energies of Ti and O before and after UV irradiation.

Figure 2. Schematic showing the experimental procedure for the formation of TiO₂ films with a hydrophilic surface.

3. Result and Discussion

The as-fabricated films possessed a TiO_x structure, because the samples were fabricated by DC reactive sputtering. The TiO_x films initially exhibited a low hydrophilicity; after thermal treatment, TiO_x was converted to anatase TiO₂ and the water contact angle drastically decreased. In addition, when the annealed TiO₂ thin films were subjected to UV irradiation, the water contact angle decreased to the extent that the surface was almost superhydrophilic. The variation in the water contact angle is illustrated in Figure 3, and indicates that UV irradiation and thermal treatment contributed to the hydrophilicity of the surface of the TiO₂ films [18,23]. Therefore, subsequent sections focus on the effects of these methods on the hydrophilicity of the surface. The summaries of analytical data of samples are shown in Table 3. Below, we discuss these results.

Figure 3. Variation in water contact angle with thermal treatment and UV irradiation (Sample D: 150 W, 60 min, R.T., Sample H: 150 W, 60 min, 500 °C, Sample H + UV: Sample H and UV irradiation).

Table 3. The summaries of the analytical data of all samples.

Samples	A	B	C	D	E	F	G	H
Water contact angle Before UV irradiation (°)	77.5	75.6	72.9	78.7	35.5	34.0	37.4	35.7
Water contact angle After 12 h UV irradiation (°)	36.9	36.7	32.0	20.0	18.4	16.1	11.0	10.8
Thickness (nm)	90.9	45.5	91.0	136.4	90.9	45.5	91.0	136.4
Phase (Amorphous: AP) (Anatase: AT)	AP	AP	AP	AP	AP	AP	AT	AT
Band gap (eV)	3.6	3.6	3.4	3.3	3.6	3.6	3.4	3.3

3.1. Generation of Light-Induced Surface Oxygen Vacancies

To observe the variation in the lattice structure of TiO_2 with UV irradiation, the binding energy of Ti was measured by XPS and is shown in Figure 4. For the measurement, each sample was cut into two pieces ($1 \times 1 \text{ cm}^2$); one piece was stored in a dark room for 12 h and the other was subjected to UV-C irradiation for 12 h, following which both samples were measured simultaneously. Figure 4A shows the XPS profile for the sample stored in the dark, while Figure 4B shows the XPS profile for the UV-irradiated sample. Figure 4 shows two main peaks of Ti 2p, situated at 464.3 and 458.5 eV and assigned to $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$, respectively. There are two relatively lower peaks under each main peak; Ti^{4+} peaks occur at 465.4 eV for $\text{Ti } 2p_{1/2}$ and 458.8 eV for $\text{Ti } 2p_{3/2}$, while Ti^{3+} peaks occur at 464.5 eV for $\text{Ti } 2p_{1/2}$ and 457.9 eV for $\text{Ti } 2p_{3/2}$ [24]. Several theories have been proposed for the formation of hydrophilic surfaces on TiO_2 films via photo-irradiation. Among them, Wang et al. [25] suggested the generation of light-induced surface oxygen vacancies, and reported that the structure of the TiO_2 surface changed upon UV irradiation and the contact angle decreased. TiO_2 consists of six coordinated Ti atoms and three coordinated O atoms in the bulk. However, on the surface, it comprises five coordinated Ti atoms and two coordinated O atoms. The atomic arrangement is illustrated in Figure 5. When the surface of TiO_2 is irradiated with light from a UV-C lamp, oxygen vacancies are possibly generated at the two coordinated bridging sites, converting Ti^{4+} into Ti^{3+} . Consequently, these defects increase the affinity of the OH^- ions and form a hydrophilic surface on the TiO_2 films.

Figure 4. Ti 2p XPS profiles (A) before UV irradiation and (B) after UV irradiation.

Figure 5. Atomic arrangement with the generation of surface oxygen vacancies.

Based on the above theory, comparing the profiles in Figure 4A,B, for Ti 2p_{1/2} and 2p_{3/2}, the Ti³⁺ content distinctly increased, whereas the Ti⁴⁺ content decreased with UV irradiation. The Ti 2p XPS data confirmed that Ti⁴⁺ is converted into Ti³⁺ under UV irradiation; the oxygen vacancies generated by UV-irradiation improve the hydrophilicity of the surface of the TiO₂ thin film.

3.2. Photoinduced Reconstruction of Ti–OH

Sakai et al. [26] proposed another theory for the formation of hydrophilic surfaces on TiO₂ films, according to which the photoinduced reconstruction of Ti–OH bonds occurs. They suggested that UV irradiation induces the reconstruction of hydroxyl groups on the surface. Positive holes are generated by UV irradiation, which can diffuse to the surface and get trapped at the lattice oxygen sites. Consequently, the binding energies of Ti and the lattice oxygen decrease, owing to which water molecules can be captured by this bond, leading to the formation of new hydroxyl groups. This subsequently improves the degree of hydrophilicity of the surface.

Figure 6 shows the O 1s XPS profiles. To confirm the reconstruction of Ti and OH, we also compared the O 1s spectra for the UV-irradiated and non-UV-irradiated samples. Figure 6A,B show the spectra obtained using the same samples as for Figure 4A,B. In the O 1s spectra, peaks for the O²⁻ species and OH species are observed at binding energies of 529.6 and 532.0 eV, respectively [27]. We compared the intensity ratios of OH to O in Figure 6A,B. The OH/O intensity ratio was 0.337 before UV irradiation and 0.368 after irradiation, indicating that the number of hydroxyl groups increased after UV-C irradiation. The water molecules rupture the bond between Ti and the lattice oxygen under UV irradiation, resulting in the reconstruction of hydroxyl groups. We believed that these additional hydroxyl groups enhanced the affinity for water, resulting in the formation of a hydrophilic surface.

3.3. Influence of Annealing on Water Contact Angle

Another method to form a hydrophilic surface on TiO₂ films is annealing; the obtained surface is termed a “thermoinduced hydrophilic” surface [28]. To study the influence of annealing on the hydrophilicity of the sample surfaces, the water contact angle and crystallinity of the samples were determined. Figure 7 shows the variation in the water contact angle under UV irradiation, and Figure 8 shows the XRD patterns of the TiO₂ thin films.

Figure 6. XPS spectra of O 1s (A) before UV irradiation and (B) after UV irradiation.

Figure 7. Variation in water contact angles of (A) Sample D (non-annealed) and H (annealed at 500 °C) and (B) Sample F (amorphous structure) and H (anatase structure).

Samples D and H were fabricated under the same deposition conditions, but sample H was annealed at 500 °C. As shown in Figure 7A, after annealing, the water contact angle decreased from 78.7° to 35.7°, indicating that annealing induced hydrophilicity on the surface. This phenomenon can be attributed to the following, based on previous research: (i) the effect of Ti³⁺ defect sites, (ii) organic degradation on the surface, and (iii) crystal phase transition [15,25]. Annealing produces Ti³⁺ defects on the TiO₂ surface, generating oxygen vacancies on the surface. The absence of oxygen atoms at the bridging-O site leads to the formation of two subsurface Ti³⁺ sites. Water molecules occupy these oxygen vacancies and generate OH groups, which adsorb to the surface, resulting in hydrophilicity on the surface of the TiO₂ films. Moreover, organic matter on the surface, such as carbon-based or nitrogen-based organic compounds, is largely removed by annealing. Another study confirmed through Fourier-transform infrared (FT-IR) analysis that annealing led to the decomposition of NH₃ on the surface of TiO₂ [29]. This led to the exposure of the surface of TiO₂ to water (the adsorbent), thereby improving the hydrophilicity of the thin films.

Figure 8. XRD pattern of (A) the TiO_x thin films (non-annealed) and (B) TiO_2 thin films (annealed at 500 °C).

3.4. Correlation of Crystallinity and Water Contact Angle

As shown in Figure 8B, annealing not only generated Ti^{3+} defect sites and decomposed organic matter, but also led to a crystal phase transition from an amorphous to anatase structure at 500 °C. When reactive sputtering Ti and O_2 is performed using DC sputtering, the energy of the sputtered target atoms is insufficient for crystallization in the rapidly growing TiO_2 , and it is fabricated into TiO_x structure; initially, TiO_x was annealed to form TiO_2 at 300 °C. However, although samples were annealed, they just had an amorphous structure. According to another study, although the RF sputtering system, with which it is easier to form crystallinity than when using DC sputtering, was used, samples had an anatase structure at 400 °C and maintained the anatase structure up to 650 °C [18]. Hence, all samples were annealed at 500 °C for 3 h to form the anatase structure [30,31]. Figure 8B confirms the formation of anatase TiO_2 through the (101), (200), (105), and (211) peaks. However, samples E and F did not show these peaks in the XRD data, even after annealing. We suggest two reasons as to why sample E did not form an anatase structure. One is the low input power during deposition. When a high sputtering power is supplied, the target atoms possess a high kinetic energy and can migrate to suitable lattice sites [32]. Sample E was prepared with an input power of 100 W; however, an anatase structure was not formed. In the FTS system, the sputtered atoms possess a lower energy than those in other deposition methods, because the atoms that use energy to escape from the plasma region are deposited on the substrate. However, as mentioned earlier, FTS enables the fabrication of high-quality thin films. Therefore, we adjusted the input power from 100 to 150 W to supply enough energy to the target atoms, so that the thin films could easily grow and nucleate.

Although we increased the input power and performed annealing at 500 °C, sample F did not show any peaks in the XRD data. We suggest that this is because of the thickness of the film. In a previous study, Mukherjee et al. studied the intensity of the Raman and integral intensity of the XRD (101) peak, and they proposed that the XRD intensity depends on the thickness [31]. In other words, sample F has insufficient thickness (45.5 nm) to reveal the crystallinity. Consequently, we believe that such samples require a high sputtering power and annealing at approximately 500 °C to form the anatase structure.

We compared the contact angle of sample F, in which crystallinity was not observed, to that of sample H, in which the crystallinity was most pronounced, in order to investigate the effect of crystallinity on the hydrophilicity (Figure 7B). The two samples initially exhibited similar contact angles; however, as the UV irradiation time increased, the anatase TiO₂ sample exhibited a lower contact angle than the amorphous TiO₂ sample. This is because anatase TiO₂ (101) would form the OH species on the surface from H₂O gas present in atmosphere under UV irradiation. In other words, the transition in the crystal structure from amorphous to anatase improved the hydrophilicity of the TiO₂ films [18,33].

3.5. Crystal Size and Surface Structure of TiO₂ Films

The crystallite size of the samples was calculated by the Scherrer equation based on the XRD data in Figure 8B [34]. The Scherrer equation can be written as follows:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

According to this equation, β , the full width at half maximum (FWHM), is inversely related to the crystallite size τ . Therefore, a large FWHM, i.e., a broad XRD pattern, implies a small crystallite size. Based on the average of the (101) and (200) peaks in Figure 8B, it was confirmed that the crystallite sizes depend on the deposition time (sample G: 29.25 nm, sample H: 37.32 nm). We studied the surface structure through SEM images. Figure 9A,B show the morphologies of sample C and sample G, while Figure 9C,D show those of sample D and sample H. Both samples exhibit a smooth and homogeneous surface.

Figure 9. Surface SEM image of samples before and after annealing: (A) sample C (before), (B) sample G (after), (C) sample D (before), and (D) sample H (after).

3.6. Optical Properties and Sustainability of TiO₂ Films

The optical properties of TiO₂ were measured using a UV/Vis spectrometer, and the optical bandgap energy was determined. Figure 10A,B show the UV/Vis results before and after annealing, respectively. Sample D shows the highest transmittance in the visible-light region before annealing, while sample H shows the same after annealing. The average transmittances in the visible region (400–700 nm [35]) are 79.1% for sample D and 78.7% for sample H. There is no significant difference in the transmittance before and after annealing.

The plot of data reveals interference fringe, indicating that the surface of the films is homogeneous and smooth, as can be seen from the surface SEM image [36]. The optical bandgap energy was also evaluated by the Tauc plot and is shown in Figure 10B, assuming that the absorption product $\alpha h\nu$ is given the following [37]:

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^n \quad (5)$$

where α_0 is a fixed material constant; $h\nu$ is the photon energy ($= 1240/\lambda$); E_g is the optical bandgap energy; and n is the power coefficient, which can be 3, 2, 3/2, or 1/2 depending on the type of transition (indirect forbidden, indirect allowed, direct forbidden, or direct allowed, respectively). As noted by Zakrzewska, anatase TiO_2 possibly permits indirect allowed and direct forbidden transitions [38]. We used the equation for an indirect allowed transition to calculate the Tauc plot. The highest bandgap was 3.6 eV for sample F and sample E and the lowest bandgap was 3.3 eV for sample H. Thus, this optical bandgap energy indicates that a photoreaction of TiO_2 occurs under UV wavelength.

Figure 10. UV/Vis spectra of (A) TiO_x thin films (non-annealed) and (B) TiO_2 thin films (annealed at 500 °C), and Tauc plot of TiO_2 .

After fabricating a hydrophilic surface on the TiO_2 films, we finally verified whether the hydrophilicity would be sustained under sunlight (UV light constitutes 3%–5% of the solar spectrum) [39]. To evaluate the sustainability of the films under sunlight, the changes in the optical properties and water contact angles of the samples after UV irradiation were determined. The experimental process for this evaluation is illustrated in Figure 11. Sample H, on which a hydrophilic surface was formed by annealing and UV irradiation, was used for this evaluation. The sample was stored in a dark room for five weeks, and then irradiated under sunlight when the weather was sunny. The water contact angle was measured every two hours. Figure 12 shows that the water contact angle decreases with increasing sunlight irradiation time, from 35.7° to 15.2° in 8 h. Therefore, we believe that the TiO_2 thin films fabricated by FTS can sustain their hydrophilic surfaces under sunlight.

Figure 11. Schematic illustrating the procedure of the sustainability evaluation.

Figure 12. Variation in water contact angle with solar irradiation times.

4. Conclusions

TiO₂ films were deposited by an FTS system and hydrophilic surfaces were obtained by annealing the films at 500 °C and by UV irradiation. We investigated the influence of annealing and UV irradiation on the water contact angle using XPS and crystallinity data. XPS data revealed that Ti⁴⁺ is converted to Ti³⁺ and the Ti–OH bond is reconstructed under UV irradiation. The annealed TiO₂ films exhibited an amorphous or anatase structure depending on the input power and thickness of the sample; further, their hydrophilicity was affected by the crystallinity. Films with an anatase structure exhibited a lower contact angle than those with an amorphous structure as the irradiation time increased. No significant change was observed in the visible-light transmittance before annealing or UV irradiation. Post restoration of its hydrophilic property by placing the sample in a dark room, the contact angle of the hydrophilic surface decreased to 15.2° with 8 h of sunlight exposure. Thus, the results indicate that the hydrophilicity of TiO₂ thin films is sustained under natural sunlight. From these results, it is expected that it can be applied to the surface of the sensor or the solar module.

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