



Enhanced Hydrophilic Property of TiO₂ Thin Film Deposited on Glass Etched with O₂ Plasma

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TiO₂ films were deposited on glass substrates with and without O₂ plasma etching by using the RF-magnetron sputtering method. We focused on the effect of surface structure on the photoinduced hydrophilic properties of TiO₂ films, fabricated on different surface conditions according to the presence or absence of the O₂ plasma treatment on glass substrates. The wettability and photoinduced hydrophilic properties of the TiO₂ films were investigated according to the changes in water contact angles under UV light irradiations with a very low intensity of 0.1 mW/cm². The photoinduced hydrophilic properties on the TiO₂ formed above the plasma treated glass were also superior to those on the TiO₂ formed above the bare glass. This enhanced TiO₂ film has been used practically for self cleaning and anti-fogging glasses.

Keywords: TiO₂, Self cleaning, Hydrophilic, Plasma etching, RF-magnetron sputtering

1. INTRODUCTION

Titanium dioxide (TiO₂) has been well known as an efficient photocatalyst material [1-4]. When ultra-violet (UV) light is irradiated on, electron and hole pairs are generated in the TiO₂ and they, respectively, reduce and oxidize adsorbates on the surface, generating radical species such as O₂ and OH. These radicals can decompose most organic compounds [5,6], and extensive research has been performed on TiO₂ in terms of applications for water and air purification [7].

In particular, the generation by UV illumination of a super-hydrophilic TiO₂ surface with a water contact angle (WCA) of 0° has attracted significant attention [8-13]. This material has been successfully applied as a transparent super-hydrophilic coating with anti-fogging [14] and self-cleaning properties [15].

In general, the wettability of a solid surface is well known to be governed by both the chemical composition and the geometrical microstructure of the surface [16].

In this work, the glass substrates are etched with O₂ plasma prior to the coating of TiO₂ in order to form the geometrical microstructure on the TiO₂ surface, and the microstructure dependence of TiO₂ thin films on the hydrophilic property is investigated. In particular, we focused on the effect of surface structure on the photoinduced hydrophilic properties of TiO₂ films, fabricated on different surface conditions of glass substrates according to the presence or absence of O₂ plasma etching. The sputtered TiO₂ film has been used practically for glass with self-cleaning and anti-fogging properties.

2. EXPERIMENTS

A radio frequency (RF) magnetron sputtering apparatus was used to fabricate TiO₂ film on soda-lime glass substrates with a size of 50×50 mm². After thoroughly stirring TiO₂ powder (99.99%) for 2 hours using a Ball-Mill, the powder was calcined at 500°C in

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the air for 2 hours. The calcined powder was molded as a cylindrical type pellet with a diameter of 2 inch and a height of 50 mm with a pressure of 11 tons. This pellet was used as a sputter target for TiO₂ films. Prior to deposition of TiO₂, the glass substrates were etched with plasma for 30 min in an oxygen atmosphere of 2×10⁻² Torr. The applied RF-power was fixed at 50 W for all films. The thicknesses of the TiO₂ films deposited on the glass substrates were measured from 50 nm to 200 nm, which were controlled by deposition time. The surface morphologies of TiO₂ films were analyzed using a field emission scanning electron microscopy (FESEM: Jeol Co.). The hydrophilicity and crystalline phase of TiO₂ films were investigated by measuring the water contact angle and X-ray diffraction (XRD: Co.) pattern, respectively. The contact angle measurements were carried out at room temperature using a Kruss DSA100 goniometer following a very standard and commonly used experimental procedure as reported in the literature [17].

The photoinduced hydrophilic conversion was evaluated according to the changes in the water contact angle under UV light irradiation using black light bulbs (BLB, Toshiba lighting & Technology). The UV light irradiation was stopped when measuring the water contact angle. The photo-catalytic activity of the film was assessed for the degradation of commercial gear oil (TOYOTA gear oil super GL-5). Prior to UV irradiation, the as-deposited films were contaminated by dropping oil onto the surfaces and wiping to ensure even coverage. The samples were washed with distilled water, to remove excess oil. During the photo-catalytic degradation, the humidity was maintained at 40% RH at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the thickness change as a function of deposition time for TiO₂ films deposited on glass substrates with RF-power of 50 W. It is shown that the thicknesses of TiO₂ films linearly increase as deposition time increases. Therefore, the deposition rate calculated from the slope of Fig. 1 is found to be 1.67 nm/min. In addition, the XRD pattern of the 200 nm-thick TiO₂ film is represented in the inset of Fig. 1. Since no crystalline peaks are observed in the X-ray diffraction pattern, the as-deposited TiO₂ films have an amorphous structure.

Figure 2 shows the change of WCA as a function of thickness for TiO₂ films deposited on the glass etched with oxygen plasma. For comparison, the change of WCA as a function of thickness for TiO₂ films deposited on the bare glass substrate is also shown. In the case of TiO₂/glass, the WCAs are almost constant with a thickness of between 17° and 18°. However, TiO₂ films deposited on the etched glass show lower WCAs of between 4° and 7° compared with those of TiO₂/glass. This enhanced hydrophilic property of TiO₂ film can be explained by Wenzel's model. Consider a rough solid surface with a typical size of roughness detail smaller than the size of the droplet, as shown in Fig. 3(a). For a droplet in contact with a rough surface without air pockets, referred to as a homogeneous interface (or Wenzel's model), according to Wenzel, the contact angle is given as follows.

$$\cos\theta = R_f \cos\theta_0 \tag{1}$$

- R_f : roughness factor
- θ : contact angle for the rough surface
- θ_0 : contact angle for a smooth surface

Figure 3(b) shows that the dependence of the contact angle on the roughness factor is predicted for various values of θ_0 , based on Wenzel's model. The model predicts that a hydrophobic sur-

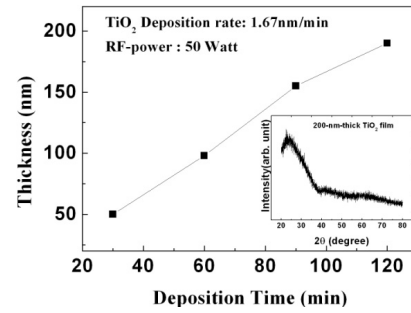


Fig. 1. Changes of thickness as a function of deposition time for TiO₂ films deposited on the glass substrate under RF-power of 50 watt.

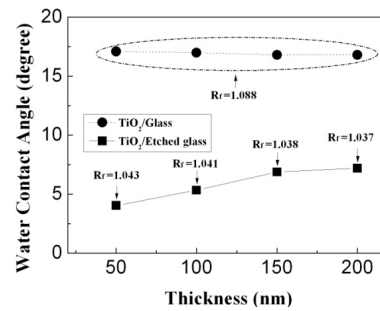


Fig. 2. Change of WCA as a function of thickness for TiO₂ films according to presence (rectangular) or absence (circle) of oxygen plasma etching on the surface of glass substrates.

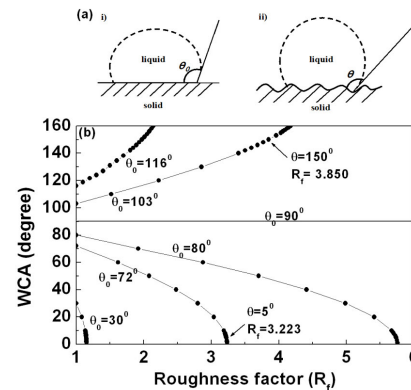


Fig. 3. (a) Schematic of a liquid droplet in contact with (i) a smooth solid surface (contact angle, θ_0) and (ii) a rough solid surface (contact angle, θ). And (b) the dependence of the contact angle on the roughness factor is predicted for various values of θ_0 , based on Wenzel's model, where, $\theta_0=30^\circ$ (for a flat glass), $\theta_0=72^\circ$ (for a flat p-Si), $\theta_0=103^\circ$ (for a flat p-Si coated with PTFE), and $\theta_0=116^\circ$ (for a flat Al surface).

face ($\theta > 90^\circ$) becomes more hydrophobic with an increase in R_f , and that a hydrophilic surface ($\theta < 90^\circ$) becomes more hydrophilic with an increase in R_f .

Thus, the enhanced hydrophilic property of TiO₂ films deposited on the etched glass shown in Fig. 2 is attributed to the surface roughness formed after the plasma etching on the glass substrate. The roughness is observed in Fig. 4, which shows SEM images for (a) unetched glass and (b) etched glass and TiO₂ films with various thicknesses deposited on them. In the case of glass substrate, nano protrusions are formed on the surface of the glass after plasma etching, as shown in Fig. 4(b), which is com-

pared to the smooth surface of unetched glass.

A calculated roughness factor of the etched glass, based on Wenzel's model, is 1.088, where WCAs of unetched and etched glass surfaces are considered to be $28^\circ (= \theta_0)$ and $16^\circ (= \theta)$, respectively. These roughness factors will decrease with increasing thickness of TiO_2 layer because the thicker films may further alter the geometrical microstructure formed on the etched glass surface. The roughness factors corresponding to each thickness of TiO_2 films deposited on the etched glass, based on Wenzel's model, are described in Fig. 2, where WCA (θ_0) on the flat TiO_2 surface was considered to be 17° , which is an average value of WCAs for TiO_2 films deposited on the unetched glass, showing that the TiO_2 film has a hydrophilic surface.

The photoinduced hydrophilic properties are shown in Fig. 5, where Fig. 5(a) indicates the changes in water contact angles on both films under UV light irradiation with intensity of 0.1 mW/cm^2 . The reciprocal of water contact angles is also plotted against irradiation time, a linear relationship is obtained, as shown in figure (b). This straight line is defined as the rate constant for the hydrophilic conversion process. A distinguished difference was observed in the critical water contact angles and the rate constants for the hydrophilic conversion between TiO_2 /etched glass films and the TiO_2 /glass films. It is clear that the TiO_2 /etched glass film became highly hydrophilic compared to the TiO_2 /glass film. This indicates that the photoinduced hydrophilic reaction of the TiO_2 surface was also enhanced by oxygen plasma etching on the surface of the glass.

When TiO_2 is illuminated with UV light, electron and hole pairs are generated, which reduce and oxidize adsorbates on the surface, respectively. These reactions are known as photocatalysis [1-6].

Thus, the enhanced photoinduced hydrophilic reaction TiO_2 film deposited on the etched glass in comparison with that of TiO_2 coated on the bare glass may be attributed to an increase of the light receiving area due to the nano protrusions formed on the glass after the plasma etching, which results in an increase of photogenerated electron and hole pairs.

Because of the high hardness, adhesion, and highly photoinduced hydrophilic reaction of the sputtered TiO_2 film, the sputtered TiO_2 films are suitable for application in many outdoor uses, especially in the exterior rear view mirrors and windshields of automobiles (see Fig. 6). The TiO_2 films have been used practically for large-area glass with anti-fogging [14] and self-cleaning properties [15]. These products promise a clear view on rainy days.

4. CONCLUSIONS

In this work, TiO_2 films were deposited on glass substrates with and without O_2 plasma etching by using the RF-magnetron sputtering method, and the wettability and sensitization of photocatalytic reactions were investigated. We focused on the effect of surface structure on the photoinduced hydrophilic properties of TiO_2 films, fabricated on different surface conditions of glass according to the presence or absence of the O_2 plasma etching. The surface structures of TiO_2 films were observed from SEM images and their wettability and photoinduced hydrophilic properties were investigated according to the changes in water contact angles under UV light irradiations with intensity of 10 mW/cm^2 . As a result, the enhanced hydrophilic property of TiO_2 film deposited on the etched glass can be explained by the increase of roughness factor calculated, based on Wenzel's model.

On the other hand, the photoinduced hydrophilic properties on the TiO_2 formed above the etched glass were also superior to those on the TiO_2 formed above bare glass. The enhancement of

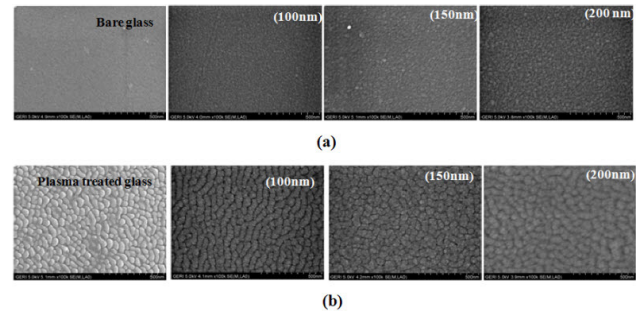


Fig. 4. SEM images for surfaces of (a) bare and TiO_2 films with various thicknesses coated on the bare glass and (b) plasma treated glass and TiO_2 films with various thicknesses coated on the plasma treated glass.

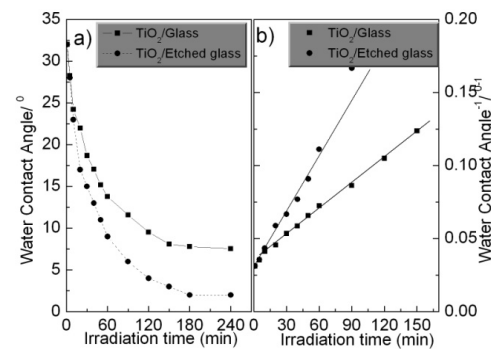


Fig. 5. (a) Change in water contact angles of the 200 nm-thick TiO_2 films deposited on the etched glass and unetched glass under 0.1 mW/cm^2 UV light irradiation. (b) The TiO_2 layers were coated at a thickness of 200 nm reciprocal of the water contact angles of both films.

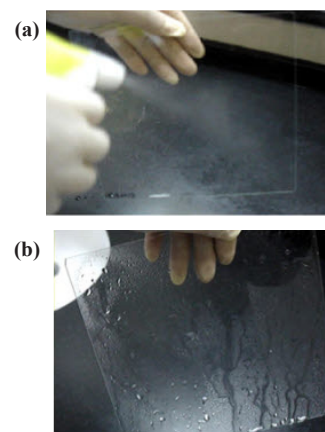


Fig. 6. Comparison between the visibilities of (a) the plasma treated glass with TiO_2 layer and (b) that of bare glass.

the hydrophilic conversion of the TiO_2 film/etched glass can be explained by an increase of the light receiving area due to the surface structure formed on the surface of the TiO_2 film, resulting in further accumulation of photogenerated electrons and hole pairs at the surface of TiO_2 . The sputtered TiO_2 films are applicable for outdoor uses because of the high hardness, adhesion to the glass substrates, and highly photoinduced hydrophilic reac-

tion, the TiO₂ films have been used practically for glass with self-cleaning and anti-fogging properties. Therefore, we suggest that these products can be applied to the exterior rear view mirrors and windshields of automobiles to ensure clear vision on rainy days.

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