

Wettability control on surface of titanium dioxide by mechanical rubbing method

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Abstract We found that a position-controlled high-speed hydrophilic to hydrophobic transition was possible on polycrystalline anatase-TiO₂ surfaces applying a new mechanical rubbing method. This method is to rub the TiO₂ surface softly with clean paper. This new kind of mechanical rubbing treatment realized switching of the hydrophilic surface with water contact angle 5.7° to a hydrophobic surface with 67.9° angle within 5 sec at arbitrary position on the surface. We have verified that, if the super-hydrophilic TiO₂ surface is mechanically rubbed, the quantity of hydroxyl groups on the surface decreases. This fact demonstrates that the mechanical rubbing process to be discussed in this paper can change the photoexcited structure of the TiO₂ surface.

Keywords [Photocatalysis, Sputtering, Titanium oxide, Water wetting]

1 Introduction

Titanium dioxide (TiO₂) is well known as a photocatalyst because of the strong oxidizing power of photogenerated holes.¹⁾ When the TiO₂ is illuminated by UV light with higher energy than the TiO₂ band gap, an inter-band electron-hole pair is formed. Such excited electrons or holes can diffuse to the TiO₂ surface and generate various radicals or ions which can decompose organic compounds absorbed on the TiO₂ surface.²⁾ Its photoinduced self-cleaning properties in particular have attracted considerable attention in various application fields. In recent years, photoinduced hydrophilicity has been observed on rutile and anatase TiO₂ surfaces, where the water contact angle decreased to less than 1° after UV illumination in air.³⁾ This phenomenon was elucidated as the formation and extinction of a surface hydroxyl group^{4, 5)} and widely noticed, especially from the viewpoint of application in the surface wettability control technologies. However, a period of several weeks' storage in the dark was necessary for the complete recovery of the hydrophobic surface of TiO₂, which was too long for

a processing time in the busy surface wettability control technologies.

In this paper we present a new surface wettability control method, which enables a very fast (< 5 sec) hydrophilic to hydrophobic transition of TiO₂ surfaces. This surface wettability control method also realized a position selective surface wettability control; hydrophobic drawings could be made on hydrophilic surfaces.

2 Experimental

TiO₂ films were deposited by DC reactive magnetron sputtering (CFS-4ES, Shibaura Mechatronics Corporation) on SiO₂-coated soda-lime-silica glass at substrate temperature of 300°C using Ti metal target (99.99%, Techno Fine). The deposition was carried out at total gas pressure of 3.0 Pa and DC sputtering power was kept at DC 200W. Ar was used as the sputtering gas, and O₂ was used as a reactive gas. The partial pressure of O₂ was defined as the quantity of O₂ [Pa] ÷ sputtering pressure [Pa] × 100 [%]. O₂ partial of O₂ was defined as the quantity of O₂ [Pa] ÷ sputtering

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pressure [Pa] x 100 [%]. O₂ partial of O₂ was defined as the quantity of O₂ [Pa] ÷ sputtering pressure [Pa] x 100 [%]. O₂ partial pressure were maintained 40%, where the target surface should be fully oxidized and the reactive sputtering mode was in “oxide mode” (O₂ flow was over the “transition region”).⁶⁾ A layer thickness of 100nm was deposited by controlling the deposition rate. Film thickness was measured by a surface profiler (Alpha Step KLA Tencor). Film composition and crystallinity were analyzed by infrared spectrometry (ATR-FTIR) (IFS-120HR Bruker) and X-ray diffraction (XRD) (MultiFlex, Rigaku). The photo-induced hydrophilicity was evaluated by measurement of contact angles to pure water after UV illumination (black light lamp, 1000μW/cm²) with the maximum intensity centered at 365 nm. Water contact angle measurements were performed at room temperature in ambient atmosphere using a contact angle meter (DM-300, Kyowa Interface Science) with an experimental error of less than 1°.

3 Results and discussion

Fig. 1 show the spectrum of the film obtained using XRD. Only peaks that are characteristic of anatase were observed in the spectral region associated with the anatase structure (101) at around 2θ=25.2°. It is clear that the peaks is (101) oriented polycrystalline anatase, because the observed position of the diffracted beam is in good agreement with that of anatase TiO₂ described in the ASTM card. The initial water contact angle of the anatase TiO₂ film was approximately 83.3° before UV irradiation.

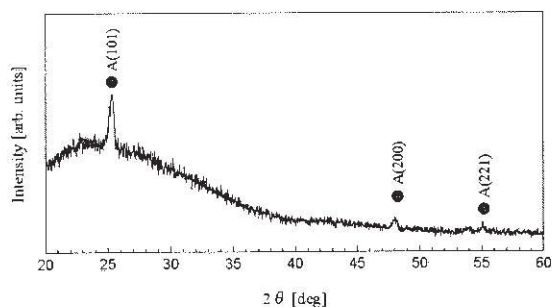


Fig.1 XRD patterns of TiO₂ films deposited on the SiO₂-coated soda-lime-silica glass.

Fig.2a shows the change in the water contact angle after UV illuminated. Two water droplets spread out on the film, both showing identical water contact angle of 5.3 and 5.9°. Soft rubbing by clean paper five times across the water spread on the left was done, and dried spontaneously.

This quick mechanical rubbing process, which lasted for only 5 sec or less, surprisingly reconverted the rubbing region into a hydrophobic one, while leaving the rest of the surface hydrophilic (Fig.2b). A spread of water with contact angle 5.7° and a droplet of water with 67.9° angle were clearly observed side-by-side on the same surface. It was previously reported that a storage period of two to three weeks in the dark was necessary for the complete reversion of TiO₂ surfaces from hydrophilic to hydrophobic^{4, 5, 7)}. However, this new mechanical rubbing method provides immediate as well as position-controlled reversion into a hydrophobic surface. This means that drawings can

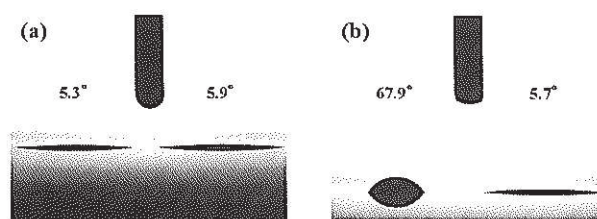
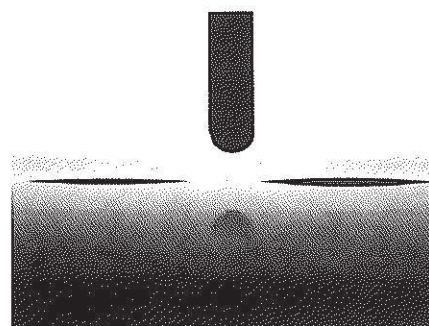


Fig.2 Photographs of the water droplets contacting on the surface of 1h UV irradiated. (a) Before mechanical rubbing process, (b) After mechanical rubbing process.



F.g3 Effect that nitrogen gas treatment process gives to the water contact angle of TiO₂ film.

be made by hydrophobic paintbrush on hydrophilic canvases, and this technology would be of great importance in many fields, such as the surface wettability control technologies. Rubbing or just pushing of a hydrophilic surface several times using carefully cleaned metallic or glass sticks also induced this transition, excluding the possibility that this transition was induced by hydrophobic contaminants from clean papers. Instead of mechanical rubbing, blowing away the water spread from the surface by nitrogen gas was performed. However, this process was no longer effective for contact angle recovery, as shown in Fig.3. Blowing by air was also not effective for the contact angle recovery. Next, the water spread was left until spontaneous evaporation completed, revealing that this process was also ineffective.

The surface hydrophobic/hydrophilic switching on TiO_2 surfaces was attributed to the formation and extinction of a surface hydroxyl group^{4, 5, 8)}. Fig. 4 shows the ATR-FTIR difference spectrum obtained by subtracting a rubbing sample from a no rubbing sample. The spectrum from 1500 to 4000 cm^{-1} is magnified in Fig. 5. Absorption peaks corresponding to Ti-O bending and stretching vibrations were observed at approximately 800 cm^{-1} . Absorption peaks corresponding to Ti-OH bending and stretching vibrations were also observed at approximately 1600 cm^{-1} and 3400 cm^{-1} , respectively. Absorption peaks corresponding to Ti-CH bending and stretching vibrations were observed at approximately 2800 cm^{-1} . This spectrum is quite similar to a standard FTIR spectrum.^{9, 10)} The results show that the no rubbing films include a large number of OH groups, whereas the rubbing film added contains no OH groups. N. Sakai et al. have reported that the mechanism responsible for the TiO_2 super-hydrophilicity parallels that of generally known oxidation decomposition type photocatalysis, in that photoexcitation or exposure to light generates pairs of positive electron holes. They inferred that, when the TiO_2 surface enters a super-hydrophilic state, some of the positive electron holes react with the crystal lattices of TiO_2 itself, not with materials adsorbed to the TiO_2 surface. More specifically, positive holes release lattice oxygen, simultaneously with the reduction of tetravalent titanium by electrons, thus generating oxygen gas and oxygen deficiencies

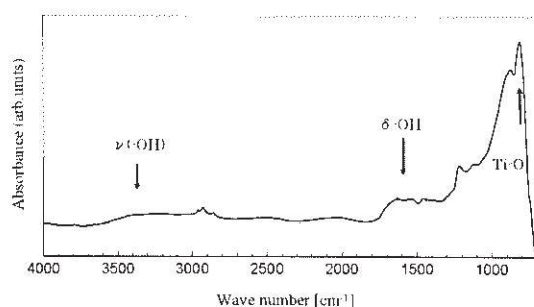


Fig.4 ATR-FTIR difference spectrum obtained by subtracting rubbing film from no rubbing film.

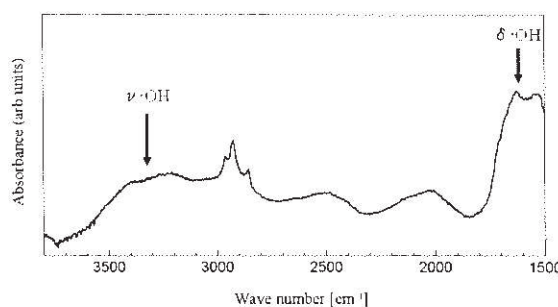


Fig.5 ATR-FTIR difference spectrum obtained by subtracting rubbing film from no rubbing film. Expanded spectrum from 1500 to 4000 cm^{-1} .

(V_o^{2+}).

It is thought that, although the oxygen deficiencies and the reduced Ti^{3+} are usually oxidized and mitigated immediately by oxygen in the air, the oxygen deficiencies might bind with dissociated water, not oxygen, if the photoexcited hydrophilic reaction is in progress^{4, 5)}. As a result, a hydrated state ($\text{Ti}^{3+}\text{-OH}$) occurs. This hydrated state is different from a state ($\text{Ti}^{4+}\text{-OH}$) in which water is adsorbed on the surface of TiO_2 , in that it is a metastable state in the air and that, if the irradiation by light ceases, oxygen in the air reacts with the surface of TiO_2 , turning this metastable hydrated state into a hydrophobic state^{4, 5, 7)}. It is inferred from the reaction mechanism so far described that “mechanically rubbing the super-hydrophilic surface,” which we term a mechanical rubbing process, exerted a strong influence on the oxygen deficiencies and the reduced Ti^{3+} , and that this

influence caused the hydrophilic process to be retarded. However, at the present moment, the manner by the mechanical rubbing process influences the oxygen deficiencies and the reduced Ti^{3+} is unknown.

4 Conclusion

In summary, we found that a position-controlled high-speed hydrophilic to hydrophobic transition was possible on poly crystalline anatase- TiO_2 surfaces applying a new mechanical rubbing method. This method can change the surface from hydrophilic to hydrophobic only by softly rubbing the surface with clean paper. This mechanical rubbing process promise a new technology, especially in field of the surface wettability control technologies, since this method enables the voluntary control of the local water contact angle on the TiO_2 surface.

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