

Enhancement of Photoinduced Highly Hydrophilic Conversion on TiO₂ Thin Films by Introducing Tensile Stress

Tatsuo Shibata, Hiroshi Irie, and Kazuhito Hashimoto*

Research Center for Advanced Science and Technology, The University of Tokyo,
4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

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Utilizing differences in the thermal expansion from TiO₂, we fabricated sputtered anatase TiO₂ thin films with tensile stress and without stress on NEX-C and quartz substrates, respectively. The differences in the photocatalytic oxidation activity and photoinduced hydrophilicity on these anatase TiO₂ thin films are reported. The photocatalytic oxidation activities, which were identical for the two films, were evaluated by the initial photodegradation rate constants of *cis*-9-octadecenoic acid ($k = 1.7 \pm 0.1 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ for NEX-C and $1.6 \pm 0.1 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ for quartz.). The photoinduced hydrophilic conversion rate, which was evaluated by monitoring the changes in water contact angles, however, was 5 times greater for the film with tensile stress than for the film without residual stress. Because the surface morphologies and the charge-separation efficiencies of these two thin films are nearly identical, it is concluded that the hydrophilic conversion on the anatase thin film can be enhanced by introducing tensile stress.

Introduction

TiO₂ has attracted much attention as a photocatalyst in recent years because of its potential in coating materials.¹ TiO₂ in thin films reveals a photoinduced highly hydrophilic conversion on its surface.^{2,3} In addition, irradiating with UV light causes conventional photocatalytic oxidation reactions on the film surface.^{4–9} These reactions result in useful properties such as self-cleaning, antifogging, and antibacterial¹⁰ functions.

Thin films deposited onto substrates involve residual stress, such as tensile and compressive stress, due to the thermal stress caused by the mismatch in the thermal expansion coefficients between the deposited film and the substrate or the intrinsic stress from the deposition technique or both. The residual stress affects not only the mechanical properties but also other physical properties that are caused by a deformation in a crystal structure.^{11–13} Furthermore, the presence of residual stress greatly affects phenomena involving structural changes such as stress corrosion of the glass.¹⁴

Therefore, it is expected that the photochemical properties, including photocatalytic oxidation processes and photoinduced hydrophilic conversion, of TiO₂ are also affected by residual stress. In the present study, the photochemical activities of TiO₂ thin films, which were prepared with residual tensile and without residual stress using a radio frequency (rf) reactive magnetron sputtering method, were investigated.

Experimental Section

TiO₂ films were deposited onto SiO₂-coated quartz and SiO₂-coated NEX-C (main components are SiO₂, Al₂O₃, and Li₂O, OHARA Inc., Japan) substrates by a rf reactive magnetron sputtering method at 400 °C, 1.0 Pa (Ar/O₂ = 60:40). Under these conditions, the residual stress originated mainly from

thermal stress. Thus, using substrates with different thermal expansion coefficients (α) from anatase TiO₂ ($\alpha = 8.6 \times 10^{-6}/^\circ\text{C}$)¹⁵ can control the residual stress. NEX-C, which has a negative thermal expansion coefficient $\alpha = -2.0 \times 10^{-6}/^\circ\text{C}$, and quartz, which has a *c*-plane $\alpha = 13.4 \times 10^{-6}/^\circ\text{C}$, were the substrates.

The crystal phases of the films were identified by glancing incidence X-ray diffraction (RINT-2100, Rigaku Denki Ltd., Japan) at a constant incident angle of 0.8° using Cu K α radiation operated at 40 kV and 30 mA. The residual stress was characterized by X-ray diffraction analysis (XRD) and Raman spectroscopy. The microstructures of these films were observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Approximately 10 mg of *cis*-9-octadecenoic acid was also deposited onto the 6.25 cm² samples. The photocatalytic oxidation activity of these films was measured by the weight changes of *cis*-9-octadecenoic acid under UV light irradiation with intensity of 1 mW/cm² (approximately 300–400 nm) using a cylindrical black-light lamp. The weight was determined averaging three different measurements from the same sample. Details of the setup have been given elsewhere.⁹ According to ref 9, the initial kinetics of the photocatalytic oxidation reaction for several adsorbed organic compounds (including *cis*-9-octadecenoic acid) under the present conditions can be assumed to be a pseudo-zero-order reaction. Therefore, the photocatalytic oxidation activity was evaluated by the initial slope. To confirm the reproducibility of the obtained initial slope, the same experiments were carried out three times in total, and the rate constant (k) was determined averaging three slopes. The photoinduced hydrophilicity was evaluated by measuring the water contact angles (θ) with a water contact angle meter (CA-X, Kyowa Interface Science, Japan) while irradiating with UV light (0.1 mW/cm²). The UV intensities of the light sources were corrected by a UV radiometer (UVR-2, TOPCON, Japan). Averaging at least five different measurements from the same sample determined the contact angle value.

* To whom correspondence should be addressed. Tel: +81-3-5452-5080. Fax: +81-3-5452-5083. E-mail address: kazuhito@fchem.chem.t.u-tokyo.ac.jp.

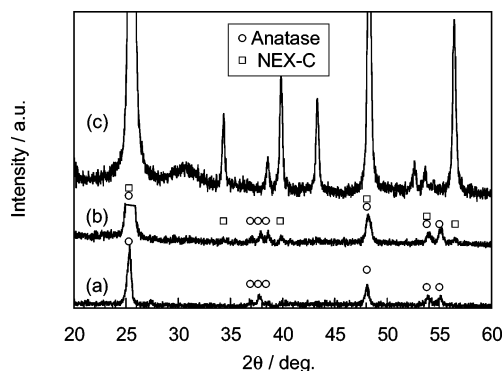


Figure 1. XRD patterns of (a) a thin film on a quartz substrate, (b) a thin film on NEX-C, and (c) NEX-C.

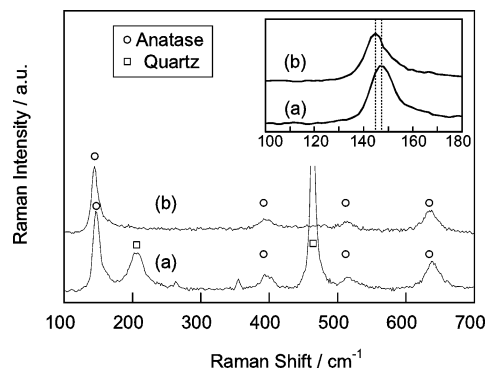


Figure 2. Raman spectra of (a) a thin film on a quartz substrate and (b) a thin film on NEX-C.

Results and Discussion

The glancing incidence XRD patterns shown in Figure 1 revealed that these two films had homogeneous anatase crystalline phases with identical crystallinity. Furthermore, a detailed analysis of the anatase (101) peak at $2\theta = 25.27^\circ$ on a quartz substrate by $\theta/2\theta$ measurements revealed a small variation from $2\theta = 25.281^\circ$ (JCPDS#21-1272). Residual stress in a film distorts the crystal lattice, which leads to a peak shift of 2θ .¹⁶ A peak shift to a smaller angle indicates compressive stress, while a shift to a larger angle indicates tensile stress. The observed value $2\theta = 25.27^\circ$ suggests that the TiO_2 film on the quartz substrate had negligible compressive stress. The peak shift of TiO_2 near $2\theta = 25.3^\circ$ on the NEX-C could not be analyzed because the peak overlapped with the NEX-C substrate.

Figure 2 shows the Raman spectra of these two TiO_2 films prepared on quartz and NEX-C. Four major Raman features were observed.¹⁷ It is noteworthy that the strongest peak of the Eg mode of the TiO_2 on NEX-C showed a characteristic shift to lower wavenumber compared to the quartz substrate. The shift of the peak position can be related to the stress state of the film.¹⁸ In that work, Exarhos et al. demonstrated that the shift of the Raman peak position is proportional to the TiO_2 film stress. The presence of a compressive stress usually shifts the peak to higher wavenumber, while tensile stress lowers the peak position. Therefore, the Raman result revealed that TiO_2 on NEX-C had a relatively large tensile stress compared to the almost neutral state of the quartz substrate. A phonon confinement effect due to the reduced size of the anatase crystals may explain the shifts from the Eg mode of anatase single crystal (144 cm^{-1}).¹⁹ The residual stress was caused by a thermal bimetal effect between the film and the substrate, which was determined by the following equation: $\sigma = E_f(\alpha_f - \alpha_s)\Delta T$, where E_f is Young's modulus of the film and α_f and α_s are

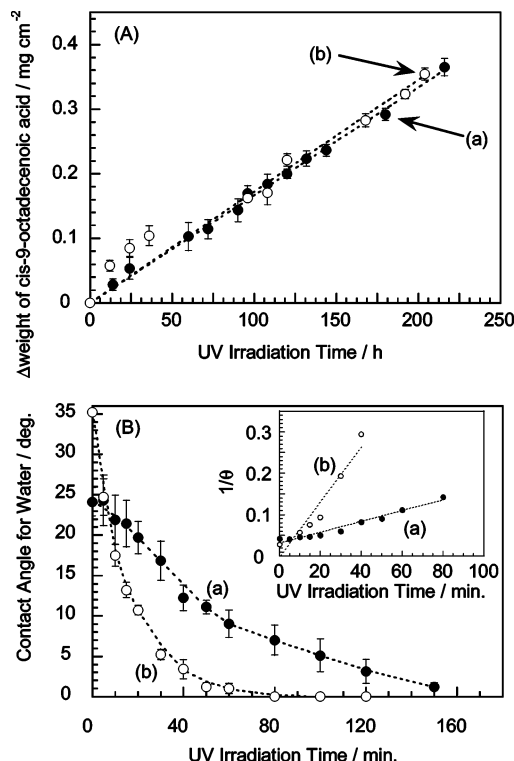


Figure 3. Weight changes (A) of *cis*-9-octadecenoic acid adsorbed onto (a) a thin film on quartz substrate and (b) a thin film on NEX-C when irradiating with 1 mW/cm^2 UV light and (B) changes in water contact angles when irradiating with 0.1 mW/cm^2 UV light (a) a thin film on a quartz substrate and (b) a thin film on NEX-C.

thermal expansion coefficients of the film and the substrate, respectively. Because α_f for anatase is $8.6 \times 10^{-6}/^\circ\text{C}$, it is reasonable that TiO_2 on NEX-C ($-2.0 \times 10^{-6}/^\circ\text{C}$) has a relatively large tensile stress and TiO_2 on quartz ($13.4 \times 10^{-6}/^\circ\text{C}$) has minimal neutral stress.

AFM and SEM indicated that the surface morphologies (grain size, roughness) of these films were very similar. The grain sizes were identical and around 30–40 nm. The measured surface roughness were $R_a = 5.8$ and 8.7 nm for the NEX-C and quartz substrates, respectively.

Figure 3A shows the decomposition of *cis*-9-octadecenoic acid as an example of the first measurement out of three for each film. The initial slope estimated the degradation rate constants (k) to be $k = 1.7 \pm 0.1\text{ }\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ (NEX-C) and $1.6 \pm 0.1\text{ }\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ (quartz). Irradiating with UV light generates electrons and hole pairs in the bulk TiO_2 that diffuse to the surface and then react with organic materials adsorbed onto the surface directly or via various active oxygen species.^{20–24} Thus, these films showed nearly identical rates for the photocatalytic oxidation reaction, which suggests that both films had the same number of photogenerated holes at the surfaces.

Figure 3B demonstrates the changes in the water contact angle on the films when illuminating with UV light (0.1 mW/cm^2). We previously reported that plots of the reciprocal of the water contact angles versus irradiation time have a linear relationship, as shown in the inset of Figure 3B and that the slope is the hydrophilicizing rate constant.²⁵ The conversion rate of NEX-C substrate's sample ($k_f = 6.6 \times 10^{-3}\text{ deg}^{-1}\cdot\text{min}^{-1}$) was at least 5 times greater than that of the quartz substrate's sample ($k_f = 1.3 \times 10^{-3}\text{ deg}^{-1}\cdot\text{min}^{-1}$). This observation clearly suggests that the NEX-C film exhibited a significantly higher activity for the photoinduced hydrophilic conversion when irradiating with the same intensity of UV light.

We have proposed a mechanism for the photoinduced wettability change.²⁵ It was concluded that an increase in the hydroxyl groups on the TiO₂ surface, which are formed by the photogenerated holes, increases the hydrophilicity.²⁶ Thus, structural changes in the surface crystal lattice caused the photoinduced hydrophilic conversion of TiO₂. In the viewpoint of the conformational change, it can be presumed that the hydrophilic conversion involves a volume change ($\Delta V > 0$) on the outer surface because the number of hydroxyl groups increase. The reverse process proceeds gradually without UV illumination because the highly hydrophilic state is metastable and the hydrophilic state converts to the hydrophobic state. Therefore, the Gibbs free energy change (ΔG) for the photoinduced hydrophilic conversion is positive. A stress effect for the conformation change cannot be neglected when the TiO₂ film has a large residual stress. We believe that the tensile stress decreases the value of ΔG so that the hydrophilic conversion readily proceeds under the same conditions.

Conclusion

In the present study, anatase thin films were deposited onto two different substrates. The films showed different states of residual stress, according to the differences in the thermal expansion coefficients from TiO₂. The quartz substrate had negligible stress, while the NEX-C had tensile stress. Although the films had identical photocatalytic activities, the surfaces significantly differed in the photoinduced hydrophilic conversion activities. These results suggest that the residual stress affected the hydrophilic conversion reaction and that the presence of the tensile stress enhanced the reaction because this reaction involves a conformation change in the outer surface of TiO₂. The residual stress is an important factor influencing highly sensitive photoinduced hydrophilicity of a film.

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References and Notes

- (1) Fujishima, A.; Hashimoto, K.; Watanabe, T. *TiO₂ Photocatalysis Fundamentals and Applications*; BKC Inc.: Tokyo, 1999.
- (2) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431.
- (3) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Adv. Mater.* **1998**, *10*, 135.
- (4) Sitkiewitz, S.; Heller, A. *New J. Chem.* **1996**, *20*, 233.
- (5) Sopyan, I.; Watanabe, M.; Murasawa, S.; Hashimoto, K.; Fujishima, A. *J. Photochem. Photobiol., A* **1996**, *98*, 79.
- (6) Sawunyama, P.; Jiang, L.; Fujishima, A.; Hashimoto, K. *J. Phys. Chem. B* **1997**, *101*, 11000.
- (7) Romeas, V.; Pichat, P.; Guillard, C.; Chopin, T.; Lehaut, C. *New J. Chem.* **1999**, *23*, 365.
- (8) Romeas, V.; Pichat, P.; Guillard, C.; Chopin, T.; Lehaut, C. *Ind. Eng. Chem. Res.* **1999**, *38*, 3878.
- (9) Minabe, T.; Tryk, D. A.; Sawunyama, P.; Kikuchi, Y.; Hashimoto, K.; Fujishima, A. *J. Photochem. Photobiol., A* **2000**, *137*, 53.
- (10) Kikuchi, Y.; Sunada, K.; Iyoda, T.; Hashimoto, K.; Fujishima, A. *J. Photochem. Photobiol., A* **1997**, *106*, 51.
- (11) Wang, X.; Kencke, D. L.; Liu, K. C.; Tasch, A. F.; Register, L. F.; Barnerjee, S. K. *J. Appl. Phys.* **2000**, *88*, 4717.
- (12) Gleskova, H.; Wagner, S. *Appl. Phys. Lett.* **2001**, *79*, 3347.
- (13) Ohta, S.; Sekiya, T.; Kurita, S. *Phys. Status Solidi B* **2001**, *233*, 265.
- (14) Michalske, T. A.; Freiman, S. W. *Nature* **1982**, *295*, 511.
- (15) Meagher, E. P.; Lager, G. A. *Can. Mineral.* **1979**, *17*, 77.
- (16) The principal residual stress can be estimated from lattice strain ($\epsilon = [(d - d_0)/d_0]$); $\sigma = -E_f \epsilon / \nu_f$, where d and d_0 are the lattice spacing in the film and the bulk, respectively, E_f is Young's modulus, and ν_f is Poisson's ratio.
- (17) Ohsaka, T.; Izumi, F.; Fujiki, Y. *J. Raman Spectrosc.* **1978**, *7*, 321.
- (18) Exarhos, G. J.; Hess, N. J. *Thin Solid Films* **1992**, *220*, 254.
- (19) Bersani, D.; Lottici, P. P.; Ding, X.-Z. *Appl. Phys. Lett.* **1998**, *72*, 73.
- (20) Howe, R. F.; Grätzel, M. *J. Phys. Chem.* **1987**, *91*, 3906.
- (21) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735.
- (22) Ishibashi, K.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *Electrochem. Commun.* **2000**, *2*, 207.
- (23) Ishibashi, K.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Photochem. Photobiol., A* **2000**, *134*, 139.
- (24) Tatsuma, T.; Tachibana, S.; Fujishima, A. *J. Phys. Chem. B* **2001**, *105*, 6987.
- (25) Sakai, N.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Phys. Chem. B* **2003**, *107*, 1028.
- (26) Sakai, N.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Phys. Chem. B* **2001**, *105*, 3023.