Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 180 (2006) 75–79

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photoinduced surface roughness variation in polycrystalline TiO_2 thin films

Ken-ichi Katsumata[a], Akira Nakajima[a,*], Tadashi Shiota[a], Naoya Yoshida[b], Toshiya Watanabe[b], Yoshikazu Kameshima[a], Kiyoshi Okada[a]

[a] *Department of Metallurgy and Ceramics Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152-8552, Japan*

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

Received 9 June 2005; received in revised form 15 August 2005; accepted 27 September 2005

Abstract

Photoinduced microstructural changes in transparent anatase thin films with large-grain polycrystallites (−200 nm) were evaluated using atomic force microscopy (AFM). Films were subjected to a vacuum ultraviolet (VUV) pretreatment before heating at 500 °C. Photoinduced wettability of the films was subsequently confirmed. Upon UV illumination, the surface image became blurred with an apparent increased surface roughness. The image sharpened gradually as the surface returned to its initial state. This microstructural surface change is most pronounced at grain boundaries.

Keywords: Surface morphology; Surface roughness; Titanium dioxide; Wetting

---

1. Introduction

Titanium dioxide (TiO_2) is a well-known photocatalyst material [1]. Electron–hole pairs are generated when TiO_2 is illuminated by ultraviolet (UV) light, thereby both reducing and oxidizing adsorbates on the surface, and producing free radicals, such as OH and O_2^-. These radicals will decompose most organic compounds or even bacteria [2–6]. Numerous previous studies have demonstrated the efficacy of TiO_2 for water and air purification [7].

Photoinduced hydrophilicity and associated conventional applications of the TiO_2 photocatalyst were discovered in 1995 [8–11]. A highly hydrophilic surface is generated when UV light is illuminated onto a TiO_2 surface. This surface exhibits both antifogging and self-cleaning properties. Aside from fundamental investigations into this phenomenon [12–23], polycrystalline TiO_2 film coatings have been applied onto various commercial products to use this property: automobile side mirrors, window films, exterior tiles, highway wall panels, and others [24].

A friction force microscopy (FFM) study of TiO_2 rutile single crystals revealed that UV illumination can produce a unique microdomain structure with a contrast difference in the surface [8]. This contrast is attributable to a microstructural distribution of hydrophilic and hydrophobic domains. Further study clarified that the domains align particularly along the direction of the bridging-site oxygens, which are the most reactive sites for producing vacancies by photo-illumination [9,10]. Although the detailed mechanism of the generation of this specific structure remains unclear, these microdomains are considered to act as flow channels for water and oil, analogously to a two-dimensional capillary, thereby creating an amphiphilic surface.

Recently, Horiuchi et al. used a totally reflected X-ray in-plane diffraction method to confirm lattice expansion of a rutile single crystal under UV illumination [25]. They revealed that the rutile (1 1 0) lattice spacing and its full width half maximum (FWHM) increase gradually during UV illumination, but decrease abruptly when UV illumination ceases. Moreover, surface potential studies using Kelvin force microscopy (KFM) revealed that the dipole moments presumably induced by atomic displacements caused by the UV illumination generate a localized surface charge. These results suggest that photoinduced hydrophilicity of a rutile single crystal accompanies structural change.

---

* Corresponding author. Tel.: +81 3 5734 2525; fax: +81 3 5734 3355.
E-mail address: anakajim@ceram.titech.ac.jp (A. Nakajima).

1010-6030/$ – see front matter
doi:10.1016/j.jphotochem.2005.09.023

A polycrystalline TiO_2 thin film typically comprises anatase grains without specific orientation. The anatase phase does not consist of bridging-site oxygen. Therefore, change in the rate at which the surface becomes hydrophilic at each anatase grain is proposed as the mechanism of the wettability change in this film [20]. It is assumed that the hydrophilic conversion rate differs among grains in the film because of variations in crystallite face orientation in the surface. It is further assumed that the microstructural distributions of hydrophilic and hydrophobic domains are attainable under proper UV illumination conditions.

Shibata et al. investigated the stress effect on photoinduced hydrophilicity of polycrystalline anatase thin films using substrate materials with different thermal expansion coefficients [19]. They prepared polycrystalline anatase films using sputtering and found that external tension enhances photoinduced hydrophilicity, whereas compression inhibits it. Moreover, they recently revealed that a polycrystalline anatase film surface hardens under UV illumination [26,27]. These results suggest that photoinduced hydrophilicity of polycrystalline anatase films also accompanies structural expansion. However, volume expansion behavior of polycrystalline anatase films under UV illumination has not been observed directly. Two main reasons are the difficulties inherent in preparing a pure large anatase single crystal and in detecting the small amount of volume change caused by the fine grain size of the polycrystalline anatase film.

Very recently, we developed a transparent sol–gel derived polycrystalline anatase film with large grain size and diminished surface roughness using vacuum ultraviolet (VUV) illumination before heat treatment [28]. The photoinduced structural expansion might be enhanced because of large grain size if it occurs. The present study examines the sequential surface microstructural change in the film by UV illumination using tapping-mode atomic force microscopy (AFM).

2. Experimental

Reagent-grade titanium isopropoxide ($Ti(OC_3H_7)_4$; Kanto Chemical Co. Inc., Tokyo, Japan) was mixed with a commercial titanium isopropoxide solution (NDH-510C, mixing ratio = 6.1 ml: 40 ml; Nippon Soda Co. Ltd., Tokyo, Japan), for better reproducibility of dense TiO_2 thin films. After stirring for 15 min in air, the solution was hydrolyzed by adding a drop of nitric acid solution (1.44 ml, pH 1; Wako Pure Chemical Industries Ltd., Tokyo, Japan) while stirring at room temperature to form the coating solution. The amount of water for hydrolysis was four-fold in excess of the titanium concentration in the mixed alkoxide. The hydrolyzed solution was then coated on a cleaned Si (1 0 0) wafer (Aki Corp., Miyagi, Japan) by dip-coating at a fixed pulling rate of 0.5 mm/s in dry air. After coating, the film was exposed to dry ozone for 60 min to remove organic compounds in the coated film. Then, the film was illuminated by vacuum ultraviolet (VUV) light using a Xe excimer lamp (172 nm wavelength; Ushio Inc., Tokyo, Japan) for 30 min at room temperature in N_2 atmosphere. The illumination intensity of the VUV light in N_2 was 18 mW/cm^2. The film was fired at 500 °C for 1 h in air after VUV illumination.

Crystal phase, thickness, refractive index at 550 nm, and band gap of deposited films were evaluated using X-ray diffraction (XRD, PW-3050; Philips Co., Amsterdam, Netherlands), ellipsometry (V-VASE; J. A. Woollam Co. Inc., Tokyo, Japan) and UV-VIS spectrophotometry (UV-3100PC; Shimadzu Corp., Tokyo, Japan). The film's surface composition was evaluated using X-ray photoelectron spectroscopy (XPS, 5500MC; Perkin-Elmer, Physical Electronics, Eden Prairie, MN). Mg Kα radiation was used, and the photoelectrons were collected at a takeoff angle of 45° with respect to the film surface fixed in a molybdenum holder. Surface microstructure and friction were characterized using AFM (MMAFM-2; Digital Instruments, CA, USA). Water wettability conversion of the TiO_2 thin film by UV illumination was examined by the sessile drop method using a commercial contact angle meter (CA-X; Kyowa Interface Science Co. Ltd., Saitama, Japan). The experimental error of the measurement was 1°. The droplet size used for the measurements was 2 μl. Ultraviolet illumination was carried out using a fluorescent black-light bulb with UV intensity of 1.0 mW/cm^2. Once the water contact angle was saturated under the UV illumination for a long period, the film was stored within a vessel filled with clean air in a dark place; the hydrophobic conversion behavior of the film during this storage was also evaluated.

The film was then set on the stage of the AFM. Initial surface structure and roughness were evaluated with tapping mode AFM using a Si cantilever. Subsequently, UV illumination (0.7 mW/cm^2) was performed for 150 s using a Hg–Xe lamp with an optical-fiber coupler. After illumination, the surface structure and roughness were recorded 13 times successively without additional UV illumination. Each measurement required about 10 min for recording. Consequently, the overall measurement period was about 2.5 h.

3. Results and discussion

A polycrystalline TiO_2 thin film prepared using the process described above was composed only of anatase with random crystallite orientation. The respective film thickness, refractive index at 550 nm, and the band gap were 104 nm, 2.20, and 3.22 eV. Analysis using XPS with etching revealed that a negligible amount of carbon and nitrogen remained in the films. Fig. 1 shows AFM image of the prepared film. Grain size and average surface roughness were around 200 and 0.47 nm respectively. The large crystallite grains in the film were composed of several smaller grains, indicating that the large grain is on the way of grain growth. It is noteworthy that this large grain formation does not occur if the starting alkoxide is only a commercial titanium isopropoxide solution or a reagent-grade titanium isopropoxide. Detailed discussion on the relationship between film preparation conditions and microstructure evolution will be described elsewhere [29].

Fig. 2 shows the time dependence of the water contact angle of the film under 1.0 mW/cm^2 UV illumination (Fig. 2(a)) and in the dark (Fig. 2(b)). The contact angle of water on the film became less than 10° within 4 min. The contact angle was saturated to almost 2.5° after 2-h UV illumination. Then, the contact angle increased gradually during dark storage after halting the

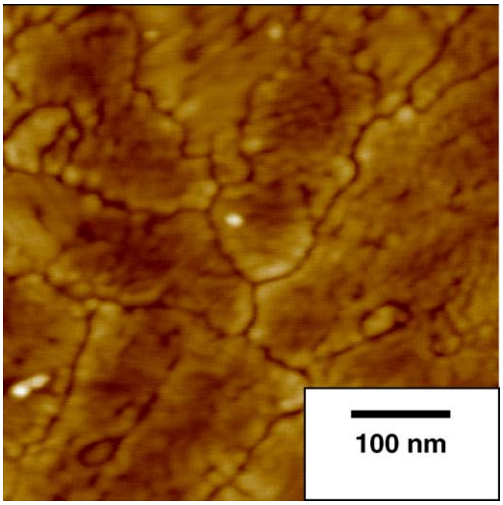

Fig. 1. AFM image of prepared anatase thin film.

UV illumination. These results indicate that the films exhibit photoinduced wettability conversion like normal polycrystalline anatase films.

Fig. 3 shows the AFM images recorded sequentially (1–13 times) after 0.7 mW/cm^2 UV illumination for 150 s. Fig. 4 shows the average surface roughness measured for each sample corresponding to the AFM images shown in Fig. 3. The initial surface roughness of the area shown in this figure was 0.47 nm (evaluated in 500 nm × 500 nm). Once UV light was illuminated, the surface image was blurred with increasing apparent surface roughness and the contrast at the grain boundary, mainly around large grains. That trend continued until the fourth image, and surface roughness increased to 1.08 nm. After that, the image sharpened gradually as the surface returned to its initial state. However, even after recording 13 times, the surface had not become identical to that of the initial state; the contrast difference remained at the small grain boundary. The changes of the AFM images (Fig. 3) and the roughness (Fig. 4) were not observed when the same experiment was carried out on the uncoated Si substrate or Pyrex glass. Based on the film thickness (ca. 100 nm) and roughness change order (0.6–0.7 nm), it is hard to explain this result from thermal expansion of the film (thermal expansion coefficients are $3.8–9.5 \times 10^{-6}$ (*a*-axis and *b*-axis) and $7.8–20.4 \times 10^{-6}$ (*c*-axis) at temperatures of 50–690 °C [30]).

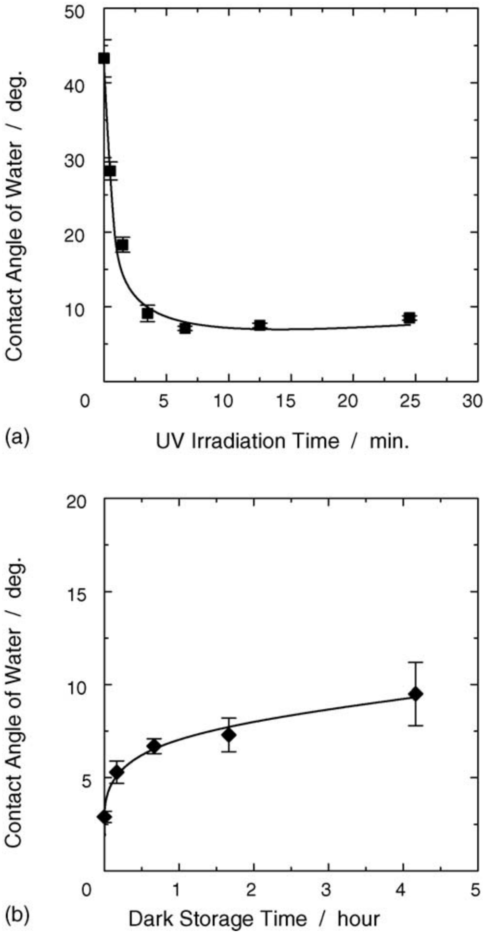

Fig. 2. Contact angle change of water on the polycrystalline anatase thin, film: (a) under 1.0 mW/cm^2 UV illumination and (b) during dark storage.

This result implies that the change in the image is triggered by UV illumination and attributable to the continuous change of height and depth of the film shown in Fig. 5. Before UV illumination, the film surface is stable and a clear image is obtainable. Once UV illumination was carried out, the proper distance between the cantilever and the film surface is hard to feed-back into the AFM because of the continuous change of the film's height and depth. For that reason, the image was blurred. This structural change is gradually terminated and the scanning image returns to its initial state when UV illumination was stopped. It is noteworthy that the contrast change is more apparent at the grain boundary than inside the grain. Anatase crystals exhibit strong thermal expansion anisotropy [30]. Consequently, high residual stress was generated during cooling after firing at the grain boundary. Because the polycrystalline film contains anatase with random orientation, some grain boundaries are under tension, but some grain boundaries suffer compression before UV illumination. Therefore, the contrast change is remarkable at the grain boundary and image brightness depends on the magnitude of the local stress.

Following UV illumination, surface roughness continues to increase until the fourth image in Fig. 3. However, it remains unclear whether this increase results from the time required for the photoinduced volume change under a residual stress field in this film, or other reasons such as the time for the diffusion of holes that are generated in the film, which can diffuse from near the substrate to the film surface. Further investigation is required to clarify the cause of this phenomenon.

We attempted this observation on normal films – those without VUV pretreatment – but we could not obtain a clear microstructure change in AFM images such as that seen in the film with VUV pretreatment. A plausible explanation of this result is the difference of stress grading from substrate to film surface caused by microstructure difference. The current work demonstrates that photoinduced roughness changes occur in polycrystalline anatase thin films with large grains. This result suggests that photoinduced structural change can occur on anatase like rutile.

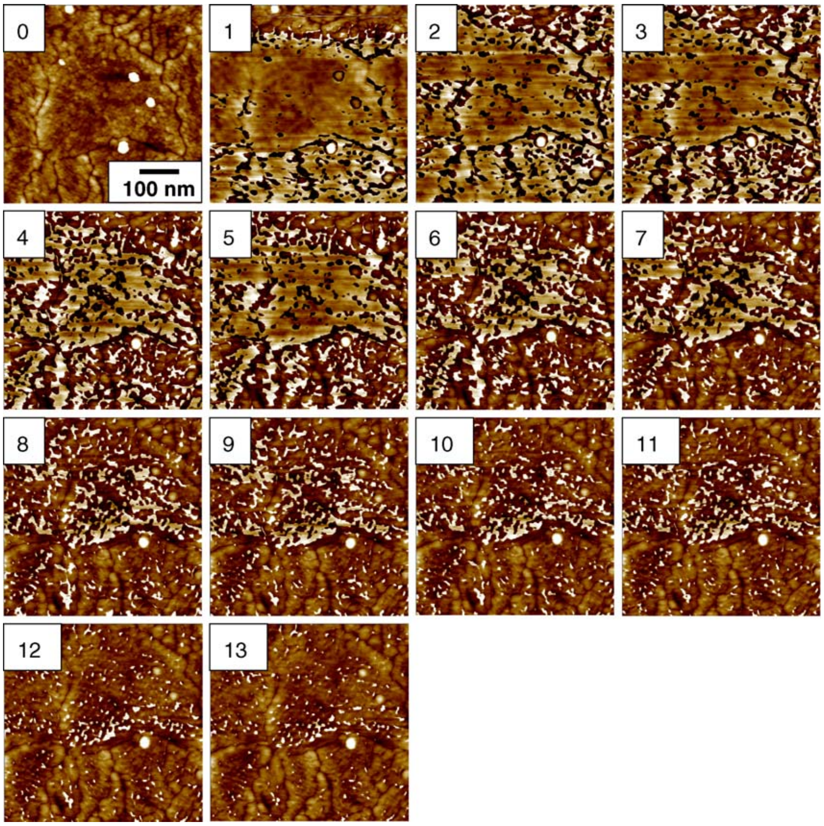

Fig. 3. Changes of microstructure on the surface of polycrystalline anatase thin film after 0.7 mW/cm^2 UV illumination for 150 s. AFM images were recorded each time (1–13 times) sequentially after UV illumination.

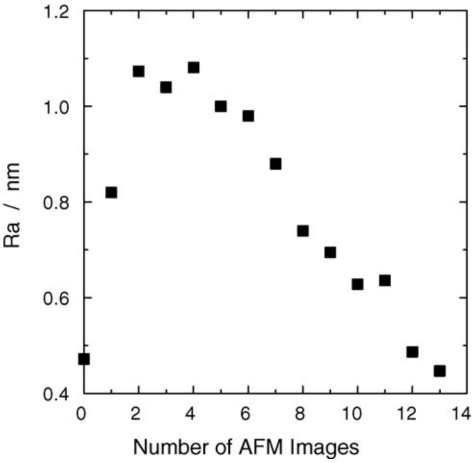

Fig. 4. Change of apparent roughness on the surface of polycrystalline anatase thin film after 0.7 mW/cm^2 UV illumination for 150 s. The apparent roughness was measured each time (1–13 times) sequentially after UV illumination.

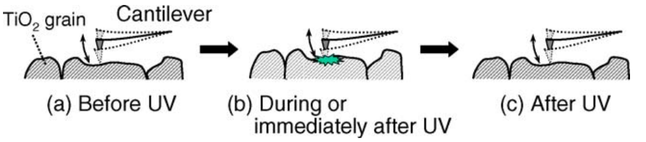

Fig. 5. Schematic illustration of the relationship between an AFM cantilever and a film surface: (a) before UV illumination, (b) during or immediately after UV illumination and (c) after UV illumination.

Fig. 6 shows the time dependence of the water contact angle of the film under the same conditions of AEM image recordings in Fig. 3. Before UV illumination, the water contact angle was about 40°. This state corresponds to the initial image (number: 0) in Fig. 3. The contact angle was less than 10° when UV illuminated onto the film surface for 150 s. Then, the contact angle increased gradually during dark storage. Although the contact angle saturates gradually, it still continues to increase even after 2 h. The result depicted in Fig. 3 corresponds mainly to

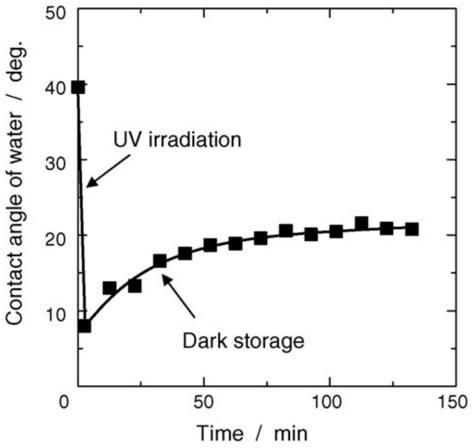

Fig. 6. Contact angle change of water on the film under the same conditions as those depicted in Fig. 3. 0.7 mW/cm^2 UV illumination for 150 s and during dark storage (same conditions as those of the AFM experiment in Fig. 3).

hydrophobic conversion behavior, and there will be a correlation between photoinduced wettability conversion and photoinduced surface roughness variation. Detailed analyses of this relationship are under way and will be presented in future reports.

4. Conclusions

Photoinduced microstructural changes of transparent anatase polycrystalline thin films with large grain size (−200 nm) were evaluated using AFM. The film was obtained using vacuum ultraviolet (VUV) pretreatment before heating at 500 °C, and photoinduced wettability conversion of the film was confirmed. Once UV light was illuminated, the surface image was blurred with increasing apparent surface roughness, then, the image sharpened gradually as the surface returned to its initial level. This surface-microstructure change is remarkable at the grain boundary.

Acknowledgment

The authors are grateful to Mr. C.D. Madhusoodana for critical reading and editing of the manuscript. The present research is supported in part by a grant from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (#17029017).

References

[1] K. Honda, A. Fujishima, Nature 238 (1972) 37–38.

[2] T. Kawai, T. Sakata, Nature 286 (1980) 474–476.

[3] J. Schwitzgebel, J.G. Ekerdt, H. Gerischer, A. Heller, J. Phys. Chem. 99 (1995) 5633–5638.

[4] K. Sunada, T. Watanabe, K. Hashimoto, J. Photochem. Photobiol. A: Chem. 156 (2003) 227–233.

[5] K. Sunada, Y. Kikuchi, K. Hashimoto, A. Fujishima, Environ. Sci. Technol. 32 (1998) 726–728.

[6] C.C. Trapalis, P. Keivanidis, G. Kordas, M. Zaharescu, M. Crisan, A. Szatvanyi, M. Gartner, Thin Solid Films 433 (2003) 186–190.

[7] A. Mills, S. LeHunte, J. Photochem. Photobiol. A: Chem. 108 (1997) 1–35.

[8] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Nature 388 (1997) 431–432.

[9] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Adv. Mater. 10 (1998) 135–138.

[10] R. Wang, N. Sakai, A. Fujishima, T. Watanabe, K. Hashimoto, J. Phys. Chem. B 103 (1999) 2188–2194.

[11] T. Watanabe, A. Nakajima, R. Wang, M. Minabe, S. Koizumi, A. Fujishima, K. Hashimoto, Thin Solid Films 351 (1999) 260–263.

[12] J. Yu, X. Zhao, Q. Zhao, G. Wang, Mater. Chem. Phys. 68 (2001) 253–259.

[13] A. Nakajima, S. Koizumi, T. Watanabe, K. Hashimoto, J. Photochem. Photobiol. A. Chem. 146 (2001) 129–132.

[14] N. Sakai, A. Fujishima, T. Watanabe, K. Hashimoto, J. Phys. Chem. B 105 (2001) 3023–3026.

[15] J.C. Yu, J. Yu, W. Ho, J. Zhao, J. Photochem. Photobiol. A. Chem. 148 (2002) 331–339.

[16] M. Miyauchi, N. Kieda, S. Hishita, T. Mitsuhashi, A. Nakajima, T. Watanabe, K. Hashimoto, Surf. Sci. 511 (2002) 401–407.

[17] L. Sirghi, Y. Hatanaka, Surf. Sci. Lett. 530 (2003) L323–L327.

[18] N. Sakai, A. Fujishima, T. Watanabe, K. Hashimoto, J. Phys. Chem. B 107 (2003) 1028–1035.

[19] T. Shibata, H. Irie, K. Hashimoto, J. Phys. Chem. B 107 (2003) 10696–10698.

[20] A. Nakajima, S. Koizumi, T. Watanabe, K. Hashimoto, Langmuir 16 (2000) 7048–7050.

[21] R. Nakamura, K. Ueda, S. Sato, Langmuir 17 (2001) 2298–2300.

[22] J.M. White, J. Szanyi, M.A. Henderson, J. Phys. Chem. B 107 (2003) 9029–9033.

[23] C. Wang, H. Groenzin, M.J. Shultz, Langmuir 19 (2003) 7330–7334.

[24] A. Fujishima, K. Hashimoto, T. Watanabe, TiO_2 Photocatalyst, Fundamentals and Applications, BKC Inc., Tokyo, 1999, p. 66.

[25] T. Horiuchi, H. Ochi, K. Kaisei, K. Ishida, K. Matsushige, Mater. Res. Soc. Symp. Proc. 751 (2003) 145–148.

[26] T. Shibata, H. Irie, K. Hashimoto, Proceedings of the 10th Symposium on Recent Studies on Photocatalytic Reactions, 2003, p. 110 (in Japanese).

[27] T. Shibata, H. Irie, K. Hashimoto, Proc. Photocatal. 14 (2004) 24 (in Japanese).

[28] K. Katsumata, A. Nakajima, H. Yoshikawa, T. Shiota, N. Yoshida, T. Watanabe, Y. Kameshima, K. Okada, Surf. Sci. 579 (2005) 123–130.

[29] K. Katsumata, A. Nakajima, N. Yoshida, T. Watanabe, Y. Kameshima, K. Okada, Surf. Sci., in press.

[30] J.A. Kuszyk, R.C. Bradt, J. Am. Ceram. Soc. 56 (1973) 420–423.