

Thickness Effect in the Photocatalytic Activity of TiO₂ Thin Films Derived from Sol-Gel Process

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Abstract—TiO₂ films in various thicknesses were prepared by sol-gel method, and their photocatalytic activities in the decomposition of gaseous 2-propanol were evaluated. It was found that the photocatalytic activities of transparent TiO₂ films increase with the increase of film thickness: The photocatalytic activity of TiO₂ films in 670 nm-thickness was 3.7 times that of films in 70 nm-thickness. We proposed that the higher photocatalytic activities for the thicker TiO₂ films originate from the greater amount of photogenerated electron and hole pairs, which are transferred from the inside to the surface of TiO₂ films. We also provided some experimental evidences supporting this mechanism.

Key words: Photocatalyst, TiO₂, Thickness, Thickness Effect, Photocatalytic Film

INTRODUCTION

It has been known that TiO₂ demonstrates one of the highest photocatalytic activities among semiconductors for the elimination of organic pollutants in aqueous solution or in gas phase [Matthew, 1985; Nozik, 1978; Hoffmann et al., 1995; Chai et al., 2000; Lee et al., 2000; Fujishima et al., 1997; Anpo et al., 1997]. Especially, TiO₂ photocatalysts in thin film form have promising application for the decomposition of gas phase pollutants or as a self-cleaning smart material [Lee et al., 2001; Jung et al., 1997]. Moreover, TiO₂ surface presents super-hydrophilic character with an irradiation of light [Fujishima et al., 1997, 1998]. Hence, the TiO₂ thin films coated on window glass, light bulbs, ceramic tiles, or walls can purify the polluted air in the room, and can self-clean or defog their surfaces. For these industrial applications of photocatalytic TiO₂ films, many practical problems, such as fabrication of transparent TiO₂ films, adhesion to glass substrate, blocking of impurity migration from the substrate, determination of optimum film thickness, etc., have to be solved. Among them, in this work, we have focused on the correlation of photocatalytic activity with film thickness.

In the case of thin TiO₂ films, the photocatalytic reactions take place only on the surfaces. Thus, it is expected that the photocatalytic activity is irrelevant to the thickness of TiO₂ film, since the surface area of film is not appreciably affected by the change of thickness. However, it has been found that photocatalytic activity is strongly dependent on the thickness of film. In the literature, a few researchers reported on the thickness dependence on the photocatalytic activity of TiO₂ films [Yu et al., 2000; Cui et al., 1993], but they did not mention the reason why thicker films demonstrate higher photocatalytic activities in the photocatalytic oxidation reactions. In this work, we made a scrupulous observation on the photocatalytic behavior of TiO₂ films as a function of film thickness, and suggested a plausible mechanism. We also provided some experimental evidence supporting this suggestion.

EXPERIMENTAL

1. Preparation of TiO₂ Films

TiO₂ films were prepared by sol-gel method, as described in following sentences. Titanium tetraisopropoxide [Ti(OⁱPr)₄, Aldrich] was diluted in n-propanol, and two equivalents of 2,4-pentanedione (AcAc, Aldrich) were added dropwise to this solution at 0 °C. With this ligand exchange reaction, Ti(OⁱPr)₂(AcAc)₂ was synthesized. The concentration of Ti-precursor solution was then adjusted to 0.5 M by adding additional n-propanol. The prepared solution was spin-coated at 2,200 rpm, and subsequently baked at 350 °C. To obtain the desired thickness, spin-coating and baking cycles were repeated (About 70 nm-thickness was obtained by each coating cycle). Finally, baked films were heat-treated at 500 °C for 1 hr in oxygen environment to obtain crystallized structure and to get rid of carbon impurities in the TiO₂ film. Instead of Pyrex or sodalime glass, silica glass in 25 mm×25 mm was utilized as substrate, in order to avoid contamination in the fabricated TiO₂ film with a migration of alkaline or alkali earth metal ions.

2. Characterization of TiO₂ Films

The surface morphology and cross sectional image of TiO₂ films were observed by a field emission scanning electron microscope (FESEM, Hitachi S-4500). Glancing angle mode X-ray powder diffraction (XRD) patterns of the TiO₂ films were obtained by using a Philips diffractometer (PW3020) with a monochromated high intensity CuK_α radiation. Since the glancing angle is adjusted to as large as 5°, crystallographic information is not confined to the film surface, but comes from the whole medium of the film. From the atomic force microscope (AFM, TopoMetrix ACCUREX), the roughness of TiO₂ film was analyzed.

3. Evaluation of Photocatalytic Activity of TiO₂ Films

TiO₂ films prepared by sol-gel method in various thicknesses were tested as photocatalysts for the decomposition of 2-propanol in gas phase. The gas reactor system used for this photocatalytic reaction is described elsewhere.¹⁸ The net volume of gas tight reactor was 200 ml, and a TiO₂ film was located in the center of the reactor. The whole area of TiO₂ film (25 mm×25 mm) was irradiated by a 300

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W Xe lamp through the 2-inch diameter silica window on the reactor. After evacuation of the reactor, a stoichiometric amount of 2-propanol and water vapor was added (the partial pressures are 2.0 and 16 Torr, respectively). The reactor pressure was then controlled to 700 Torr by the addition of oxygen gas. Under these conditions, 2-propanol and H₂O remained in vapor phase. The gas mixtures in the reactor were magnetically convected during the irradiation. After the irradiation, every few minutes 0.5 ml of gas sample in the reactor was automatically picked up and sent to a gas chromatograph (Young Lin M600D) by using an autosampling valve system (Valco Instruments Inc., A60). For the detection of CO₂, a methanizer was installed between the GC column out-let and FID detector.

4. Photochemical Deposition of Au Particles on TiO₂ Films

AuCl₃ (Aldrich) was reduced to Au on the surface of TiO₂ films by photochemical decomposition. A 30 ml of a 5×10^{-4} M AuCl₃ aqueous solution was added to a silica reaction vessel. TiO₂ film was then immersed in this AuCl₃ aqueous solution, and the sample was irradiated by 15 sec with a 300 W Xe lamp. The irradiated TiO₂ film was thoroughly rinsed with distilled water, and the deposited Au particles on the surface of TiO₂ film were then observed with FESEM.

RESULTS AND DISCUSSION

Several TiO₂ thin films in the thickness of 70–670 nm were prepared by sol-gel method. FESEM images of TiO₂ film in about 300 nm-thickness deposited on silica glass are shown in Fig. 1. From

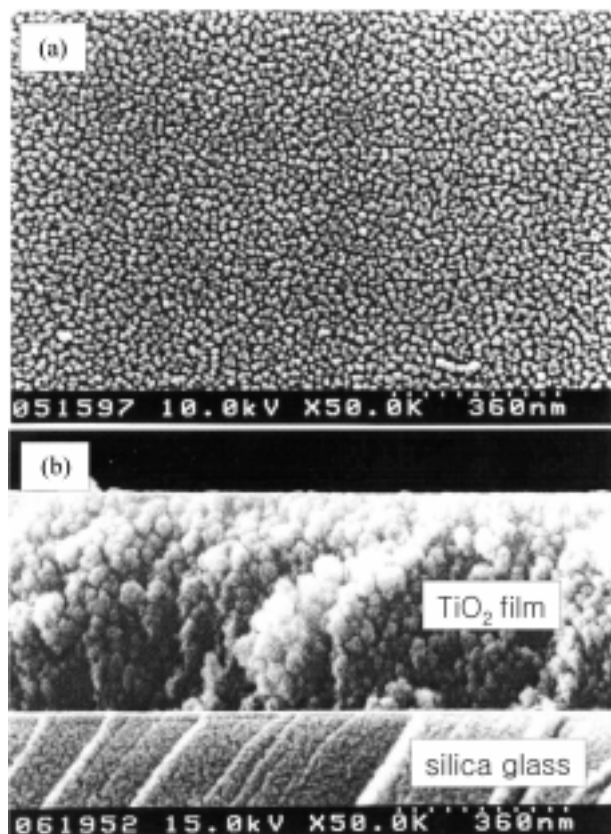


Fig. 1. FESEM images of TiO₂ film in 300 nm-thickness deposited on silica glass: (a) plan-view; (b) cross-sectional-view.

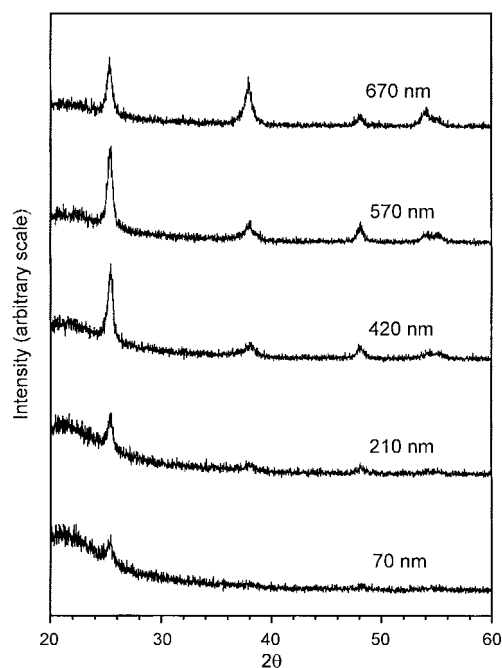


Fig. 2. XRD patterns of TiO₂ films in various thicknesses. Sol-gel derived TiO₂ films were annealed at 500 °C for 1 hr.

the plan-view and cross-sectional-view images, the grains in the TiO₂ films are spherical shape, and their diameters are 20–30 nm. XRD patterns in Fig. 2 indicate that TiO₂ films annealed at 500 °C in 1 hr are pure anatase phase regardless of film thickness.

We evaluated the photocatalytic activities of TiO₂ films whose thicknesses were in the range of 70–670 nm. Gaseous 2-propanol was utilized as a model compound for the evaluation of photocatalytic activity. It has been known that 2-propanol is primarily decomposed to acetone, and then finally decomposed to CO₂ and H₂O [Fujishima et al., 1997]. Thus, in this work, the photocatalytic activity

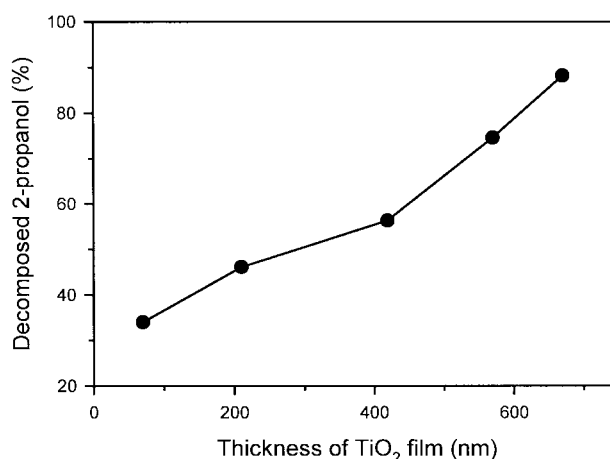


Fig. 3. Decomposition percentage of 2-propanol by the photocatalytic reaction with TiO₂ films as a function of film thickness (After 15 min of irradiation with 300 W Xe lamp, the decomposed percentage of 2-propanol was measured. The gas composition in the reactor: 2-propanol, 2.0 Torr; H₂O, 16 Torr; O₂, 682 Torr).

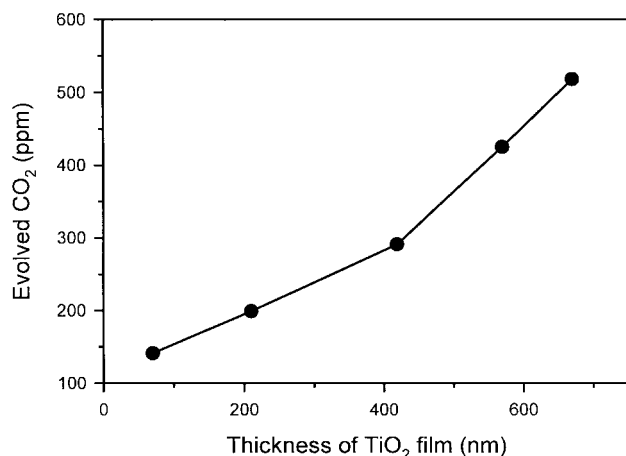


Fig. 4. Photocatalytic oxidation rate of 2-propanol to CO₂ with TiO₂ films as a function of film thickness (After 15 min of irradiation with 300 W Xe lamp, the concentration of CO₂ evolved was measured. The gas composition in the reactor: 2-propanol, 2.0 Torr; H₂O, 16 Torr; O₂, 682 Torr).

was estimated by two ways. First of all, the decomposition of 2-propanol to acetone was monitored. That is, the percentages of decomposed 2-propanol in 15 min of irradiation were measured, and these values were used for the relative comparison of photocatalytic activity. Fig. 3 describes the decomposition rates of 2-propanol as a function of film thickness. The photocatalytic activity was on a continuous increase with the increase of the film thickness. The percentage of decomposed 2-propanol with the TiO₂ film in 670 nm-thickness was 88%, while that with the film in 70 nm was only 33%.

Second, the amount of CO₂ evolved was analyzed. Fig. 4 describes the amount of CO₂ evolved for the TiO₂ films as a function of film thickness. In this case, the photocatalytic activity was defined as the CO₂ evolved in 15 min of photocatalytic reaction. The amount of evolved CO₂ with TiO₂ films in 670 nm-thickness was 520 ppm, while that with the films in 70 nm was 140 ppm.

These experiments indicate that the photocatalytic activity of TiO₂ films is strongly dependent on the film thickness. Then, what makes thicker films more photocatalytically active? There are several possible factors leading to this result, as illustrated below.

Scheme I: The thicker film would have larger surface area, because the surface roughness increases in general with the increase of film thickness. Thus, it is expected that the number of active sites on the TiO₂ surface increases.

Scheme II: Some alkaline impurities, which are considered to be detrimental to photocatalytic oxidation reaction, in the glass substrate can diffuse into TiO₂ film during the annealing process. The diffusion of alkaline impurities from the glass substrate to the surface of TiO₂ film would be more difficult for the thicker film.

Scheme III: For the transparent TiO₂ film, the light can penetrate into the inside of TiO₂ surface. Thus, the TiO₂ located underneath the surface can also be excited by irradiated light. Then, the generated electron-hole pairs may be transferred to the surface of TiO₂. For the thicker films, a higher concentration of electron-hole pairs, which play key role in the photocatalytic oxidation reaction, might be generated on the TiO₂ surface.

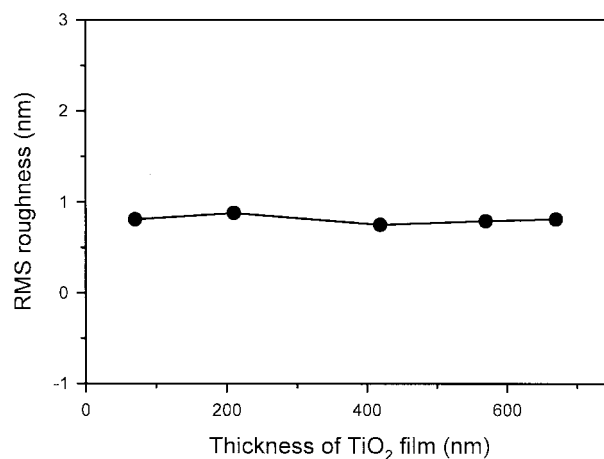
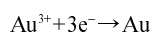


Fig. 5. RMS roughness of sol-gel derived TiO₂ films in various thicknesses.

Because the sol-gel derived TiO₂ films do not have micropores between the grains, the major factor determining the surface area of TiO₂ film would be the roughness of film surface. Thus, we evaluated the surface roughness of each TiO₂ film by AFM. As indicated in Fig. 5, the root mean square (RMS) roughness of TiO₂ films prepared by sol-gel method was not appreciably changed with the increase of film thickness, while the photocatalytic activity was greatly increased with the increase of film thickness. This suggests that Scheme I is not the main factor in determining the high photocatalytic activity for the thick TiO₂ films. In addition, a pure silica glass was used as substrate for this experiment in order to avoid the diffusion of impurity ions. Hence, Scheme II is not a dominating factor, either. Therefore, it is considered that Scheme III is a more plausible mechanism in inducing the thickness dependence of photocatalytic activity for the TiO₂ thin film.

Verification of the Scheme III mechanism requires detection of the amount of electron-hole pairs generated on the surface of TiO₂ films in various thicknesses. Since the direct measurement is not a trivial matter, we estimated it indirectly by performing the following two experiments. First, we performed a photochemical deposition experiment with TiO₂ films. As we know, AuCl₃ dissolved in aqueous solution is not appreciably decomposed to metallic Au with the irradiation of light in 380 nm. However, AuCl₃ can voluntarily be decomposed to metallic Au with the photocatalytic reaction of TiO₂, under the light in the same wavelength. That is, Au³⁺ ion in solution accepts photoexcited electrons from TiO₂ surface, and it forms metallic Au, as indicated at following formula.



As a result, photodecomposed metallic Au is deposited only on the surface of TiO₂ film. Thus, it is deduced that the amount of photo-deposited Au on TiO₂ surface is proportional to the density of charge-separated electron and hole pairs on the surface of TiO₂. In this experiment, we observed the amount of photodeposited Au on the surface of TiO₂ films in various thicknesses. Photodecomposition reaction time was adjusted to 15 sec for all experiments. All TiO₂ films were sol-gel derived, and their surface roughness was not appreciably different, as indicated in Fig. 3. Fig. 6 shows FESEM images for the photodeposited Au. No Au was deposited on the silica

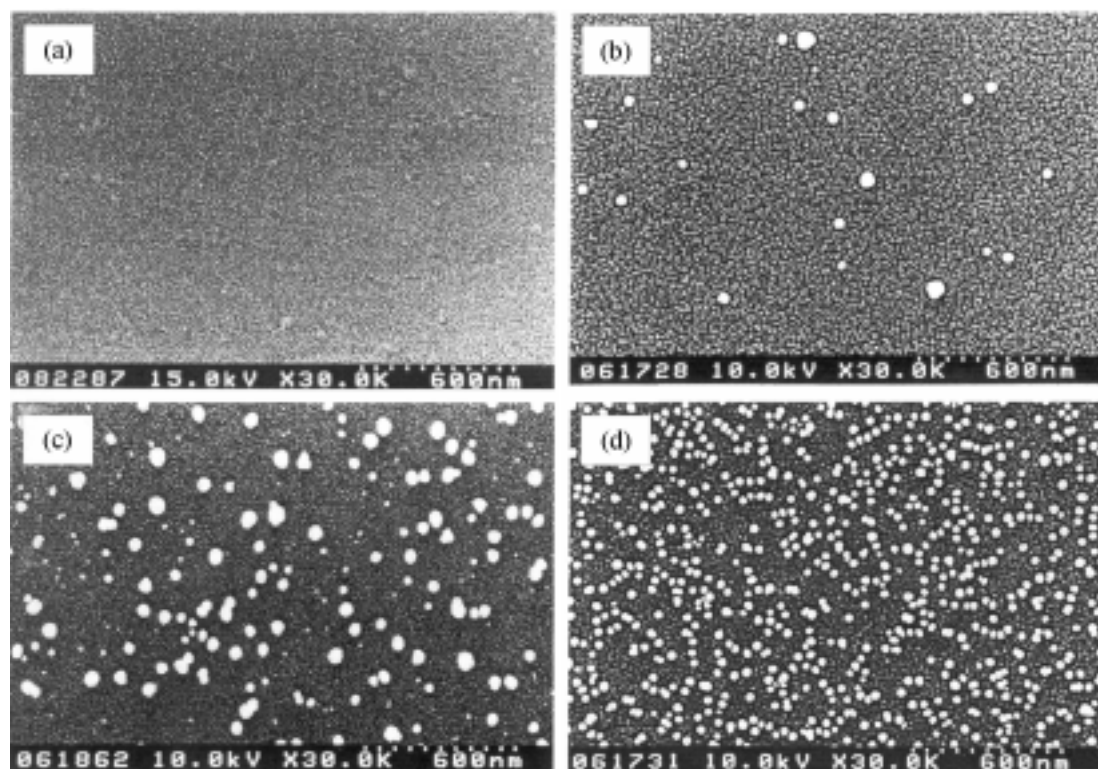


Fig. 6. FESEM images for the photodeposited Au on TiO_2 films in various thicknesses: (a) on silica glass; (b) on TiO_2 films in 70 nm; (c) on TiO_2 films in 305 nm; (d) on TiO_2 films in 670 nm.

glass without TiO_2 film, as we had expected. On the TiO_2 films, metallic Au is deposited as a form of particle in the size of about 50–100 nm. With the increase of film thickness, the number of Au particles is greatly increased. This indicates that more electron and hole pairs are generated on the surface of TiO_2 with the increase of film thickness. It is derived that the electron and hole pairs generated in the bulk TiO_2 are transferred to the surface of TiO_2 film.

Second, we determined the kinetic parameters for the TiO_2 films in the photocatalytic decomposition reaction of gaseous 2-propanol. Langmuir-Hinshelwood kinetic treatment was introduced to determine the kinetic parameters for the TiO_2 films. This is a very simple model, but it would be a reasonable model in describing our photocatalytic reaction, since our photocatalytic reaction is a kind of gas phase reaction taking place on the surface of heterogeneous catalysts. From the traditional derivation of Langmuir-Hinshelwood kinetics, K represents the equilibrium binding constant, while k reflects the reaction rate constant, that is, a measure of intrinsic reactivity at the surface of catalyst. The rate of reaction (r) can be expressed by

$$r = kKP / (1 + KP) \quad (1)$$

At an initial vapor pressure (P_o), above equation can be modified to

$$1/r_o = 1/k + 1/(kKP_o) \quad (2)$$

Initial reaction rate (r_o) can be measured simply by

$$r_o = (P_o - P) / \Delta t \quad (3)$$

where P is the vapor pressure of reactant (2-propanol) after a given

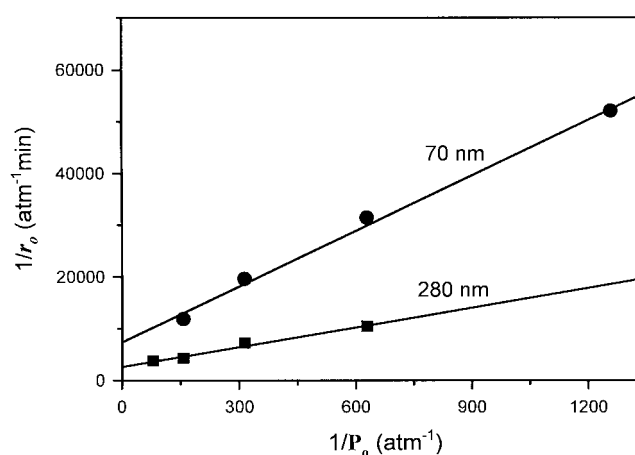


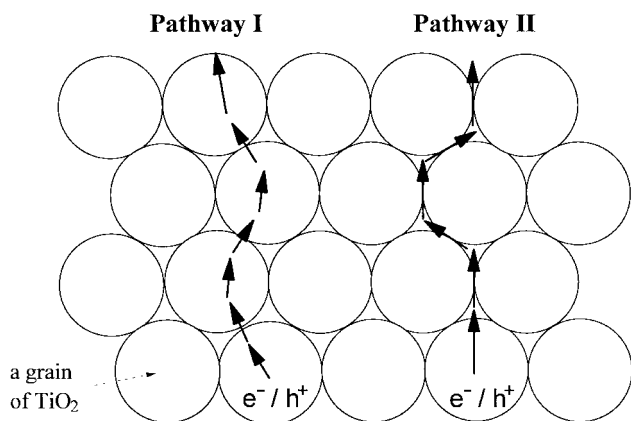
Fig. 7. Concentration dependence of initial reaction rate. The partial pressure of initial 2-propanol was varied from 8×10^{-4} atm to 1.3×10^{-2} atm.

time interval (Δt).

In this experiment, Δt was chosen to be 3 min and the initial vapor pressure of 2-propanol (P_o) was varied from 8×10^{-4} to 1.3×10^{-2} atm. By plotting $1/r_o$ vs. $1/P_o$ as shown in Fig. 7, the reaction rate constants (k) and equilibrium binding constants (K) of TiO_2 films in different thickness were determined (see Table 1). In the photocatalytic reaction, k indicates the decomposition rate constant for the adsorbed reactant molecules, and it is closely related to the density of electron-hole pairs generated on the TiO_2 surface. K represents the number of active sites, and it is related to the microstructure or

Table 1. Kinetic parameters for TiO₂ films in different thicknesses

Thickness of TiO ₂ film	k (atm·min ⁻¹)	K (atm ⁻¹)
70	1.3×10^{-4}	210
280	3.8×10^{-4}	217

**Fig. 8. Suggested possible pathways for the transfer of electron-hole pairs generated in the bulk to the surface of TiO₂.**

surface area of TiO₂ film. Compared to TiO₂ films in 70 nm, the TiO₂ films in 280 nm have 2.9 times higher reaction rate constant, while **K** is not basically different. It is believed that the higher reaction rate constant for the thicker TiO₂ film is closely related to the higher number of electron and hole pairs on the surface of TiO₂. On the other hand, the equilibrium binding constant (**K**) was not much different between the thick and thin TiO₂ films. This implies that the number of active sites is not appreciably changed with the increase of thickness. Therefore, this experiment also supports Scheme III mechanism.

Then, how would the electron-hole pairs, generated in the bulk TiO₂, be transferred to the surface of TiO₂? In a single crystal the transfer of electron and holes to the crystal surface would be very efficient, if the recombination was not considered. In this case, the electrons and holes may simply drift through the same conduction and valence band, respectively. For the polycrystalline films, however, the transfer of electron and hole pairs would be much more complicated. The generated electron and hole pairs must pass through the many grain boundaries. We have suggested two possible pathways for the transfer of electron and hole pairs generated in the bulk to the film surface, as shown in Fig. 8. Pathway I seems to be relatively difficult, because the electron and hole pairs should pass through many interfaces. Pathway II indicates that the generated electron and hole pairs are once moved to the grain boundary, and then transferred to the surface of film along the grain boundary. We believe that this is a more plausible mechanism.

CONCLUSIONS

The photocatalytic activities of TiO₂ films in decomposing gaseous 2-propanol were greatly increased with the increase of film thickness. The amount of CO₂ evolved with TiO₂ films in 670 nm-

thickness was about 3.7 times that of films in 70 nm-thickness. Au photochemical deposition result indicates that the number of deposited Au particles on the surface of TiO₂ film greatly increases with the increase of TiO₂ film thickness. The reaction rate constant (**k**) of the TiO₂ film in 280 nm-thickness was 2.9 times that of the film in 70 nm, while the equilibrium binding constant (**K**) of the thick film was not much different from that of thin film. These results indicate that the photogenerated electron and hole pairs inside of the TiO₂ surface are transferred to the film surface.

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