

Feature Article

Photocatalytic Behavior of TiO₂ Films : Thickness and Roughness Dependence

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ABSTRACT Transparent TiO₂ films in various thicknesses were prepared by sol-gel and MOCVD method, respectively, and their photocatalytic activities in decomposing gaseous 2-propanol were evaluated. The surfaces and grain structures of the prepared films were characterized by FESEM, XRD, and AFM. It was found that the photocatalytic activities of TiO₂ films were greatly dependent on the film thickness and surface roughness: The photocatalytic activity increases with the increase of film thickness, while it decreases with the increase of surface roughness. We have proposed that these phenomena originate from the transfer of photogenerated electron and hole pairs from the bulk to the surface of TiO₂ film. Several experimental evidences supporting this mechanism have also been provided.

INTRODUCTION

TiO₂ photocatalysts in thin film form have promising industrial applications for the elimination of organic pollutants in aqueous solution or in gas phase, and they are also well-known as self-cleaning and super-hydrophilic smart materials working under an irradiation of light.¹⁻⁴ Hence, the TiO₂ thin films coated on the surface of window glass, mirrors in automobile, eye glasses, light bulb, ceramic tiles, plastics or wall can self-clean, defog their surfaces, and purify the polluted air in a confined space.^{4,5} For these industrial applications, the most important properties required to the photocatalytic TiO₂ films would be high photocatalytic efficiency and optical transparency.

So far, the investigations toward the improvement of photocatalytic activity or fundamental studies on the behavior of photocatalytic reaction have mainly been focused on the particulate TiO₂.⁶⁻⁸ On the contrary, TiO₂ in thin film form has scarcely been studied in

these aspects, and the concepts obtained from the particulate TiO₂ have been applied to the thin film without further consideration. However, it is expected that the photocatalytic behaviors of TiO₂ in thin film form are somewhat different from those of particulate TiO₂, since the photocatalytic reactions take place only on the surface, and the surface area of thin film is much smaller than that of fine particles.

A markable characteristic of photocatalytic thin films distinguished from that of particles would be "thickness of film". One might expect 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 is not correct. As we have observed, the photocatalytic activity is strongly dependent on the thickness of TiO₂ film. In the literature, a few researchers reported on the thickness dependence of photocatalytic activity for TiO₂ films. Wold et al. reported the thickness dependence of activity for the photocatalytic TiO₂ films derived from sol-gel and spray pyrolysis method, respectively, in decomposing aqueous salicylic acid.⁹ The photocatalytic activities increased with the raise of film thickness and finally reached a plateau level from 500~600 nm. Recently, Yu et al. also indicated that for the sol-gel derived TiO₂ films in decomposing the methyl orange coated on the TiO₂ surface, the photocatalytic activities were steadily increased until saturated at 1.1 μ m-thickness.¹⁰ However, the reason why thicker film shows higher photocatalytic activity and why photocatalytic activity of film is maximized at a certain thickness has not been reported so far.

In this work, our investigation is focused on the photocatalytic behavior of TiO₂ films as a function of film thickness. We propose a mechanism explaining the thickness dependence, and provided several experimental evidences supporting this mechanism. We also report that the roughness of surface is another crucial factor in determining the photocatalytic activity of TiO₂ films.

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EXPERIMENTAL SECTION

TiO₂ films were prepared by sol-gel method, and metal organic chemical vapor deposition (MOCVD) technique, respectively. The sol-gel derived TiO₂ films were prepared by following procedures. Titanium tetraisopropoxide [Ti(OPrⁱ)₄] was diluted in n-propanol, and two equivalents of 2,4-pantanedione were added at 0°C. By adding additional n-propanol and acetic acid, the concentration of Ti(OPrⁱ)₂(AcAc)₂ solution was adjusted to 0.8M. The prepared solution was spin-coated at 2500 rpm, and baked at 250°C. To obtain the desired thickness, spin-coating and baking cycles were repeated. Finally, the baked films were heat-treated at 500°C for 30 min in oxygen environment in order to obtain anatase phase and to get rid of carbon impurities in the TiO₂ film.

TiO₂ films were also prepared by MOCVD technique. Ti(OPrⁱ)₄ was vaporized at 35°C, and carried to the deposition chamber by dehydrated N₂ with a flow rate of 50 ml/min. The mixed gas of oxygen and nitrogen (200/150 ml/min) was used as reaction gas, and the pressure of deposition zone was maintained to 3 Torr. The growth rate of TiO₂ films at 450°C was about 10 nm/min. The deposited films were post-annealed at 500°C for 30 min under an oxygen environment. Silica glass (electronic grade) was used as substrate both in sol-gel and MOCVD process.

Glancing angle mode X-ray powder diffraction patterns of the TiO₂ films were obtained by using a Philips diffractometer (PW3020) with a monochromated high intensity CuKα radiation. The surface morphology and cross sectional image of TiO₂ films were observed by a field emission SEM (Hitachi S-4500). The surface roughness of film was observed by an atomic force microscope (AFM, TopoMetrix ACCUREX).

The TiO₂ films prepared by sol-gel or MOCVD 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.¹¹ 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 (2cm x 2cm) was irradiated by a 300 W Xe lamp through the 2-inch diameter silica window on the reactor. After evacuation of the reactor, stoichiometric amounts of 2-propanol and water vapor were added (the molar concentrations were 200 and 400 ppm, 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 30 min, 0.5 ml of gas sample in the reactor was automatically picked up and sent to a Gas Chromatography (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.

AuCl₃ (Aldrich) was reduced to Au on the surface of TiO₂ films by photochemical decomposition.¹² A 30 ml of a 5 x 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

Characterization of TiO₂ films prepared by sol-gel and MOCVD technique. Transparent TiO₂ thin films in various thicknesses were prepared by sol-gel and MOCVD technique, respectively. FESEM images for the TiO₂ films deposited on silica glass are shown in Figure 1.

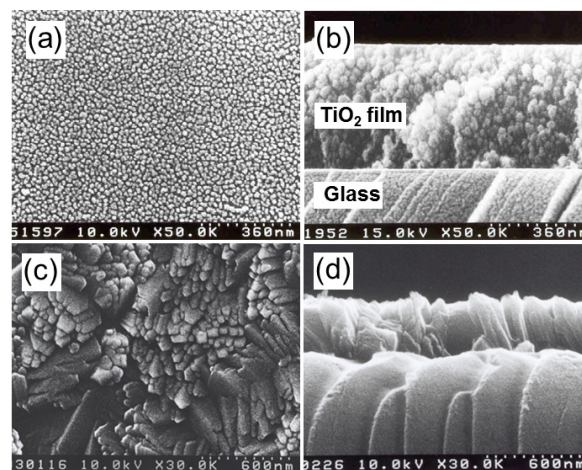


Figure 1. FESEM images of TiO₂ films in about 300 nm-thickness deposited on silica glass: (a) plan-view of sol-gel derived film; (b) cross-sectional-view of sol-gel derived film; (c) plan-view of MOCVD derived film; (d) cross-sectional-view of MOCVD derived film.

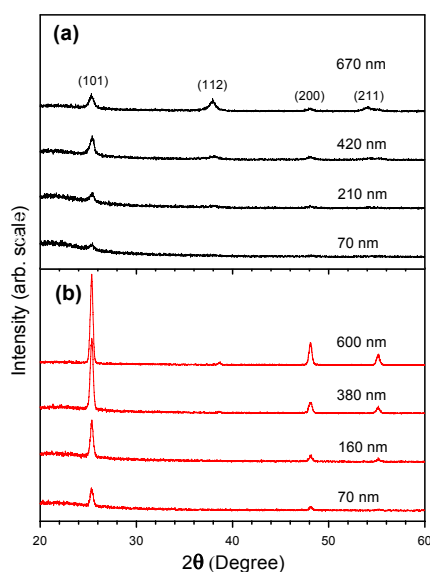


Figure 2. XRD patterns of TiO₂ films in various thicknesses. (a) Sol-gel derived TiO₂ films; (b) MOCVD derived films.

It was found from the plan-view and cross-sectional-view images that the shapes of grains for the sol-gel derived TiO₂ films in about 400 nm-thickness were spherical and their diameters were only 20-40 nm, while the films derived from MOCVD technique were highly crystallized and their grains were grown in columnar structure. XRD patterns in Figure 2 also indicate that the TiO₂ films derived from MOCVD technique are much more crystallized than those from sol-gel method. For the both films, however, pure anatase phase were formed regardless of film thickness.

The surface roughnesses of films in various thicknesses were measured by AFM. As indicated in Figure 3, the RMS roughness of TiO₂ films prepared by sol-gel method was only 0.8 nm, and it was not appreciably changed with the increase of film thickness. On the other hand, the roughness of films deposited by MOCVD technique was more than 10 times higher than that by sol-gel method, and it was greatly dependent on the film thickness. Especially, the roughness was sharply increased for the films thicker than 300 nm, while it was relatively less changed in the range of 70~300 nm.

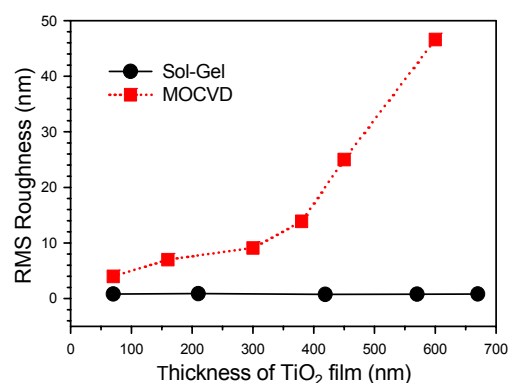


Figure 3. RMS roughness of TiO₂ films in various thicknesses.

Photocatalytic activity of TiO₂ films. We evaluated the photocatalytic activities of TiO₂ films in various thicknesses. The thicknesses of TiO₂ films prepared by sol-gel and MOCVD techniques were controlled in the range of 70~670 nm and 70~600 nm, respectively. 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 CO₂.³ Thus, the photocatalytic activity was estimated by two ways in this work.

First of all, the decomposition of 2-propanol to acetone was monitored. Figure 4a describes the decomposition rates of 2-propanol as a function of TiO₂ film thickness. Photocatalytic activity was simply defined as the percentage of decomposed 2-propanol in 60 min of photocatalytic reaction. For the films derived from sol-gel method, the photocatalytic activity was continuously increased, as the thickness of TiO₂ film increased. On the other hand, for the films derived from MOCVD, photocatalytic activity was maximized at 370 nm-thickness, and it was then decreased at higher thickness. Compared with the films in 70 nm, the films at 370 nm demonstrate 4 times of photocatalytic activity. However, the photocatalytic activity of films in 600 nm was about 1/4 of that of films in 370 nm.

Second, the amount of CO₂ evolved was analyzed. Figure 4b describes the amount of CO₂ evolved for the both kind of TiO₂ films as a function of thickness. In this case, the photocatalytic activity was defined as the CO₂ evolved in 15 min of photocatalytic reaction. For the sol-gel derived TiO₂ films, the evolved CO₂ with TiO₂ films in 670 nm-thickness was 520 ppm, while that with the films in 70 nm-thickness was 140 ppm. For the MOCVD derived TiO₂ film, the evolution of CO₂ was

maximized at 370 nm-thickness. For the both kind of TiO₂ films, the behaviors of CO₂ evolution as a function of thickness were in accord with those of 2-propanol decomposition.

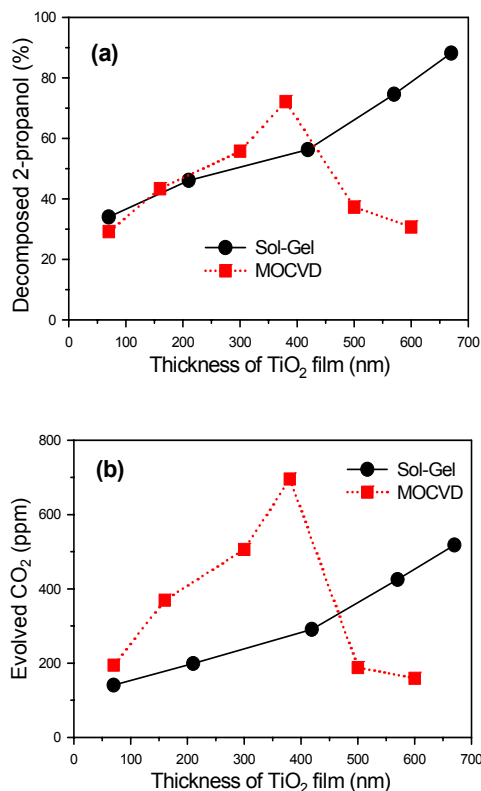


Figure 4. Decomposition percentage of 2-propanol (a) and evolved CO₂ (b) by the photocatalytic reaction with TiO₂ films as a function of film thickness (After 15 min of irradiation with 300 W Xe lamp, the decomposed percentage of 2-propanol was determined.).

Thickness effect on the photocatalytic activity. Then, why does thicker film demonstrate higher photocatalytic activity? There are several factors to take into account.

Factor I: Alkaline impurities, which are regarded to be detrimental to photocatalytic oxidation reaction,¹³ in the glass substrate can diffuse into TiO₂ film during the heat treatment process. The migration of alkaline impurities from the glass substrate to the surface of TiO₂ film would be suppressed with the increase of thickness.

Factor II: The thicker TiO₂ film would have larger surface area with the increase of surface roughness. Thus, the number of active sites may be increased.

Factor III: TiO₂ films might have voids among the

grains. This may lead to larger surface area for the thicker film.

Factor IV: For the transparent TiO₂ film, the irradiated light can reach the inside of TiO₂ surface. Thus, the bulk TiO₂ can also be photo-excited, and the generated electron-hole pairs could be transferred to the surface of film. As a result, greater number of electron-hole pair is generated on the surface of thicker TiO₂ film, and this may expedite photocatalytic oxidation reaction.

In this work, pure silica glass was used as substrate for the deposition of TiO₂ films in order to avoid diffusion of impurity ions. Hence, the Factor I is excluded here. For the sol-gel derived TiO₂ films, the roughness of film was not appreciably changed with the increase of film thickness as indicated in Figure 3, while the photocatalytic activity was continuously elevated with the increase of film thickness as shown in Figure 4 and 5. This suggests that the Factor II is not a major factor.

We have analyzed the existence of voids in the films indirectly, as described below, since the direct measurement of surface area for the thin film is not a simple matter. The sol-gel derived TiO₂ films in different thicknesses were dipped in 10 mM Basic Blue-41 (Aldrich) aqueous solution several hours.¹⁴ Then, the surface of films was rinsed by water, and the absorbance by the adsorbed Basic Blue-41 was measured with UV-visible spectrophotometer. It was found that the absorbance of dye for each TiO₂ film was not appreciably affected by the change of thickness. This indicates that dye molecules are adsorbed only on the TiO₂ surface, and the TiO₂ films do not have voids between the grains, nor internal surfaces. Thus, the Factor III is not a major factor, either. As a result, it is suggested that Factor IV is a dominating factor in describing the thickness dependence of photocatalytic activity for TiO₂ thin films.

For the consolidation of this suggestion, however, the information on the amount of electron-hole pairs generated on the surface of TiO₂ films during the photocatalytic reaction has to be provided as a function of film thickness. We set up two experiments for this purpose. First of all, we performed a photochemical deposition experiment with TiO₂ films in various thicknesses. AuCl₃ dissolved in aqueous solution is not appreciably decomposed to metallic Au with the irradiation of light in 380 nm-wavelength. With the photocatalytic reaction by TiO₂, however, AuCl₃ can voluntarily be decomposed to Au. That is, Au³⁺ ion in solution accepts photoexcited electrons from TiO₂ surface, and forms metallic Au, as indicated at following formula.



As a result, photochemically generated metallic Au is deposited preferentially on the surface of TiO₂ film. Thus, it is derived that the quantity of photodeposited Au on TiO₂ is proportional to the amount of space-charge separated electron and hole pairs on the surface of TiO₂. We measured the amount of photodeposited Au on the surfaces of TiO₂ films in various thicknesses. The light-irradiation time was adjusted 15 sec for all experiments. All TiO₂ films were sol-gel derived, and their surface roughnesses were not appreciably different. Figure 5 indicates FESEM images for the photodeposited Au. As expected, no Au was deposited on a silica substrate without TiO₂ film. On the TiO₂ films, metallic Au was deposited as a form of island structures. With the increase of film thickness, the number of spherical Au grain was greatly increased. This indicates that more electron and hole pairs are generated on the surface of TiO₂, as the thickness of film increases.

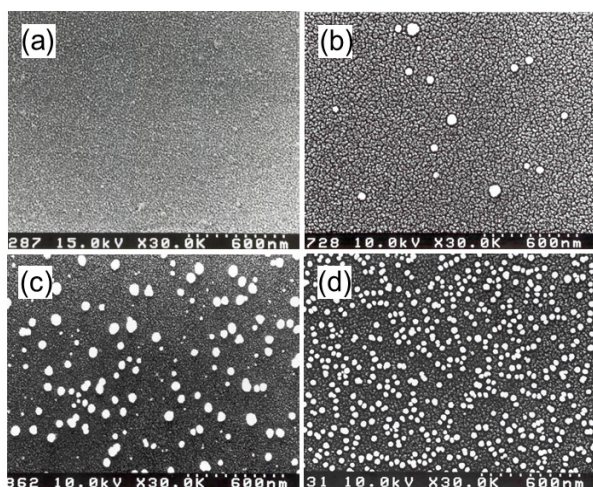


Figure 5. FESEM images for the photodeposited Au on TiO₂ films in various thicknesses: (a) on silica glass; (b) on TiO₂ films in 70 nm; (c) on TiO₂ films in 305 nm; (d) on TiO₂ films in 670 nm. All TiO₂ films were sol-gel derived and roughnesses were not appreciably different.

It was also found that the size of Au nanoparticles formed on the thicker TiO₂ film is relatively smaller. Generally, crystals are formed by the nucleation and grain growth steps. With increasing the nucleation sites, the crystal size becomes smaller. The number of Au nucleation site will be dependent on the supply of electrons. Thicker TiO₂ film can produce more

electrons, which in turn induces more nucleation sites for the Au growth. Thus the relatively smaller grain size is considered to be due to the larger number of nucleation sites formed on the thicker TiO₂ film, as shown in Figure 5.

Second, we determined the kinetic parameters for the TiO₂ films in the photocatalytic decomposition reaction of gaseous 2-propanol. Langmuir-Hinshelwood kinetic treatment was introduced to determine the kinetic parameters for the TiO₂ films. This is a simple model, but would be a reasonable model in describing our photocatalytic reaction, since the photocatalytic reaction is a kind of gas phase reaction taking place on the surface of heterogeneous catalysts. From the traditional derivation of Langmuir-Hinshelwood kinetic, **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

$$r = \frac{kKP}{1 + KP} \quad (1)$$

At an initial vapor pressure of reactant (**P**₀), above equation can be modified to

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{(kKP_0)} \quad (2)$$

Initial reaction rate (**r**₀) can be measured simply by

$$r_0 = \frac{(P_0 - P)/\Delta t}{V} \quad (3)$$

, where **P** is the vapor pressure of reactant (2-propanol) after a given time interval (**Δt**).

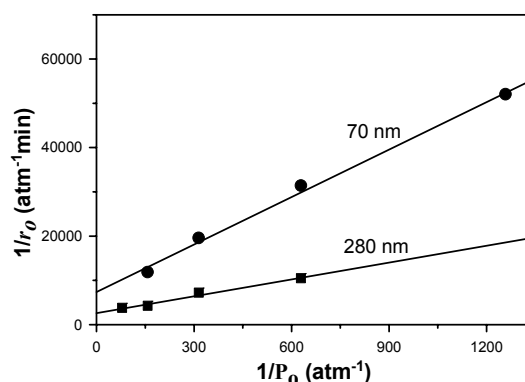


Figure 6. Concentration dependence of the initial reaction rate. The partial pressures of initial 2-propanol were varied from 8×10^{-4} atm to 1.3×10^{-2} atm.

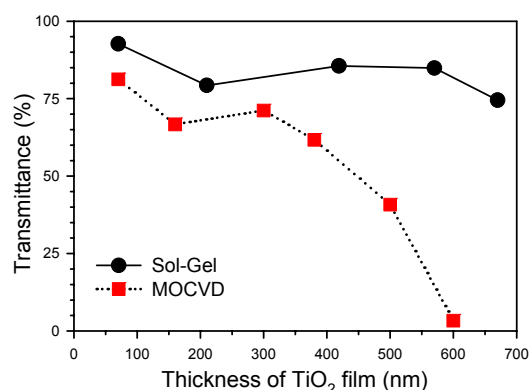
Table I. Kinetic parameters for TiO₂ films in different thicknesses.

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

In this experiment, sol-gel derived TiO₂ films in different thickness but in similar roughness were used. In the photocatalytic reaction Δt was chosen to 3 min, and the initial vapor pressures of 2-propanol (P_0) were varied from 8×10^{-4} to 1.3×10^{-2} atm. By plotting $1/P_0$ vs. $1/r_0$ as shown in Figure 6, the reaction rate constants (k) and equilibrium binding constants (K) of TiO₂ films in two different thicknesses 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 TiO₂ surface. K represents the number of active sites, and it is related to the microstructure or surface area of TiO₂ film. Compared to the TiO₂ films in 70 nm, the TiO₂ films in 280 nm had 2.9 times higher reaction rate constant, while K was 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. No difference of equilibrium binding constant implies that the number of active sites is not appreciably changed with the increase of thickness. This is consistent with the RMS roughness result by AFM.

Roughness effect on the photocatalytic activity. For the TiO₂ films derived from MOCVD method, the photocatalytic activity was maximized at 370 nm, and then decreased down with further increase of film thickness, as shown in Figure 4. We guess that the decrease of photocatalytic activity at the thickness above 370 nm is related to the increase of surface roughness. The increase of roughness in TiO₂ film induces the increase of surface area, which may promote the photocatalytic activity. On the other hand, however, it might be detrimental to the photocatalytic activity because of low transmittance of light into the film, since the incident light is scattered on the

surface. We estimated the transmittance of TiO₂ films utilizing the light in the spectral range of 400-500 nm, in order to avoid intrinsic absorption by TiO₂ film. The transmittance was estimated as average value at this wavelength range, since the transmittance value is fluctuated along the film thickness with spectral interference. Figure 7 shows the change of transmittance as a function of film thickness. For the sol-gel derived films, the transmittance was only decreased from 92% to 76%, with the increase of thickness from 70 nm to 670 nm. On the other hand, for the films derived from MOCVD technique, the transmittance was dropped from 82% to 5%. This indicates that the transmittance is critically dependent on the roughness of film surface. As the roughness of TiO₂ film increases, the number of photons penetrated into the surface will be sharply decreased, and as a result smaller amount of electron and hole pairs will be transferred to the surface of TiO₂ film.

**Figure 7.** The average transmittance of light into TiO₂ films as a function of film thickness. The spectral range of light was 400–500 nm.

In common thin film process, the surface roughness of film is gradually elevated with the increase of thickness. Therefore, it is expected that the photocatalytic activity of TiO₂ film be maximized at a certain thickness, since the roughness and thickness factors play a role in the opposite direction. If the surface roughness can be controlled to constant, we believe that the photocatalytic activity of transparent TiO₂ film would increase steadily until its thickness reaches several microns.

Then, how are the electron and hole pairs generated in the bulk TiO₂ carried to the surface? In a single crystal, the transfer of electrons and holes to the crystal surface would be simple and efficient, if

the recombination is not considered. The electrons and holes will simply be drifted through the same conduction band and valence band, respectively. However, for the polycrystalline films, the transfer of electron and hole pairs would be much more complicated, because the generated electron and hole pairs have to pass over the grain boundaries.

As described in Figure 4, TiO₂ thin films in 70~370 nm-thickness derived from MOCVD technique showed appreciably higher photocatalytic activity than those derived from sol-gel process. The grains of TiO₂ films by sol-gel method were in spherical shape and the sizes were only about 20~40 nm, while that of films derived from MOCVD technique were well-developed columnar structure, as shown in Figure 1. Therefore, the transfer of electron-hole pairs will be more efficient for the films derived from MOCVD, and the higher photocatalytic activity can be achieved as a result.

CONCLUSIONS

The photocatalytic activities of transparent TiO₂ films in decomposing gaseous 2-propanol were greatly increased with the increase of film thickness. From the photochemical deposition of Au with TiO₂ films, it was found that the amount of deposited Au clusters on TiO₂ film surface increased with the increase of 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*) was not appreciably different.

These results indicate that the photogenerated electron and hole pairs at the inside of TiO₂ surface are transferred to the film surface.

It was also found that the increase of surface roughness was detrimental to the photocatalytic activity of TiO₂ film because of low transmittance of light into the film surface, while the increase of surface area caused by the elevation of roughness played a minor role.

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KEYWORDS: TiO₂, Photocatalysis, Photocatalytic film, Thickness, Roughness, Photocatalytic efficiency.

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