JOURNAL OF MATERIALS SCIENCE **34** (1999) 6201–6206

Low-temperature formation of photocatalytic Pt-anatase film by magnetron sputtering

J. SHENG, L. SHIVALINGAPPA, J. KARASAWA, T. FUKAMI
Faculty of Engineering, Shinshu University, Nagano-shi, Japan 380
E-mail: fusheng@gipwc.shinshu-u.ac.jp

Films of TiO_2 dispersed or coated with platinum were deposited on glass and Pt-buffered polyamide substrates respectively by magnetron sputtering. The photocatalytic activity of the films was evaluated through the decomposition of acetic acid under UV irradiation. The Pt-dispersed TiO_2 film of approximately 1.5 wt% platinum shows a maximum activity due to for the formation of anatase phase with a fine grain size. Platinum particles $\sim$20 Å in thickness coated on anatase film greatly improves activity. The activity shows a steplike dependence of film thickness where the critical thickness varies between 150 and 200 nm depending on the deposition temperatures. The correlation between defects and activity was verified by measuring either the temperature dependence of electric resistance or the shift of binding energy from XPS. © *1999 Kluwer Academic Publishers*

1. Introduction

Photoelectrochemical properties of titania have been studied by many authors in the field of solar energy conversion and storage since the pioneering work of Fujishima and Honda [1, 2]. Recently, many scientists have focused on application of TiO_2 photocatalyst to purification and treatment of air and water, e.g., through the photolysis of organics and toxic gases [3, 4].

Photocatalytic chemical reactions occuring in the surface of semiconductor materials start from absorption of light and result in attainment of photo-activated electrons and holes in the surface layer. This process is predominantly determined by fundamental physical properties of the materials. Either TiO_2 or noble metal-TiO_2 powder has attracted extensive attentions mainly for its large specific surface area [5–9]. However, the use of conventional powder catalyst results in disadvantages for stirring during the reaction and for separation of powder after the reaction. Preparation of film catalysts will make it possible to overcome these disadvantages and to extend the industrial applications. Photocatalytic TiO_2 thin films were prepared using different techniques, for instance, by spray-coating [10] or sol-gel techniques [11]. However, a heating process at about 600 °C is indispensable in these methods in order to decompose metallorganics, causing a limitation in the use of non-refractory substrate. In this paper, an attempt has been made to prepare photocatalytic Pt-TiO_2 films with special attention to the formation of anatase at temperature as low as 200 °C and to the use of flexible substrate (e.g., polyamide) to widen the application of film photocatalysts.

2. Experimental

Thin films were prepared using tripole magnetron sputtering system, the details of which were described elsewhere [12–14]. In this sputtering system it is possible to prepare multicomponent films by alternately moving the erosion area by switching the polarity of electromagnet which was located between the permanent magnets.

The Pt-TiO_2 film (type I) was prepared by alternately sputtering co-axially placed platinum and titanium targets of 150 and 90 mm in diameter, respectively. The deposition time of platinum was kept at 2 s whereas that of titanium is varied from 20 to 140 s in each cycle in order to obtain different compositions. The films were deposited onto Corning 7059 glass. The Pt-TiO_2 film (type II) was prepared by depositing at first a pure TiO_2 film on polyamide sheet (TORAY-DUPON Co., Ltd), followed by coating small amount of platinum particles on the surface, rather than by using alternate sputtering mechanism. Prior to the deposition of TiO_2 film, a platinum (or nickel) buffer layer of 200–300 Å thick was deposited on polyamide in order to improve affinity between the film and polyamide sheet. Table I shows the typical sputtering conditions. All the samples are one-side coated unless otherwise specified.

The thickness of the films was measured using stylus profilometer. The crystallinity of the films was identified by X-ray diffractometer (XRD), and the microstructure by atomic force microscopy (AFM). The compositions of the films were analysed by fluorescence X-ray analyser. The photocatalytic activity of the thin films was evaluated through the decomposition of acetic acid. The sample (15 × 35 × 1 mm) was immersed in 6.5 ml aqueous acetic acid with a concentration of 0.002 mol $^{-1}$ (120 ppm) in a glass test tube. A high pressure mercury lamp (100 W) was used as a UV source. One face of the film was irradiated along the normal direction. During irradiation, the acetic acid solution was bubbled with 2 ml/min O_2. The

0022–2461 © *1999 Kluwer Academic Publishers*

TABLE I Sputtering conditions for Pt-TiO_2 films

Film types	Pt-dispersed (I)	Pt-coated (II)[a]
Substrate	Corning 7059	Polyamide
Targets	Ti/Pt	Ti
Discharge I/V	150/550	150 mA/550 V
Gas/pressure	O_2/30	O_2/30 mTorr
Substrate temperature	200	200–400 °C
Growth rate	7.5	7.2 Å/min

[a] Pt-coating sputtering: 200 °C/50 mA/6–12 s.

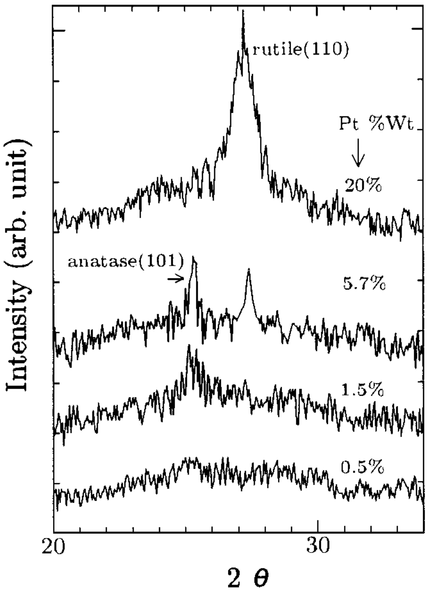

Figure 1 XRD patterns of platinum dispersed TiO_2 films on glass at 200 °C.

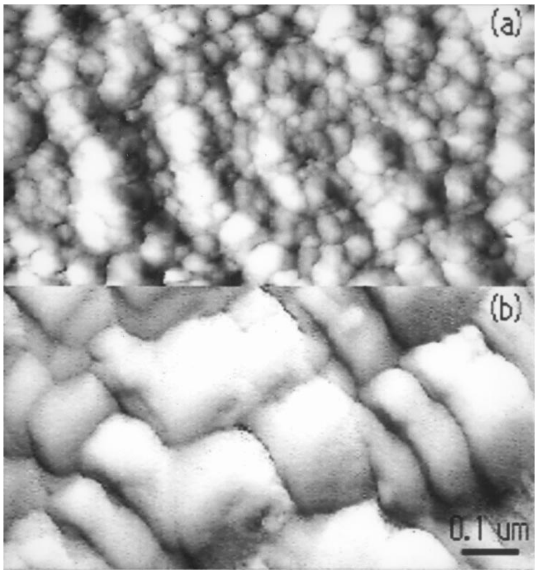

Figure 2 AFM images of platinum dispersed titanium films with (a) 1.5% and (b) 20% (wt) of platinum, respectively.

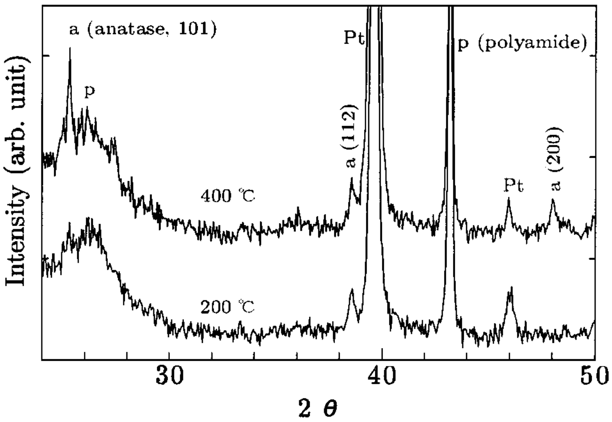

Figure 3 XRD patterns of TiO_2 films on Pt-buffered polyamide deposited at different temperatures.

concentration of the acetic acid was tested using FET pH meter (±0.05)* and gas chromatography (M-80B, HITACHI, Co.) for every 5 h UV irradiation.

3. Results and discussion

3.1. Physical characteristics

As shown in Fig. 1, the crystal structure of type I Pt-TiO_2 films strongly depends on the content of platinum dispersed. When the content of platinum is high (e.g., 20 wt %), there forms pure rutile phase. With decreasing the content of platinum, rutile phase gradually disappears and anatase phase of 101 preferential orientation grows. With further decreasing platinum content, the film becomes pure anatase and finally tends to be amorphous. The peak of platinum is not found in as-deposited film but detected after treatment at 700 °C, suggesting that platinum is amorphous in as-deposited film. Fig. 2 shows the influence of platinum content on the microstructure of films. As the content of platinum is decreased the grain size of the films is remarkably reduced. Platinum buffer layer in type II Pt-TiO_2 films not only modifies the bonding strength of film/polyamide interface but also makes it possible to deposit anatese film at temperature as low as 200 °C. As shown in Fig. 3, (1 0 1) and (1 1 2) peaks of anatase structure were clearly observed.

3.2. Photocatalytic activity

3.2.1. Platinum dispersed TiO_2 film

Concerning the effect of crystal phase on the photocatalytic activity, it has been established recently that the anatase phase is much more effective than amorphous and rutile phase [4, 10]. Fig. 4 shows the change in the concentration of acetic acid on type I Pt-TiO_2 films as a function of platinum content. When the content of platinum was greater than 10 wt %, the films show weak photocatalytic activity because of the formation of rutile phase. When the platinum content is reduced, the concentration of the solution decreases and activity gets stronger due to the formation of anatase phase. The maximum activity was observed in the film of 1.5% platinum for which the concentration of acetic acid was reduced from 120 to 0.02 ppm. The observed difference in photocatalytic activity for anatase and rutile phases is

---

* According to the ionization equilibrium of acetic acid, the concentration of HAC, [C], can be calculated by $[C] = [H]^2/K_i + [H]$, where, K_i is the ionization equilibrium constant (1.82×10^{-5}, 20 °C), and [H] the concentration of proton ($\log [H] = -pH$). The deviation of the calculated [C] for standard HAC solutions is found to be within ±5%.

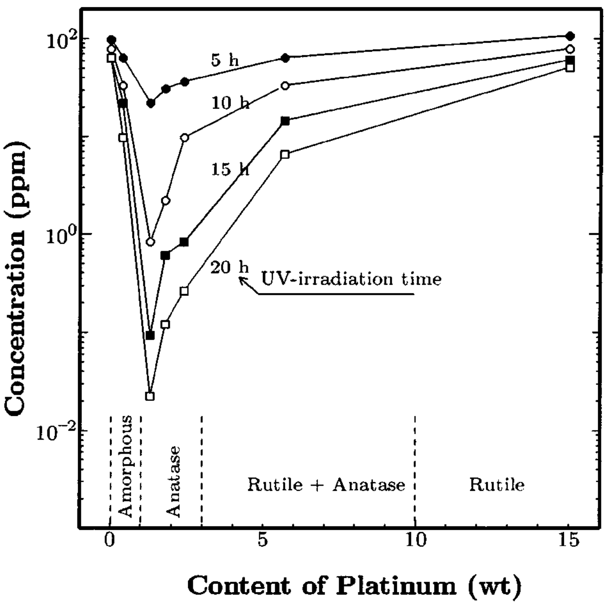

Figure 4 Photocatalytic activity of platinum dispersed TiO_2 films of various platinum contents.

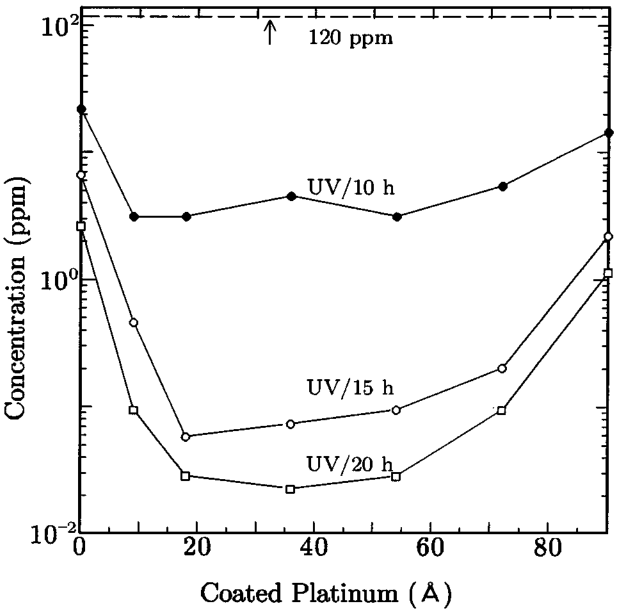

Figure 5 Photocatalytic activity as a function of the amount of platinum coating (film thickness: 540 nm).

consistant with the results reported by Takahashi [10], which is presumably due to the discrepancy either in bandgap structure [15] or in atomic alignment of lattice [4].

As reported for TiO_2 powder photocatalyst [9], small grain size is very important for the modification of photocatalytic activity because of its high specific surface area. The high activity for Pt-TiO_2 film of 1.5% platinum is not only due to the formation of anatase but also for its minute grain size as shown in Fig. 2.

3.2.2. TiO_2 film coated with Pt particles

Strong interaction between platinum and TiO_2 for photocatalytic activity has already been verified in type I Pt-TiO_2 films. Since photocatalytic reaction merely takes place on surface and the platinum buried inside the film is useless, the introduction of the platinum particles on TiO_2 film was believed to be as effective as the dispersion of platinum inside TiO_2 film. As shown in Fig. 5, platinum particles of approximately 20 Å in thickness can improve the activity remarkably because these superfine platinum particles can form large amount of individual photochemical cells with TiO_2. In this system, the photogenerated electrons move towards platinum so as to get separated from positive holes [2]. The separated holes play an important role in photocatalytic reaction by directly reacting with organics, or by generating atomic oxygen to oxidize organics by following photoelectrochemical process [2]

$$H_2O + 2h^+ \rightarrow 2H^+ + O(\rightarrow 1/2O_2).$$

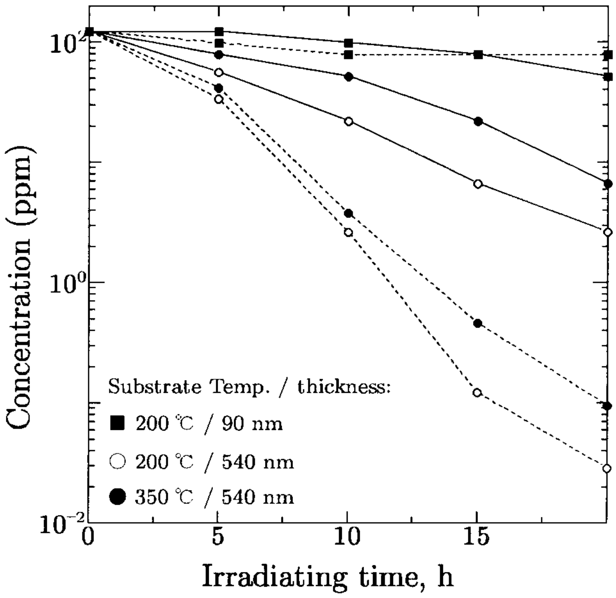

Figure 6 Comparison of photocatalytic activity of TiO_2 films prepared at different conditions (solid line: as-deposited; dot line: coated with 18 Å platinum on surface).

The second mechanism is in agreement with the fact that acetic acid can be photocatalytically oxidized in a sealed test tube (i.e., without the introduction of oxygen gas). The electrons and positive holes in TiO_2 film without platinum are not efficiently separated and hence are easily extincted due to the re-combination of them, resulting in lower activity than TiO_2-Pt binary system, as shown in Fig. 6.

The photocatalytic activity did not depend strongly on the amount of coated platinum. As shown in Fig. 5, the activity changes slightly while increasing platinum coating from 15 to 55 Å. However, the overcoated platinum will form a continuous platinum layer to mask TiO_2 film, consequently causing a degradation or even ineffectiveness in activity. As a result, when coating platinum both the amount of platinum particles and the exposed surface of TiO_2 should be optimized and fairly balanced.

From Fig. 6 it is clear that the coated platinum does not change the order of activity in three samples. If the TiO_2 film is initially ineffective, the deposition of

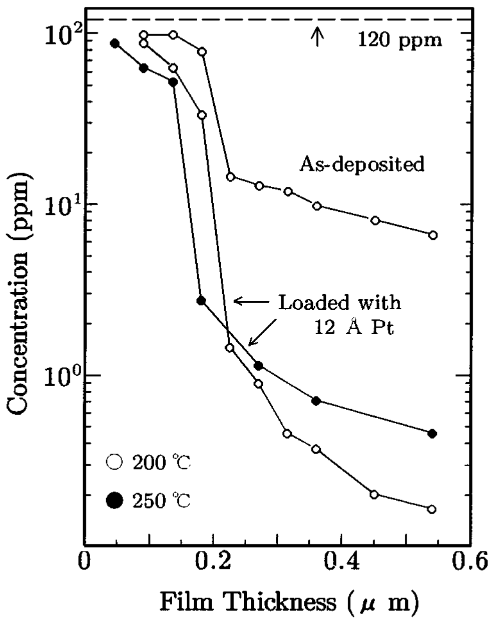

Figure 7 Thickness dependence of photocatalytic activity for TiO_2 films deposited at different temperatures (tested after 15 h UV-irradiation).

Pt particles is not effective to modify the activity, suggesting that the validity of TiO_2 is the prerequisite for photocatalytic activity and platinum only plays a supplementary role in the photocatalysis evolution.

Interestingly, film thickness t dependence of photocatalysis was observed, though the photocatalytic reaction is fundamentally surface reaction. As shown in Fig. 7, the film deposited at 250 °C shows very weak activity at t less than 150 nm whereas an abrupt increases around 150 nm. The critical thickness t_c varies depending on the deposition temperature of thin film but shows no relation with the coated platinum. Takahashi and others [10] have observed a similar phenomenon in the spray-coated Pt-TiO_2 films at thickness of around 50 nm, and has ascribled this phenomenon to the influence of amorphous substrate on film crystalization during the initial stage of film growth. Moreover, it is anticipated that the thickness dependence of UV-absorbance may be another reason for thickness dependence of activity because the concentration of positive hole is determined by the absorbance of UV light. However, according to the relation $A = 1 - e^{-\mu t}$ where μ is constant, the absorbance A and hence the photocatalytic activity should be a continuous change with film thickness t, other than a drastic change indicated in Fig. 7. On the other hand, upon contacting with solution, a Schottky barrier will be formed on the film/solution interface. The moving of the photogenerated holes out of TiO_2 film should be assisted by the built-in potential in Schottky barrier to become active in photocatylysis. The surface layer corresponding to a thickness of Schottky barrier plays a decisive role in photocatalytic activity, just like *p-n* conjuction in solar cell. If film thickness t is less than the depletion layer width x_d, the photocatalytic activity will be dramatically decreased. As a result, the critical thickness t_c in Fig. 7 is presumably corresponding to the depletion layer width x_d. The surface state and donor concentration N_d of the films affect either the width or the height of Schottky barrier, consequently causing a change of t_c in different thin films.

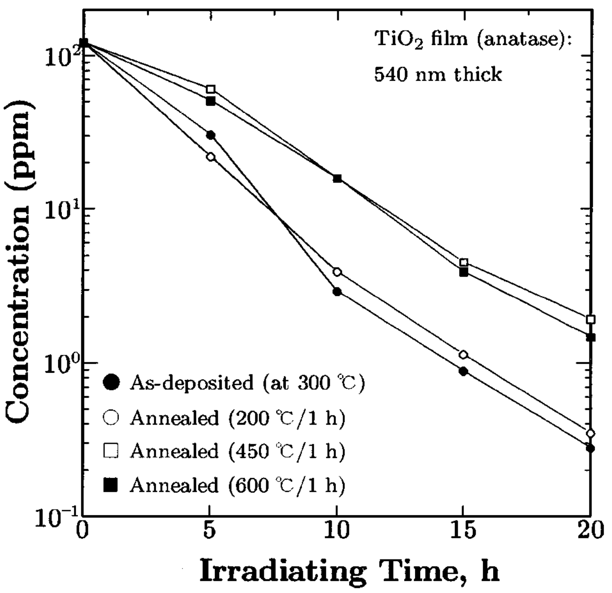

Figure 8 Change of photocatalytic activity of pure TiO_2 films (on glass, double-sided) after heated in air at various temperatures.

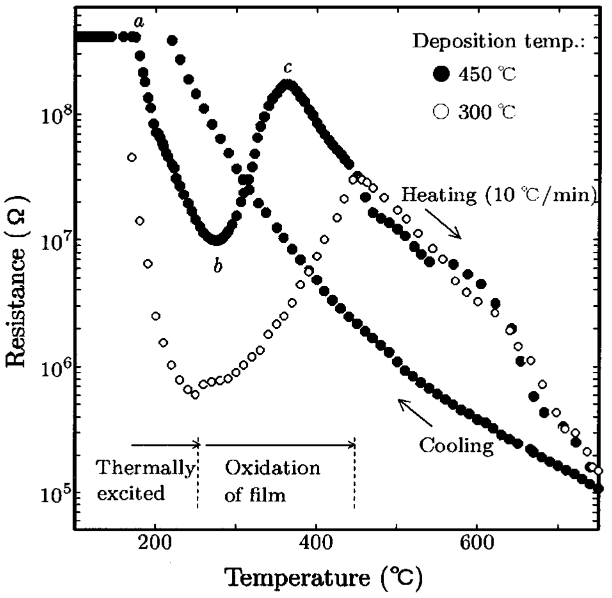

Figure 9 Abnormal resistance change of TiO_{2-x} films during the heating-up process. The cooling curve was measured after 2 h soaking period at 750 °C.

3.3. Correlation between defect and photocatalysis

As shown in Fig. 8, the film treated at 200 °C in air shows a negligible change in photocatalytic activity whereas a degradation in activity if treated at 450 and 600 °C. This phenomenon is thought to be due to the decrease of nonstoichiometric defect, according to the abnormal change in electric resistance measured during the heating-up process of the as-deposited TiO_{1-x} film, as shown in Fig. 9. Usually, the as-deposited film is nonstoichiometric and has a considerable number of oxygen vacancies [16]. At low temperature (before point *a* in Fig. 9), the quasi free electrons required to preserve electric neutrality are bound to defect sites. With increasing the temperature, these trapped electrons are thermally agitated and become free, thus greatly modifying the electric conduction (point $a \rightarrow b$). With further increase in temperature, the concentration of either $V_O^{\cdot\cdot}$ or e' decreases rapidly because oxidation of the oxygen-deficient film gives rise to a stoichiometric composition. As a result, the resistance increases dramatically after point *b* until the film is fully oxidized at point *c*. The fully oxidized film shows normal NTC characteristics of electric resistance (see cooling curve). Accordingly, if the film is oxidized at temperature higher than point *b*, the photocatalytic activity will be weakened because of the decrease of oxygen vacancy. Therefore, attention should be paid to maintaining or even increasing the defect density in the film. However, it was found that the film annealed in reducing atmosphere (e.g, CO + Ar) shows no modification in activity presumably because such process can not generate more defects than in as-deposited film [17].

In addition, compared with the film deposited at 450 °C, the film deposited at 250 °C shows more dramatic change of resistance in this temperature range as shown in Fig. 9, implying that the film deposited at low temperature contains more defects and should show higher activity, fairly consistant with the results in Fig. 6.

Additional evidence for the variation of oxygen vacancy is available from XPS spectra. As shown in Fig. 10, the O_{1s} core level emission shows a peak at around 531 eV in as-deposited sample and a shift to lower energy area after annealed at 600 °C, suggesting a variety in the chemical environments, especially in the coordination state of atoms. The as-deposited film is nonstoichiometric oxide which may be regarded as a solid solution of TiO_2 and Ti_2O_3. Thus the O_{1s} emission is ascribled to O^{-2} ions coordinated by both Ti^{+4} and Ti^{+3} ions. While in the fully oxidized sample, O^{-2} ions are coordinated only by Ti^{+4}, resulting in a shift of binding energy. The spectra for $Ti_{2p(3/2)}$ are quite similar to those for O_{1s}. The Ti^{+4} ions in as-deposited film is partially coordinated to oxygen vacancies, while those in the fully oxidized film are coordinated to O^{-2} ions. This discrepancy leads to a slight shift in the $Ti_{2p(3/2)}$ core emission. A similar phenomenon has been observed for Ba^{+2} ions in $YBa_2Cu_3O_{6.9}$ [18] and for defect on the surface of TiO_2 (1 1 0) single crystal [19].

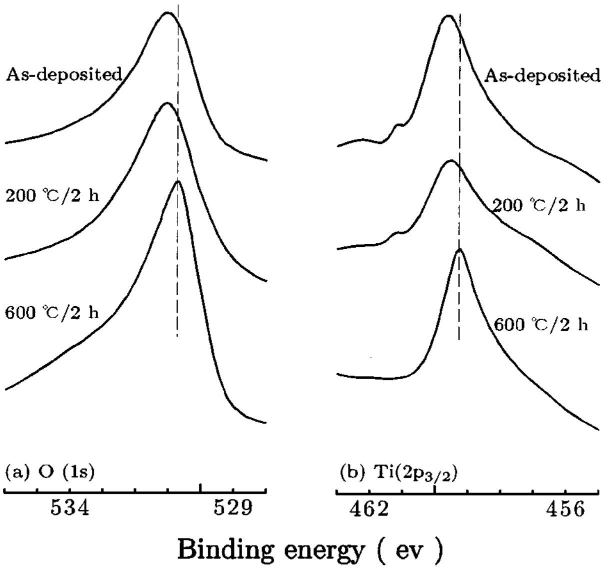

Figure 10 XPS spectra of TiO_2 films on glass, showing a chemical shift after heat treatment.

It is widely accepted that surface defects, such as oxygen vacancy, can serve as active sites for the absorption of gases [19] which is important for chemical gas sensor. Since photocatalytic reaction is surface reaction and only the substance absorbed on the surface can react with the photogenerated active seeds (e.g., h^+, OH^- and O), defects may contribute to the photocatalysis reaction by providing active sites for chemisorption and/or decomposition of the molecules, and by modifying surface conduction necessary for the charge transfer during electrochemical reaction.

4. Conclusions

The photocatalytic activity was observed in two types of Pt-TiO_2 films. The dispersion of platinum or the use of platinum buffer layer makes it possible to form anatase phase at relatively lower temperatures and thus possible to use plastic sheet as substrate. In Pt-dispersed TiO_2 films the maximum activity was observed around 1.5% of platinum content due to the formation of anatase phase and minute microstructure. In TiO_2 film coated with platinum particles, extremely small amount of platinum can remarkably improve the photocatalytic activity due to the charge separation of *e*-*h* pair. The minimum thickness is required for photocatalyst in terms of the thickness dependence of activity. Since surface defects are useful for the photocatalytic activity, care should be taken not to expose films to high temperature (e.g., ≥400 °C) because intensive heating may result in a depletion of defects in the films.

References

1. A. FUJISHIMA and K. HONDA, *Bull. Chem. Soc. Jpn.* **44** (1971) 1148.
2. *Idem., Bull. Nature* **238** (1972) 37.
3. E. PELIZETTI and C. MINERO, *Electrochem. Acta.* **38** (1993) 47.
4. D. OLLIS and H. AL-EKABI (eds.), in “Proc. 1st Int. Conf. TiO_2 Photocatalytic Purification and Treatment of Water and Air,” London 1992 (Elsevier Science, Amsterdam, 1993).
5. S. FRANK and A. BARD, *J. Phys. Chem.* **81**(15) (1977) 1484.
6. T. KAWAI and T. SAKATA, *J. Chem. Soc., Chem. Commun.* (1980) 695.
7. S. TERATANI, J. NAKAMICHI, K. TAYA and K. TANAKA, *Bull. Chem. Soc. Jpn.* **55** (1982) 1688.
8. Y. OOSAWA, *J. Phys. Chem.* **88** (1984) 3069.
9. *Idem., Bull. Chem. Soc. Jpn.* **65** (1992) 34.
10. M. TAKAHASHI, K. MITA, H. TOYUKI and M. KUME, *J. Mat. Sci.* **24** (1989) 243.
11. K. KATO, A. TSUZUKI, H. TAODA, Y. TORI, T. KATO and Y. BUTSUGAN, *J. Mat. Sci.* **29** (1994) 5911.
12. T. FUKAMI and O. TESHIMA, in “Proc. 10th Symp. on ISIAT,” (ISIAT’86 Committee, Tokyo, 1986) p. 413.
13. *Idem., J. Inst. Electronic, Information and Communication Eng.* J70-C (1987) 408 (in Japanese).

14. A. FUJISAWA, T. RAI and T. FUKAMI, *Ionics* **21**(2) (1995) 45.
15. L. KAVAN, M. GRATZEL, S. GILBERT, C. KLEMENZ and H. SCHEEL, *J. Amer. Chem. Soc.* **118** (1996) 6716.
16. J. SHENG, N. YOSHIDA, J. KARASAWA and T. FUKAMI, in “Proc. 3rd Int. Symp. Sputtering & Plasma processes,” edited by K. Hirata (ISSP’95 Committee, Tokyo, 1995) p. 367.
17. P. KOFSTAD, “Nonstoichiometry, Diffusion, and Electric Conductivity in Binary Metal Oxides” (Krieger Publishing, USA, 1983) p. 141.
18. H. MEYER, Y. GAO, T. WAGENER and J. WEAVER, in “Amer. Inst. Phys. Conf. Proc. No.165,” edited by J. Harper, R. Colton and L. Feldman (New York, 1987) p. 259.
19. W. GOPEL and G. ROCKER, *Phys. Rev.* **28** (1983) 3427.

Received 6 December 1996
and accepted 2 June 1999