Characteristics of TiO₂ Thin Film as a Photocatalyst Prepared Using the Pulsed Laser Deposition Method

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Titanium dioxide (TiO₂) thin films as a photocatalyst were prepared using the pulsed laser deposition (PLD) method. The structural and compositional properties of the films are described. Electron binding energy peaks of (a) Ti 2p_{3/2} and (b) O1s can be observed on films prepared by the PLD method. The crystallinity of the prepared TiO₂ film was measured by X-ray diffraction as a parameter of substrate temperature (Ts). XRD measurements revealed that the substrate temperature affected the phase formation, the crystalline structure and the preferred orientation of the TiO₂ films. The structure of the films as measured by an atomic force microscopy (AFM) suggests that the films prepared at Ts ≤ 400°C are composed of particles of two sizes : small particles of ~10 nm in diameter and large particles of ~100 nm in diameter. The films prepared at Ts = 600°C were composed entirely of large particles.

Key Words : TiO₂, Thin Film, Photocatalyst, Pulsed Laser Deposition, XRD

1. Introduction

Recently, environmental damage such as water and air pollution has become an increasingly serious problem. For example, exhaust emissions from automobile engines, such as nitrogen oxides (NO_x) and particulate materials (PMs), particularly from diesel engines, are having harmful effects on the environment and on humans. Since environmental and exhaust standards have been adopted by the authorities of several countries as a means to safeguard public health, emission control of these gases has become an important task^{1),2)}.

Titanium dioxide (TiO₂) is a material having photocatalytic properties. As this photocatalytic function has a powerful decomposing effect, TiO₂ has been used in a variety of applications for purification of the environment^{3)~8)}. Many techniques have been used to produce TiO₂ films, including thermal evaporation⁹⁾, RF sputtering¹⁰⁾, reactive sputtering¹¹⁾, the sol-gel method¹²⁾, and chemical vapor deposition^{13),14)}. However, the qualities of the TiO₂ films prepared using these methods have only been slightly improved.

Over the past few years, the pulsed laser deposition (PLD) method has become a widely used technique for the deposition of thin films due to the advantages of simple system setup, a wide range of deposition conditions, a wider choice of materials and higher instantaneous deposition rates. In particular, this method is very well suited to the preparation of crystalline thin films^{15),16)}.

In this report, TiO₂ thin films are prepared as photocatalysts using the PLD method, and the structural and compositional properties of the films are measured in order to determine the condition required

to fabricate high-quality TiO₂ thin films as a photocatalyst.

2. Experimental

The schematic of the experimental apparatus is shown in **Figure 1**. In this experiment, TiO₂ thin films were prepared by pulsed Nd : YAG laser deposition. A deposition chamber was fabricated of stainless steel with a diameter of 400 mm and a length of 370 mm. The chamber was evacuated to a base pressure (below 4.0×10^{-4} Pa) using a turbomolecular pump and a rotary pump.

A pulsed Nd : YAG laser (Continuum SureliteIII ; wavelength of 532 nm, pulse duration of 3.5 ns, maximum output energy of 340 mJ) was used to irradiate TiO₂ (purity, 99.99%) or Ti (purity, 99.99%) targets. The radiated area on the target was maintained at 5.0 mm². The laser energy density was fixed at 3.8 J/cm². The Si (100) and the corning glass (SiO₂) substrates

Fig. 1 Experimental setup.

Table 1 Deposition conditions for TiO₂ thin films.

Laser	Pulsed Nd : YAG Laser Wavelength 532 nm Pulsed width 3.5 ns Energy density 3.8 J/cm ² Repetition rate 10 Hz
Target	Ti (purity 99.99%), TiO ₂ (purity 99.99%)
Substrate	Si(100), SiO ₂
Substrate Temperature	Room temp. ~700°C
Target-substrate distance	d=6.0 cm
Base pressure	<4.0×10 ⁻⁴ Pa
Gas pressure	~10 Pa (100 % O ₂)
Deposition time	30 min.

were located 6.0 cm from the target. The target was rotated at 20 rpm to avoid pitting during deposition.

The Si(100) substrate was used for film quality measurement (AFM, XRD, XPS) and corning glass (SiO₂) substrate was used for measurement of photocatalytic activity. These substrates were cleaned using an ultrasonic agitator in repeated baths of ethanol and were then rinsed in high-purity deionized water prior to loading into the deposition chamber. The substrates were heated from room temperature to 700°C using an IR lamp. The oxygen gas pressure (P_{O_2}) was varied from base pressure to 10 Pa. After 18,000 laser pulses at a repetition rate of 10 Hz, the deposition process was completed. Details of the preparation conditions for the TiO₂ thin films are given in Table 1.

The composition ratio and the bonding states were analyzed by X-ray photoelectron spectroscopy (XPS; JEOL JPS 9010). Film thickness, measured by a-step (Dektak; Ulvac), was approximately 500 nm. The crystalline structure and the crystallographic orientation of the films were characterized by glancing-angle X-ray diffraction (GXRD; JEOL JDX 3530) using CuK α radiation, where the angle of incidence was maintained at 1.0°. The surface morphology and roughness of the TiO₂ thin films on Si(100) substrates was observed using an atomic force microscopy (AFM; JEOL, JSPM 4210).

The photocatalytic properties of the prepared TiO₂ films were tested by measuring the decomposition of methylene blue (C₁₆H₁₈N₃S·Cl·3H₂O) on the TiO₂ surface under UV light irradiation. TiO₂ films were dipped into an aqueous methylene blue solution with a concentration of 0.05 mmol/l and were then irradiated using a black light lamp (362 nm, 50 mW/cm²). The transmittance of the solution was measured for 8 hours starting at intervals of 2 h using a Hitachi UV-3300 spectrometer at a wavelength of 664 nm.

3. Results and Discussion

Electron binding energies of the TiO₂ thin film prepared using the TiO₂ target at an oxygen gas pressure of P_{O_2} =10 Pa and a substrate temperature of T_s =500°C were measured by X-ray photoelectron spectroscopy (XPS). Figure 2 shows the obtained

Fig. 2 XPS spectra of (a) Ti 2p 3/2 and (b) O1s electron binding energies of the TiO₂ thin film deposited at T_s =600°C and P_{O_2} =10 Pa (Ti target, E_d =3.8 J/cm²).

Fig. 3 XPS depth profile of the TiO₂ film deposited at T_s =600°C and P_{O_2} =10 Pa (TiO target, E_d =3.8 J/cm²).

XPS spectra of (a) Ti 2p_{3/2} and (b) O1s electron binding energies of the TiO₂ thin film prepared using the TiO₂ target at a oxygen gas pressure of P_{O_2} =10 Pa. TiO₂ thin film was prepared using the PLD method. Figure 3 shows the XPS depth profile of the TiO₂ film that was prepared using the TiO₂ target at P_{O_2} =10 Pa and T_s =600°C. In this figure, the film thickness was

Fig. 4 GXRD patterns of the TiO_2 films deposited at $P_{\text{O}_2}=10$ Pa (Ti target).

calculated from the sputtering time and the sputtering yield for the bulk TiO_2 target. The O/Ti composition ratio of the film was approximately 1.8.

Detailed XRD measurements were performed in order to investigate the crystalline properties of laser-deposited TiO_2 films that were prepared using the Ti target. At $T_s=300^\circ\text{C}$, the weak peaks of anatase TiO_2 (101) and (004) and the distinct peak of rutile TiO_2 (210) appear (Fig. 4(a)). As the substrate temperature increased to $400\sim 500^\circ\text{C}$, the weak peak of rutile TiO_2 (110) appeared (Figs. 4(b) and (c)). When the substrate temperature increased to 600°C , the peak of anatase TiO_2 (101) disappeared and the peak of rutile TiO_2 (200) appeared. (Fig. 4(d)). The intensity of rutile TiO_2 (110) increases significantly as the substrate temperature increases.

The structures of the films prepared using the Ti target were measured by an atomic force microscopy (AFM), as shown in Figs. 5(a) and (b). The measurement was performed in non-contact AFM mode. The films prepared at $T_s \leq 400^\circ\text{C}$ were found to be composed of particles of two sizes: small particles of ~ 10 nm in diameter and large particles of ~ 100 nm in diameter, as shown in Fig. 5(a). The films prepared at $T_s=600^\circ\text{C}$ are composed of large particles (~ 100 nm), as shown in Fig. 5(b). In general, large particles indicate rutile type TiO_2 and small particles indicate anatase type TiO_2 . These results suggest that substrate temperature affects the phase formation, the crystalline structure and the preferred orientation of the TiO_2 films.

Figure 6 shows the time-dependence of the transmittance of an aqueous methylene blue solution (0.05 mmol/l) for the TiO_2 films (1.0 cm 2). TiO_2 films were deposited using the Ti target at $T_s=400^\circ\text{C}$ and $T_s=600^\circ\text{C}$ in oxygen gas ($P_{\text{O}_2}=10$ Pa). Under UV light irradiation (362 nm, 50 mW/cm 2) these films decomposed the aqueous methylene blue solution. The maximum decomposition rate constant of the film calculated from the results was approximately 0.02 (h^{-1}), which was almost identical to that of the film prepared using the sol-gel method. The

(a) $T_s=400^\circ\text{C}$, $P_{\text{O}_2}=10$ Pa

(b) $T_s=600^\circ\text{C}$, $P_{\text{O}_2}=10$ Pa

Fig. 5 AFM images of the TiO_2 films deposited at $T_s=400^\circ\text{C}$ and $T_s=600^\circ\text{C}$. Bar graphs show the height of the film surface (Ti target, $P_{\text{O}_2}=10$ Pa).

Fig. 6 The temporal evolutions of the transmittance of an aqueous methylene blue solution for the TiO_2 films (Ti target, $P_{\text{O}_2}=10$ Pa).

photocatalytic activity of the film prepared at $T_s=400^\circ\text{C}$ is higher than that of the film prepared at $T_s=600^\circ\text{C}$. Generally, the decomposition ability of

anatase TiO₂ film is higher than that of rutile TiO₂ film. This result suggests that the film prepared at Ts=400°C is anatase TiO₂ and the film prepared at Ts=600°C is rutile TiO₂.

4. Conclusions

TiO₂ thin films as the photocatalyst are prepared using the PLD method, and the structural and compositional properties of the films were described. XPS measurements suggest that TiO₂ thin film prepared using a TiO₂ target at Ts=600°C and P_{O₂}=10 Pa is almost stoichiometric. The crystallinity of the TiO₂ film, as measured by X-ray diffraction, suggests that the films prepared using the Ti target at Ts=300~600°C consists of anatase type and rutile type TiO₂. The structure of the films as measured by atomic force microscopy suggests that the films prepared at Ts≤400°C are composed of particles of ~10 nm and ~100 nm in diameter. The films prepared at Ts=600°C were composed of large particles. Films prepared by the PLD method decomposed the aqueous methylene blue solution under UV light irradiation.

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