Preparation of TiO$_2$/WO$_3$ multilayer thin film by PLD method and its catalytic response to visible light

H. Shinguu$^{a,*}$, M.M.H. Bhuiyan$^a$, T. Ikegami$^b$, K. Ebihara$^b$

$^a$ Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan
$^b$ Department of Electrical and Computer Engineering, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

Available online 20 October 2005

Abstract

We report about multilayer TiO$_2$/WO$_3$ thin films deposited on silicon and quartz glass substrate by pulsed laser deposition (PLD) method. The multilayer film has higher photocatalytic activity than TiO$_2$ film under visible light irradiation. The films were characterized using an atomic force microscope (AFM), X-ray diffraction method (XRD) and UV–VIS absorption spectrometry. Photocatalytic efficiency of TiO$_2$ and TiO$_2$/WO$_3$ multilayer thin film was also evaluated by photodecomposition of methylene blue (MB) in aqueous solution. The portion of WO$_3$ layers in the multilayer film is very sensitive to photocatalytic property. The multilayer film containing 5% WO$_3$ layers in thickness showed the highest dye decomposition ratio.

© 2005 Elsevier B.V. All rights reserved.

PACS: 81.15.Fg
Keywords: Photocatalyst; Thin film; TiO$_2$; WO$_3$

1. Introduction

The photocatalytic material titanium oxide (TiO$_2$) [1,2] has been gathering much attention due to its various applications to the environmental purification and dye sensitized photovoltaic solar cell [3]. To improve photocatalytic characteristic of TiO$_2$ for practical wide range applications, it is important to prepare TiO$_2$ with large specific surface area and optical response to visible light.

Recently, there are a number of studies related to enhancement of photocatalytic response to visible light using a metal oxide catalyst with TiO$_2$. Combination of different kinds of semiconductor photocatalysts can enhance photocatalytic response by increasing the charge separation and extending wavelength for photoexcitation. At the same time, its physical and optical properties are greatly modified.

Pulsed laser deposition (PLD) method [4,5] is known as one of the excellent processes for thin film deposition and it seems suitable for fundamental research to improve properties of TiO$_2$ thin film, because it can easily deposit thin films with nano-size grains and multilayer structure. In this research we prepared multilayer TiO$_2$/WO$_3$ thin films [6,7] using Ti, TiO$_2$, WO$_3$ target by PLD method and investigate their properties.

2. Experimental procedure

The experimental setup is shown in Fig. 1. A pulsed KrF excimer laser (Lambda Physik COMPex205, $\lambda$=248 nm, rep. rate 10 Hz) was used to ablate one of Ti (DOWA), TiO$_2$ and WO$_3$ (DOWA) targets in a deposition chamber filled with oxygen of 27 Pa. A TiO$_2$ target used in this experiment was made by pressing and sintering anatase TiO$_2$ powder. Laser fluence of 3 J/cm$^2$ was used to ablate Ti and TiO$_2$ targets and fluence of 1.3 J/cm$^2$ was used for a WO$_3$ target. A silicon (100) or quartz glass substrate was set 5 cm apart from the target and kept at a temperature of 500 °C during deposition.

Fig. 2 shows the structure of the TiO$_2$/WO$_3$ multilayer thin film. The WO$_3$ layer and TiO$_2$ layer were deposited alternately by 9000 laser ablation pulses. Number of laser pulses to ablate a WO$_3$ target were changed from 3% to 15% of total laser pulses to change thickness of the WO$_3$ layer.

Fig. 3 shows experimental setup to evaluate photodecomposition ratio of the film. The film dyed with methylene blue (MB) in aqueous solution was irradiated by 15 W fluorescent
lamp at 15 cm apart and illuminated by a halogen lamp to measure intensity of the reflected red light ($\lambda = 650$ nm) with a spectrometer. Here, photodecomposition ratio was calculated from the increase ratio of the reflected light intensities.

3. Result and discussion

Fig. 4(a) and (b) show XRD patterns of TiO$_2$/WO$_3$ multilayer films deposited on a silicon substrate (100), where 5% of total laser pulses was used to deposit the WO$_3$ layers. In Fig. 4(a) and (b), Ti and TiO$_2$ targets were used to deposit TiO$_2$ layers, respectively. Clear diffraction peaks from anatase TiO$_2$ [(101), (105), (211)] are observed in both films. Weak and broad peaks from WO$_3$ [(002), (004)] may result from its thickness and low deposition temperature. The films of different WO$_3$ mixing ratio showed almost the same results.

Fig. 5 shows the AFM images of TiO$_2$/WO$_3$ multilayer films of different WO$_3$ mixing ratios deposited on a quartz glass substrate using Ti or TiO$_2$ target for TiO$_2$ layers. Multilayer films of 3% WO$_3$ mixing ratio (Fig. 5(a), (d)) have grain size of about 100 nm and 80 nm, respectively. The films of 15% WO$_3$ mixing ratio have larger grain size of (c) 150 nm and (f) 100 nm, which results from larger grain size of WO$_3$ film than that of TiO$_2$ film.

Fig. 6(a) and (b) shows the UV–VIS transmittance of TiO$_2$/WO$_3$ multilayer film deposited using a Ti target (a) and a TiO$_2$ target (b). In both cases, optical absorption edge increased from 300 nm to 350 nm with increasing WO$_3$ ratio in the film. This means that film of TiO$_2$/WO$_3$ multilayer structure can be activated by light of longer wavelength without decreasing transmittance in visible region.

Photocatalytic property of the TiO$_2$/WO$_3$ multilayer films was evaluated by photodecomposition of methylene blue (MB) in aqueous solution. Fig. 7(a) and (b) show the decomposition ratio of MB using TiO$_2$/WO$_3$ multilayer films irradiated by a fluorescence lamp ($\lambda > 400$ nm). Decomposition ratio and its temporal change depend on both WO$_3$ mixing ratio and the target (Ti or TiO$_2$) to deposit TiO$_2$ layers. Multilayer films of 5% WO$_3$ mixing ratio showed the largest decomposition ratio. With increasing WO$_3$ mixing ratio, the grain size increases and roughness of the film decreases, which means decrease of surface area contacting with MB aqueous solution. Spectral absorption edge of the multilayer film shifts to longer wavelength with increasing WO$_3$ mixing ratio, and it contributes to photo-activation of the film by visible light.
Therefore there is an optimal WO$_3$ mixing ratio for photocatalytic property of the multilayer film, and it seems about 5% in our experiment. All films showed decomposition ratio of

---

Fig. 5. AFM images of TiO$_2$/WO$_3$ multilayer thin film (1 μm × 1 μm, quartz glass substrate). (a–c) Target: Ti, (d–f) Target: TiO$_2$.

Fig. 6. Transmittance of TiO$_2$/WO$_3$ multilayer thin film. (a) Target: Ti, (b) Target: TiO$_2$ (quartz glass substrate).

Fig. 7. Comparison of decomposition ratio of TiO$_2$/WO$_3$ multilayer thin film. (a) Target: Ti, (b) Target: TiO$_2$. 
over 10% after 300 min irradiation, however TiO$_2$ films (without WO$_3$ layers) could not decompose MB under the same condition.

4. Conclusion

Multilayer TiO$_2$/WO$_3$ thin films were deposited by PLD technique using WO$_3$ target and Ti or TiO$_2$ target. Influence of mixing ratio of WO$_3$ in the film and target material on the film properties was investigated. Multilayer film mixed with WO$_3$ layers into the TiO$_2$ layers modified grain size and surface morphology of the films. Multilayer TiO$_2$/WO$_3$ films showed improvement of photocatalytic response to the visible light and 5% of WO$_3$ mixing rate showed the best photocatalytic response.

References