Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 21(2009) 741–744
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Influences of working pressure on properties for TiO_2 films deposited by DC pulse magnetron sputtering

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Abstract

TiO_2 films were deposited at room temperature by DC pulse magnetron sputtering system. The crystalline structures, morphological features and photocatalytic activity of TiO_2 films were systematically investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and ultraviolet spectrophotometer, respectively. The results indicated that working pressure was the key deposition parameter influencing the TiO_2 film phase composition at room temperature, which directly affected its photocatalytic activity. With increasing working pressure, the target self-bias decreases monotonously. Therefore, low temperature TiO_2 phase (anatase) could be deposited with high working pressure. The anatase TiO_2 films deposited with 1.4 Pa working pressure displayed the highest photocatalytic activity by the decomposition of Methyl Orange solution, which the degradation rate reached the maximum (35%) after irradiation by ultraviolet light for 1 h.

Key words: TiO_2 film; anatase; UV induced photocatalysis; DC pulse magnetron sputtering
DOI: 10.1016/S1001-0742(08)62334-7

Introduction

Over the last few years, a great attention has been focused on the titania (TiO_2) films due to its excellent chemical stability, high refractive index, nontoxicity, and good mechanical properties. Besides, the TiO_2 films can exhibit excellent photocatalytic and superhydrophilic properties after ultraviolet (UV) light irradiation (Doong *et al*., 2007; Zhao *et al*., 2008; Miyamura *et al*., 2008; Wang *et al*., 2008; Turkevych *et al*., 2008). Therefore, TiO_2 films can be utilized in many applications, such as antifogging, selfcleaning, antibacterial, self-sterilization processes and in the removal of organic pollutants from wastewater (Aubry *et al*., 2007; Tavares *et al*., 2007). But there are several drawbacks that limit a wider utilization of the TiO_2 films as photocatalyst applications. The most primary one is the formation of photoactive TiO_2 films at room temperature without post-deposition thermal annealing treatment (Heft *et al*., 2006).

There are three different crystalline phases of TiO_2 namely anatase, rutile and brookite. Among them, the anatase structure is referred to be the most photoactive structure. However, the deposition of crystalline photoactive TiO_2 films without the substrate heating or a post-deposition thermal annealing has not been fully mastered yet. Among numerous deposition methods, the magnetron sputtering is a promising one for the deposition of crystalline anatase TiO_2 films with photocatalytic at room temperature (lower than 100°C).

In this article, anatase phase TiO_2 films are deposited with direct current pulse magnetron sputtering system. This method uses high purity Ar (99.999%) as sputtering gas and high purity O_2 (99.999%) as reactive gas. High purity Titanium (Ti, 99.99%) is used as target material. By this method, the anatase TiO_2 films with excellent photocatalytic are deposited at room temperature.

1 Experiment

1.1 Sample collection

A Ti (99.99%) target (200 × 100 mm^2) was used for a reactive sputtering material for depositing transparent TiO_2 films in the Ar + O_2 mixture. The target power was supplied by a DC pulse (Sıcha *et al*., 2008). Power supply unit operating in power mode was at a repetition frequency of 100 kHz and a duty cycle of 0.1 (Pinnacle Plus + 5 kW, Advanced Energy Industries Inc., USA). Films were deposited on unheated glass substrates. The distance between substrate and target was 110 mm. The substrate surface temperature (T) was measured by thermocouple and T was lower than 100°C in all experiments. In this case, the contamination of TiO_2 films by the Na+ diffusing from the glass substrates can be neglected. The influence of working gas pressure on the TiO_2 film structure and photocatalytic activity was investigated. The detailed deposition

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conditions are listed in Table 1.

The film phase composition was determined by the X-ray diffraction (XRD) analysis using a D/max2500 diffractometer (Rigaku, Japan) working in Bragg-Brentano geometry with Cu K_α(40 kV, 40 mA) radiation. The morphological features of films were measured by atomic force microscopy (AFM) system (SPM-9500J3, Shimadzu Corporation, Japan). The thickness of films was measured by a stylus profilometer Dektak 6M (Veeco, USA) with the resolution of 0.1 nm. The photocatalytic activity of TiO_2 film was determined from a decomposition of $C_{14}H_{14}N_3NaO_3S$ (Methyl Orange, MO) solution. This solution exhibits a very good stability against UV light irradiation. The TiO_2 films were immersed in the MO solution with initial concentration (C_0 = 10 mg/L) in distilled water (10 mL) and irradiated by the UV light for 1 h. The concentration of solution was determined by measuring the absorbency of solution at wavelength 485 nm using ultraviolet-visible spectrophotometer (U-3310, Hitachi Ltd., Japan).

Table 1 Deposition parameter

Parameters	Value
Ar flow rate (cm^3/min)	16
O_2 flow rate (cm^3/min)	4
Ti target sputtering power (W)	400
Base vacuum (Pa)	1.0×10^{-4}
Working pressure (Pa)	0.5–1.4

2 Results and discussion

2.1 Growth rate analysis

Figure 1 shows the curve of the growth rate of TiO_2 films deposited at different working pressures. From Fig. 1, it can be seen that with increasing working pressure from 0.5 to 1.4 Pa, growth rate of films decreases gradually from 1.7 to 1.1 nm/min. This trend can be explained by the following reasons. First, working pressure of system controls mean free path of metastable Ar particles (Ar*) and sputtering ions (Ar^+) (Tang, 2003; Ding, 2007). As working pressure increases, the mean free paths of Ar* and Ar^+ decrease and then the energy of Ar^+ decreases. Farther, the sputtering yield of target decreases. Second, mean free paths of Ti atoms and Ti ions decrease with increasing working pressure. Then the scattering cross section of Ti particles increases with increasing working pressure in the process of Ti particles incident to the growing surface of film.

2.2 XRD analysis

Figure 2 shows the XRD patterns of TiO_2 films deposited at different working pressures. From Fig. 2 it can be seen that the structure of TiO_2 films strongly depends on the working pressure. The XRD patterns of TiO_2 films deposited at low working pressures (0.4–0.8 Pa) display no obvious diffraction peak, which means that the films are amorphous structure. When working pressure is increased from 1.0 to1.4 Pa, the XRD patterns of TiO_2 films exhibit only one diffraction peak at 2θ = 25.3°, which means that the films are pure anatase (101) phase. No rutile phase is found in XRD patterns of all the films.

The rutile phase is a high temperature TiO_2 phase and therefore higher activation energy is needed for its formation comparing with the anatase phase (Sıcha *et al*., 2008). Figure 3 gives the Ti target self-bias at different working pressures. When other deposition parameters are seted constantly, the Ti target self-bias decreases monotonously with increasing working pressure. In sputtering theory, the Ti target self-bias variation influences the energy of particles sputtered from the target directly. Finally, the particles energy incidence to the film growth surface is affected by the Ti target self-bias variation (Tang, 2003; Ding, 2007). The particles energy is higher than need for anatase phase formation but lower than that for rutile phase from 0.5 to 0.8 Pa (Sıcha *et al*., 2008). Therefore, the film displays an amorphous structure. As mentioned above, higher working pressure leads to loss more particle energy by scattering between particles. Thus pure anatase phase TiO_2 films are deposited at high working pressure (1.4 Pa).

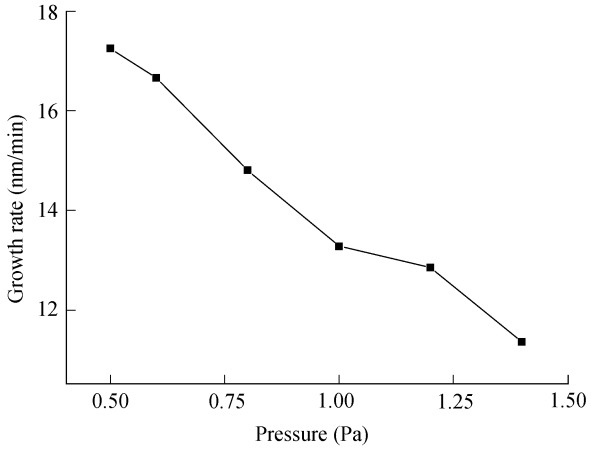

Fig. 1 Growth rate at different working pressures.

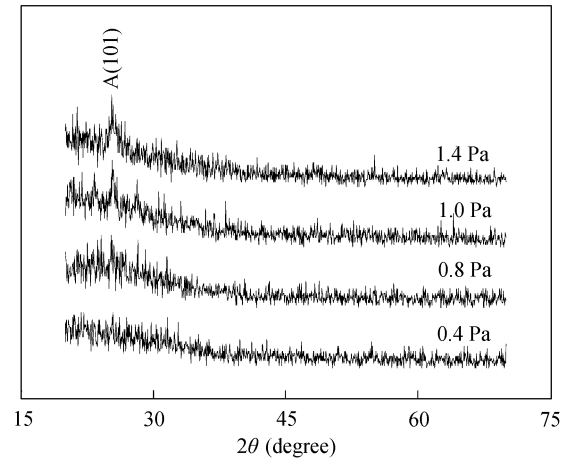

Fig. 2 X-ray diffraction (XRD) patterns of TiO_2 films deposited at different working pressures.

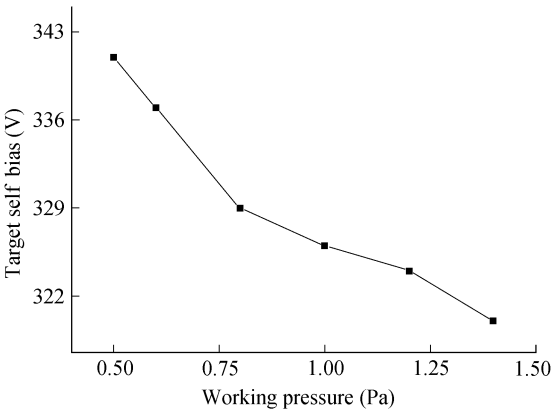

Fig. 3 Ti target self bias at different working pressures.

In order to see clearly the crystal structure of TiO_2 films, TiO_2 films deposited at different working pressures are thermal annealed at 500°C. Figure 4 shows the evolution of XRD patterns of annealed TiO_2 films. From Fig. 4, it can be seen that no rutile phase is found in all samples after thermal annealing treatment. The XRD patterns of TiO_2 films deposited at low working pressures (0.5–0.8 Pa) display diffraction peaks at $2\theta = 25.3°$, 37.8°, 48.1°, 53.9°, and 62.7°, which is generally attributed to anatase phase (101), (004), (200), (105), and (204) (00-021-1272 JCPDS card number), respectively. This phenomenon can be explained by the energy of incident Ti particles. Because the energy is lower than needed for rutile phase and the film contain little rutile phase nucleation, the XRD patterns of all films after thermal annealing treatment display no rutile phase. With a higher energy than needed for anatase phase, Ti particles incident to the film growth surface come into being anatase phase nucleation randomly. Thereby, after thermal annealing treatment, TiO_2 films deposited at low working pressure contain multi anatase crystallographic orientations. While with increasing working pressure, the incident Ti particles energy is decreased through scattering other particles, as discussed above. This results show that the films display the anatase (101) phase preferred orientation. From Figs. 2 and 4, it is seen that both films before and after thermal annealing treatment, exhibit anatase (101) phase preferred orientation deposited at high working pressure (1.4 Pa).

2.3 Photocatalytic activity

The photocatalytic activity of TiO_2 film is characterized by the degradation rate of MO solution, which the degradation rate is the change of the solution concentration. The concentration of MO solution is determined by measuring the absorbency of solution at wavelength 485 nm. The absorbency of solution is determined by its absorption coefficient, thickness, and concentration. The absorption coefficient and thickness of solution are constant in all experiments. Therefore, the absorbency of solution represents the concentration of solution directly. Figure 5 shows the evolution of degradation rate for 200 nm as deposited TiO_2 films with increasing working pressure. From Fig. 5 it can be seen that the working pressure strongly influences the degradation rate of deposited TiO_2 films. The degradation rate of TiO_2 films improves from 17% to 33% when working pressure rises from 0.4 to 1.4 Pa. This trend can be interpreted as follows. First, anatase phase is referred to be the most photoactive phase. With the increase of working pressure, more anatase phase TiO_2 structure appeared, and then the degradation rate for MO solution is improved. Second, with working pressure increasing, the structure of TiO_2 film is transformed from amorphous into crystal. The morphological features of films change accordingly. Figure 6 displays the atomic force microscopy (AFM) surface morphologies of TiO_2 films with different working pressures. From Fig. 6 it can be seen clearly that the surface of TiO_2 films deposited at 0.4 Pa is much smoother than that at 1.4 Pa, which means the latter possess much more surface area contact with MO solution. Thus, the degradation rate of TiO_2 films improves when working pressure rises up. After UV irradiation for 5 h, MO solution could be degradated completely by TiO_2 film deposited at 1.4 Pa.

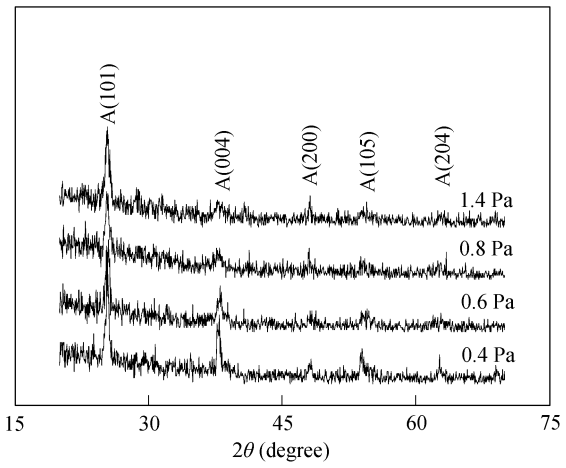

Fig. 4 XRD patterns of TiO_2 films after thermal annealing treatment at 500°C.

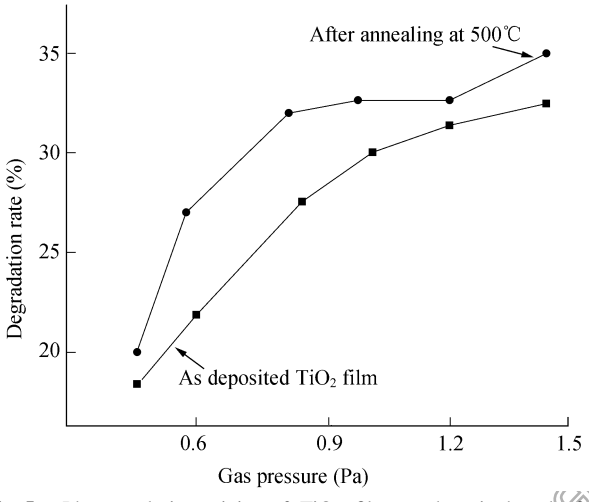

Fig. 5 Photocatalytic activity of TiO_2 film as deposited and after annealing at 500°C.

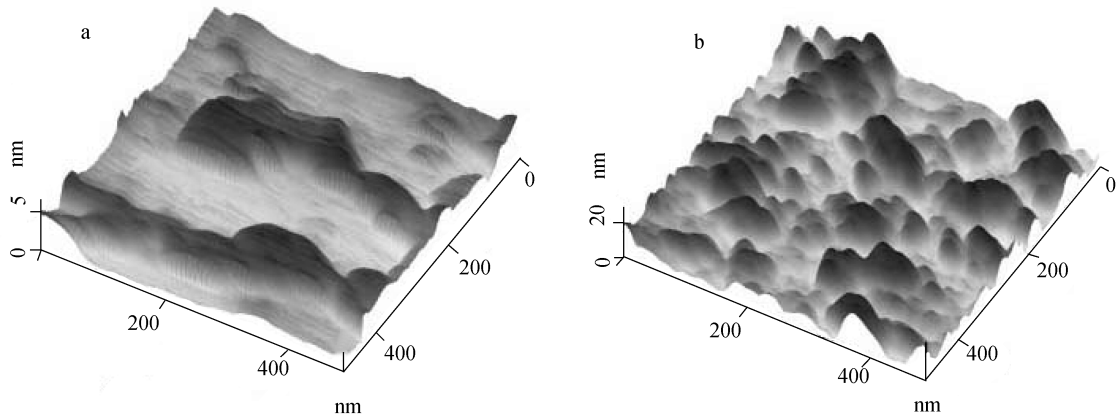

Fig. 6 Atomic force microscopy (AFM) morphological images of TiO_2 films deposited at 0.4 Pa (a) and 1.4 Pa (b).

Comparing the degradation rate of TiO_2 film as deposited with that after thermal annealing treatment at 500°C (Fig. 5), it can be seen that thermal annealing treatment does not improve the photocatylitic activity of TiO_2 films and its evolution trend obviously. From photocatalytic activity analysis, the conclusion can be drawn that TiO_2 film with high photocatalytic activity can be deposited at room temperature by direct current pulse magnetron sputtering system, which corresponds well with the results above and possess particular feature in the system. Within this technology, TiO_2 films could be utilized in a wider application.

3 Conclusions

Experiments results show that TiO_2 films of high photocatalytic activity can be obtained by direct current pulse magnetron sputtering system at room temperature (substrate temperature < 100°C). Main conclusions can be summarized as follows. 1. The working pressure is key deposition parameter, which influences the target yield and kinetic energy of Ti particles. Photocatalytic activity of films attenuated with the incident Ti particles with high kinetic energy. 2. With the increase of working pressure, the structure of TiO_2 films transforms from amorphous phase to pure anatase(101) phase and the TiO_2 films deposited at high working pressure (1.4 Pa) display excellent photocatalytic activity. The degradation rate of MO solution is slightly different between deposited TiO_2 films and after annealing treatment TiO_2 films.

Acknowledgments

This work was supported by the Dalian Foundation for Development of Science and Technology (No. 2006A13GX029). The authors appreciate Open Research Center of Saitama Institute of Technology for XRD, AFM measurements. One of the authors (DING Wanyu) would like to thank Saitama Institute of Technology for the financial support during his stay in Japan.

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