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Fabricating TiO_2 Photocatalysts by rf Reactive Magnetron Sputtering at Various Oxygen Partial Pressures

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Titanium dioxide (TiO_2) thin films were fabricated onto non-alkali glass substrates by rf reactive magnetron sputtering at room temperature using Ti-metal target at varied oxygen partial pressure [O_2/(Ar + O_2)]. The sputtering deposition was performed under an rf power of 200 W. The target to substrate distance was kept at 80 mm, and the total gas pressure was 10 mTorr after 2 h of deposition. It was found that the crystalline structure, surface morphology, and photocatalytic activities of the TiO_2 thin films were affected by the oxygen partial pressure during deposition. The XRD patterns exhibited a broad-hump shape indicating the amorphous structure of TiO_2 thin films. The thin films deposited at a relatively high value of oxygen partial pressure (70%) had a good photo-induced decomposition of methylene blue (MB) and photo-induced hydrophilicity, and had a small grain size.

Keywords oxygen partial pressure, photocatalyst, reactive magnetron sputtering, TiO_2 thin film

1. Introduction

Titanium dioxide (TiO_2) films have been extensively used as photocatalysts because of their good activity, long-term chemical stability, non-toxicity, commercial availability, and low cost (Ref 1). In the photocatalytic process, TiO_2 is activated by illumination ultraviolet (UV) light with energy higher than the TiO_2 band-gap. Inter-band transition can be induced, which results in the generation of electron-hole pairs (Ref 2). The created holes in the valence band generate hydroxyl radicals, and the excited electrons in the conduction band generate super oxide anions (Ref 3). This causes the decomposition of organic pollutants into CO_2, H_2O, and harmless intermediate organic compounds by oxidation and reduction reactions (Ref 4). TiO_2 photocatalyst thin films have been applied to various fields, such as easy-to-clean surfaces, self-cleaning windows, anti-fogging glasses, self-sterilizing and antibacterial tiles, and water purification devices (Ref 5). TiO_2 films are found in four phases: amorphous, anatase (tetragonal structure), rutile (tetragonal structure), and brookite (orthorhombic structure) (Ref 6). Anatase, the most commonly used crystal phase of TiO_2, shows good photoactivity only under UV irradiation.

The TiO_2 thin films have been prepared by various methods, such as chemical vapor deposition, ion-assisted deposition, sol-gel processing, the photoelectrochemical reduction method, liquid phase deposition, and reactive magnetron sputtering. Among these techniques, the rf magnetron sputtering process provides more advantages in controlling the microstructure and composition of the films (Ref 7), and has been used to fabricate large-area deposition (Ref 8) in industrial applications. Numerous studies have been published on the relationship between different sputtering conditions and photocatalytic activities of the films deposited by reactive magnetron sputtering (Ref 9). Herman et al. (Ref 10) studied the influence of coating parameters, such as oxygen partial pressure, film thickness and discharge current on the crystallinity of TiO_2 films. Liu et al. (Ref 11) examined the effect of oxygen partial pressure on the structure, surface morphology, and photocatalytic properties of TiO_2 film deposited by magnetron sputtering. Further, oxygen addition during sputtering as a reactive gas can assist TiO_2 film deposition (Ref 12). The aim of this study is to evaluate the effects of various [O_2/(Ar + O_2)] flow-rate ratios on the surface morphology, structure, water contact angle, and methylene blue (MB) absorbance for TiO_2 photocatalyst thin films grown onto non-alkali glass substrates by the rf reactive magnetron sputtering.

2. Experimental Procedure

The TiO_2 thin films were coated onto glass substrates (non-alkali glass, $25 \times 25 \times 1$ mm^3) for 2 h to thicknesses ranging between 1030 and 124 nm at room temperature by an rf reactive magnetron sputtering with [O_2/(Ar + O_2)] flow-rates of 0, 10,…, 90, and 100%, each. A high-purity Ti-metal target was used in an Ar/O_2 atmosphere. Total gas pressure (10 mTorr), rf power (200 W), and distance between substrate and target (80 mm) were kept constant. Reactive and sputtering gases were O_2 (purity: 99.995%) and Ar (purity: 99.995%). The argon and oxygen flow rates were controlled by mass flow meters, and the sputtering pressure was measured using an ion gauge. All the samples were deposited by rotating the substrate at 10 rpm to achieve good surface morphology. Before

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deposition, the system was vacuumed down to a pressure less than 5.0×10^{-6} Torr. The Ti-target was pre-sputtered for 10 min to remove any contamination, and the substrates were ultrasonically cleaned in acetone, rinsed with deionized water, and dried in nitrogen. The detailed deposition conditions are described in Table 1.

The photo-induced hydrophilicity was evaluated by contact angle measurements to pure water which were carried out at room temperature in an ambient atmosphere under relative humidity of 45% using a contact angle meter (FACE CA-VP150) with an experimental error of less than 1°. TiO_2 dispersed in 15 μmol MB aqueous solution was irradiated by 1.5 mW/cm^2 UV light for 4 h at room temperature to examine the photocatalytic behavior of the TiO_2 coatings. The photo-decomposition of the aqueous solution can be observed in the UV/vis spectrum (measured by UVP UVL-225D; wavelength range: 300-800 nm) by decreasing the maximum absorbance with increasing irradiation time. For visible light irradiation, a 300-W halogen tungsten lamp with a UV cut-off filter acted as a visible light source to provide light emission at 400-800 nm.

Table 1 Deposition conditions for the rf reactive magnetron sputtering of TiO_2 thin films

Substrate	Non-alkali glass; $25 \times 25 \times 1$ mm^3
Target	Ti; 99.99% purity; 50.8 mm diameter
Gas	Ar(99.995%); O_2(99.995%)
Base pressure	5.0×10^{-6} Torr
Substrate-to-target distance	80 mm
Deposition time	2 h
Substrate rotate vertical axis	10 rpm
rf power	200 W
Total gas pressure	10 mTorr
Substrate temperature	Room temperature
Oxygen-argon ratio $\left(\frac{O_2}{Ar+O_2}\right)$	0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100%

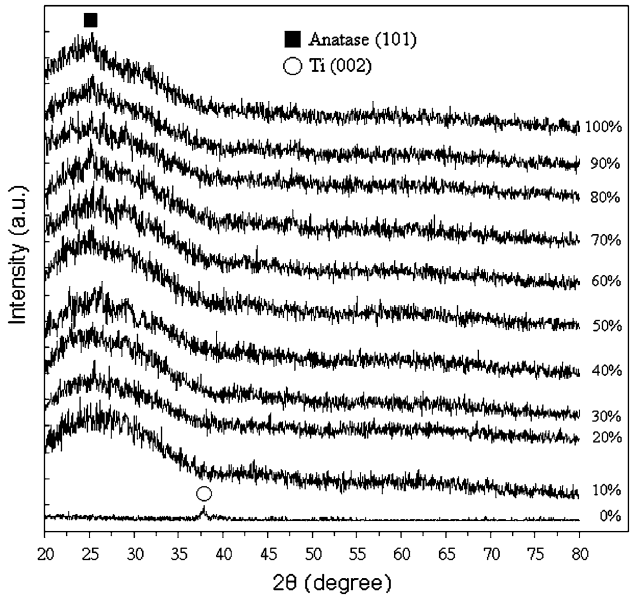

Fig. 1 XRD diffraction patterns of the TiO_2 films deposited by the rf reactive magnetron sputtering at different [O_2/(O_2 + Ar)] flow-rates

The film thicknesses were measured using a surface profilometer (α-step, AMBIOS XP-1). The surface morphologies were analyzed with a field emission scanning electron microscope (FESEM, JEOL JSM-6500F). Because of the existence of impure phase of Ti_2O in the films, the grain size was calculated from the SEM images, not from the x-ray peak broadening. The grain size of the film was considered as the crater size on the SEM image, which was averaged from an area of 4 μm^2 by the image analysis software: Image Pro Plus 5.1. The crystal structures of the films were characterized with x-ray diffraction (Rigaku-2000 spectrometer) using Cu Kα radiation.

3. Results and Discussion

The TiO_2 photocatalyst thin films grown onto glass substrates exhibited very good adherence. No cracking or peel-off of the films was noted after deposition. The deposition rate of TiO_2 films sputtered in pure Ar, i.e., [O_2/($Ar + O_2$)]

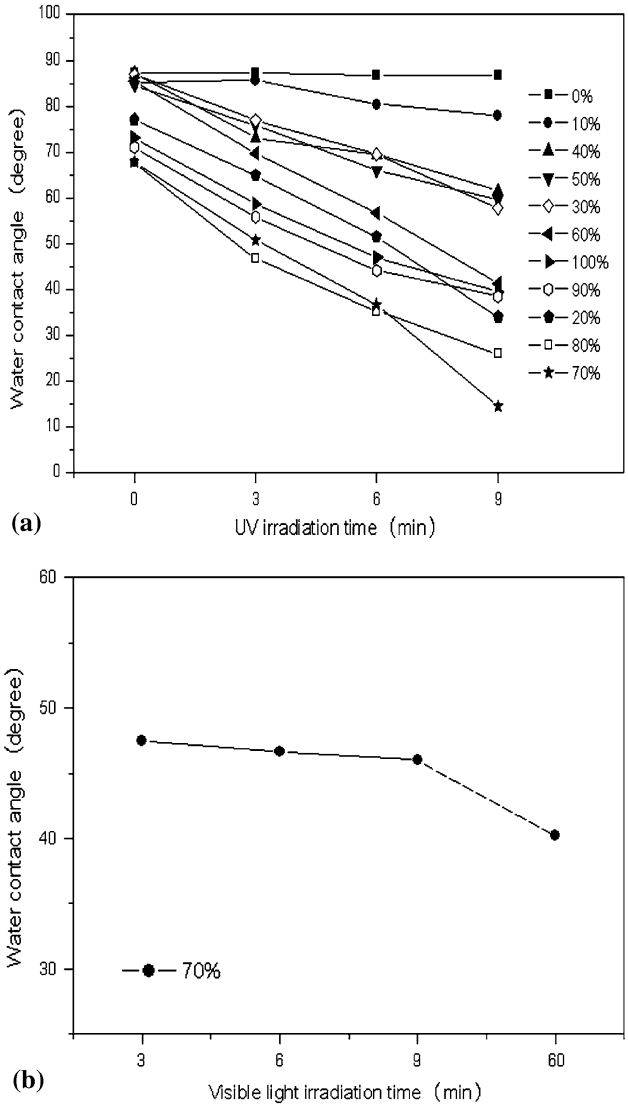

Fig. 2 (a) Plot of changes in the contact angles of the TiO_2 thin films as a function of UV light irradiation time for different [O_2/(O_2 + Ar)] flow-rates. (b) Water contact angles of the TiO_2 thin films under visible light irradiation, at [O_2/(O_2 + Ar)] flow-rate of 70%

when flow-rate ratio equals 0, was 8.58 nm/min. When the $[O_2/(Ar + O_2)]$ flow-rate ratio increased to 10%, the deposition rate of TiO_2 films decreased drastically to 1.2 nm/min. Further increase in oxygen partial pressure only resulted in gradual decrease in deposition rate. Since the dissociation energies of the argon (Ar) and oxygen (O_2) are 15.76 and 48.76 eV, respectively, Ar can be dissociated more easily than oxygen. Higher oxygen partial pressure induced more surface oxidation of the Ti target and resulted in a lower deposition rate (Ref 11).

Figure 1 shows the XRD diffraction patterns of TiO_2 films deposited onto glass substrates at various $[O_2/(O_2 + Ar)]$ flow-rates. The films deposited at the oxygen partial pressure of 0% (with pure Ar gas) display (002) preferred orientation. For all the TiO_2 films, there are no sharp diffraction lines, and these results are similar to the XRD patterns observed by Abdel-Aziz et al. (Ref 13) and Dhayal et al. (Ref 14). In this study, the main peak of TiO_2 anatase structure appears at about 25.0-25.3°, and the XRD patterns show a broad hump shape indicating the existence of amorphous structure of the film. However, it should be positioned at 25.3° for the TiO_2 anatase structure.

The photo-induced hydrophilicity of the TiO_2 thin films was evaluated by measuring the contact angles of water droplets during irradiation with the UV and visible light, as shown in Fig. 2(a) and (b), respectively. In Fig. 2(a), the initial water contact angle of the films deposited at oxygen partial pressure of 70% was about 67.7°, which was smaller than the initial contact angles of the films deposited at other oxygen partial pressures (ranging from 67.8° to 87.1°). When the film surface was irradiated by the UV light, the contact angles started to decrease. For example, the contact angle of the TiO_2 thin film deposited at oxygen partial of 70% was decreased from 67.7° to less than 15° after UV irradiation for 9.0 min, exhibiting a significant hydrophilic effect. For other oxygen partial pressures, the contact angles after the 9.0-min UV illumination ranged between 25.9° and 77.8°, which were considerably larger. On the other hand, the contact angle of the glass substrate (data not shown) and Ti thin film (oxygen partial pressure of 0%) were not decreased after the UV irradiation. It can be concluded that the glass substrate and Ti thin film have no hydrophilic characteristics. As shown in Fig. 2(b), for oxygen partial pressure of 70%, the contact angles of TiO_2 films irradiated by the UV light were higher than those exposed to the visible light. This is due to the fact that the UV light excites electrons in both the valence band and the conduction band, but the visible light only excites electrons in the conduction band (Ref 15). The UV-light-induced hydrophilicity of TiO_2 is related to the dissociative adsorption of water molecules from the ambient air at Ti^{4+} photo-reduced to Ti^{3+} sites, which are typically situated at the oxygen bridges on the surface (Ref 16). The UV-light-induced hydrophilicity is not stable and during storage in the dark, and the TiO_2 surface recovers its initial low hydrophilicity through the adsorption of oxygen (Ref 17).

The decomposition performance index is defined as the slope of the MB concentration changes versus the UV irradiation time, generally used to estimate the organics decomposition performance (Ref 18). The absorption spectrum of MB aqueous solution (15 μM, pH 7.0) degraded with the TiO_2 photocatalytic film by UV and visible light irradiation for 4 h is shown in Fig. 3. It is found that the lower absorbance of MB was obtained by the UV light irradiation. Figure 4(a)

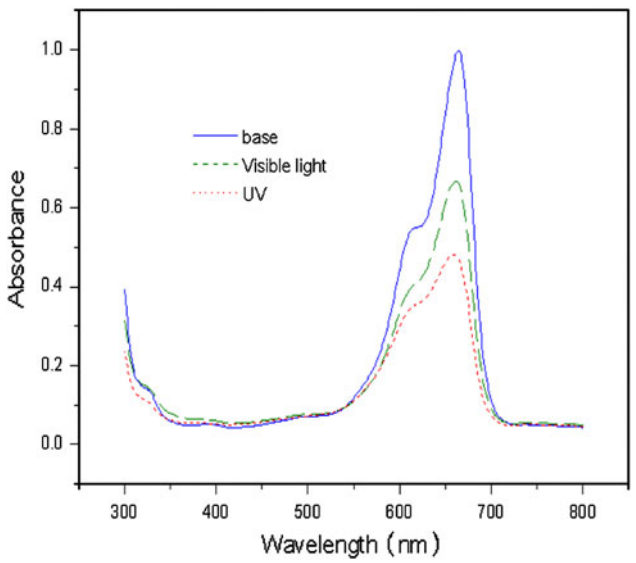

Fig. 3 The absorption spectrum of MB aqueous solution (15 μM, pH 7.0) under the UV light and visible light irradiated for 4 h, at a $[O_2/(O_2 + Ar)]$ flow-rate of 70%

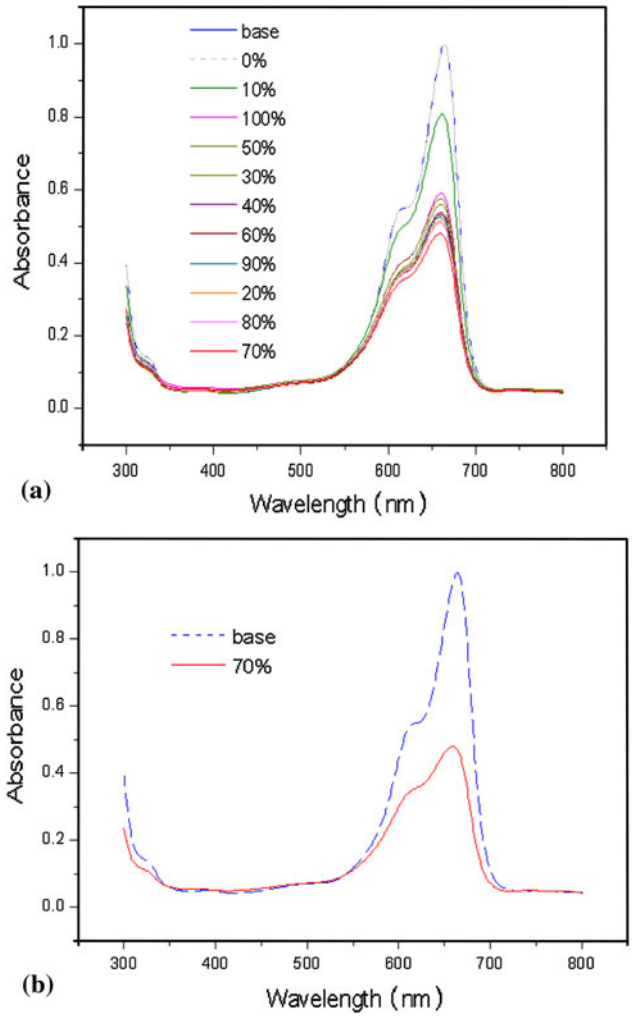

Fig. 4 (a) Absorption spectrum of MB aqueous solution (10 μM, pH 7.0) degraded with TiO_2 photocatalytic film deposited at different $[O_2/(O_2 + Ar)]$ flow-rates, for 4 h UV irradiation. (b) Confirmation run

shows the absorption spectrum of MB aqueous solution degraded with TiO_2 photocatalytic film deposited at different $[O_2/(O_2 + Ar)]$ flow-rates after 4 h of the UV irradiation. As can be seen, the TiO_2 films deposited at the $[O_2/(Ar + O_2)]$ partial pressure of 70%, exhibited the lowest absorbance of MB with a value of 0.47. For the TiO_2 films deposited at other oxygen partial pressures, the values of MB absorbance were between 0.81 and 0.50. It was found that 70% oxygen partial pressure produced TiO_2 films with higher photocatalytic decomposition ability, and more anatase phase than those deposited at other oxygen partial pressures (Ref 19). The experiments were repeated three times at the 70% oxygen partial pressure, and the average resulting absorbance of MB was 0.474, as shown in Fig. 4(b). The experimental results were highly reproducible.

Figure 5 shows the SEM micrographs of the TiO_2 thin film deposited at various oxygen partial pressures. As the oxygen partial pressure increases from 10% (Fig. 5a) to 70% (Fig. 5d), the crystallite size decreases initially and then increases with further increases in the oxygen partial pressure. The smaller the TiO_2 grain size, the shorter the average diffusion time of the conduction band electrons, which is propitious to redox of the electrons diffused to the interface (Ref 20). The TiO_2 film deposited at 70% oxygen partial pressure had a fine grain size, which may be another reason for the observed high photocatalytic activity.

4. Conclusions

This study has successfully deposited TiO_2 thin films onto non-alkali glass substrates by the rf reactive magnetron sputtering at room temperature. The flow rates of Ar, and O_2

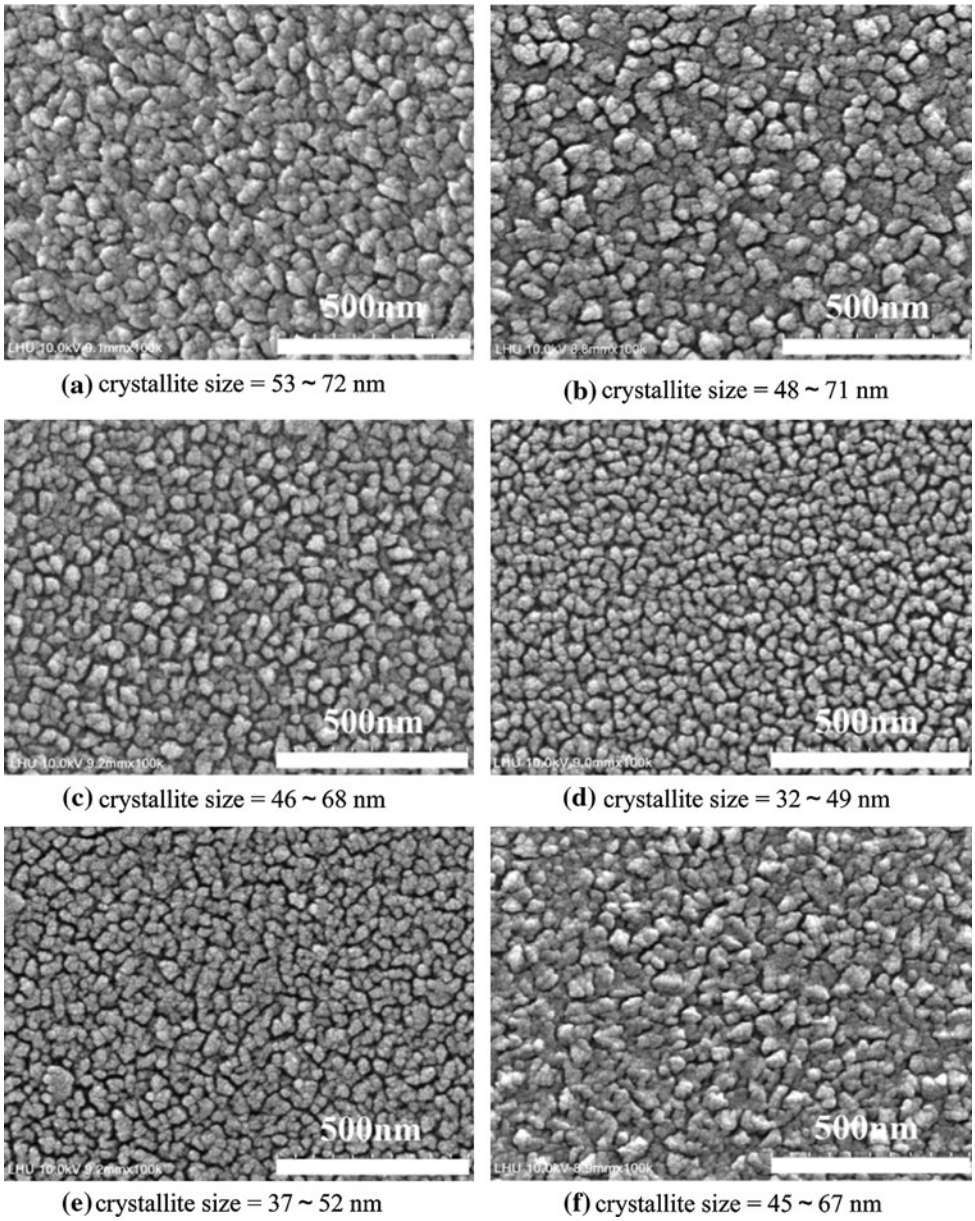

Fig. 5 SEM micrographs showing crystallite size of the TiO_2 films deposited at various $[O_2/(O_2 + Ar)]$ partial pressures: (a) 10%; (b) 30%; (c) 60%; (d) 70%; (e) 80%; (f) 90%

were varied, but rf power, total deposition pressure, target to substrate distance, and deposition time were kept constant during sputtering. The deposition rates, morphology, photo catalytic activity, and hydrophilicity were measured. The deposited TiO_2 thin film exhibited uniform and smooth surfaces. The films were mainly composed of small spherical particles. The films deposited at a relatively high value of oxygen partial pressure (70%) had a fine grain size and showed good photo-induced decomposition of MB and photo-induced hydrophilicity. It was suggested that the fine grain size of TiO_2 thin film may be one of the reasons for the observed high photocatalytic activity.

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