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Influence of oxygen flow rate on photocatalytic TiO_2 films deposited by rf magnetron sputtering

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Abstract Titanium dioxide (TiO_2) thin films having anatase (1 0 1) crystal structure were prepared on non-alkali glass substrates by rf (13.56 MHz) magnetron sputtering using a TiO_2 ceramic target under various oxygen partial pressures. At a fixed substrate temperature of 400 °C and total gas pressure of 1 Pa after 3 h deposition. Effects of oxygen partial pressure on the structural, surface morphology, and photocatalytic activities of the TiO_2 thin films were investigated. We performed both photoinduced decomposition of methylene blue (MB) and photoinduced hydrophilicity under UV light illumination. The XRD patterns exhibited a broad-hump shape indicating the amorphous structure of TiO_2 thin films. The results showed that when the $[O_2/(Ar + O_2)]$ flow rate increased to 50%, the photoinduced decomposition of MB and photoinduced hydrophilicity were enhanced. The water contact angle after 9 min UV illumination was approximately 4.5°, and the methylene blue (MB) solution decomposition from 12 down to 3.34 μ mol/L for 240 min UV irradiation.

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1 Introduction

Titanium dioxide (TiO_2) is one of the most widely used because of its outstanding optical and electrical properties, plays an important role in the fields of optics, electronics, catalysis and solar cell application [1]. It has been studied photocatalysts for environmental applications due to its nontoxic nature, long-term chemical stability, commercial availability at a low cost and robust, ability to decompose most organic pollutants, and general reactivity [2]. The hydrophilic and photocatalytic behaviour of TiO_2 films have been applied in various fields, in which the purification of air and water, anti-fogging, self-cleaning, antibacterial activities for architectural, and the side-view mirror of a typical automobile should be quite attractive [3, 4]. When TiO_2 is irradiated by ultraviolet (UV) light, it produces pairs of electrons and holes. Such excited electrons or holes can diffuse to the TiO_2 surface and generate some kinds of radicals or ions which can decompose organic compounds adsorbed on the TiO_2 surface [5, 6]. Several methods such as sol–gel [7], pulsed laser deposition (PLD) [8], metal organic chemical vapour deposition (MOCVD) [9], microwave processing [10], and sputtering [11] are available for the fabrication of TiO_2 thin films. Magnetron sputtering processes have favorable features such as lower substrate temperature, good film adhesion, good uniformity of thickness distribution, the film properties can be easily modified by doping, and it is an industrial process applicable to large-area deposition [12].

Many studies have already published on relations between different sputtering conditions and photocatalytic activities of the films deposited by magnetron sputtering [13]. Shen et al. [14] investigated the influence of TiO_2 films at various oxygen partial pressures, showed that the oxygen partial pressures had large influences on optical,

mechanical and structural properties. Liu et al. [15] studied the effect of oxygen partial pressure on the structure, surface morphology and photocatalytic properties of the TiO_2 film by magnetron sputtering. Moreover, Toku et al. [16] optimize the experimental conditions for deposition of anatase TiO_2 films on Si substrate by modifying the O_2 concentration in Ar/O_2 mixture of a DC magnetron sputtering. The aim of this study, TiO_2 photocatalyst thin films prepared by rf magnetron sputtering. The effects of various $[O_2/(Ar + O_2)]$ flow-rate ratios on structural, morphological and photocatalytic activities were discussed.

2 Experimental procedure

TiO_2 films were deposited by means of rf magnetron sputtering on non-alkali glass at substrate temperature of 400 °C. A ceramic TiO_2 disc having a 50.8 mm diameter and a 6 mm thickness was used as sputtering target, the commercially available hot-pressed and sintered (99.995% purity, Elecmat, USA). The target-to-substrates distance was 100 mm. Reactive and sputtering gases were argon (purity: 99.995%) and oxygen (purity: 99.995%), respectively. The argon and oxygen flow rates were controlled by mass flow meters and the sputtering pressure was measured using an ion gauge. The depositions were carried out at oxygen flow ratio $[O_2/(O_2 + Ar)]$ of 0, 10, 20, 30, 40, 50, 60 and 70%. The base pressure of the process chamber was about 0.6×10^{-3} Pa, the pressure during deposition was maintained at 1 Pa, and sputtering power was kept at 200 W. All samples were deposited with substrate rotation (15 rpm) to have good surface morphology. Before coating, the substrates were ultrasonically cleaned in acetone, rinsed in deionized water and dried in nitrogen.

The thicknesses of the films were measured by using a surface profiler system (Alpha-step, SURCORDER, ET4000A). The crystal structure of the TiO_2 film was evaluated using X-ray diffraction (Rigaku-2000 X-ray Generator.) using Cu Kα radiation with an angle of incidence of 1°. The surface morphology of the film was investigated using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F) and topographic images were obtained by an atomic force microscope (AFM, SPA-400). The photoinduced hydrophilicity was evaluated by measuring the changes in the contact angles for pure water, which were carried out at room temperature in ambient atmosphere using a contact angle measuring system (FACE CA-VP150) with an experimental error less than 1°. The organics decomposition characteristics were measured using the change in the methylene blue (MB) concentration. In the measures, black light lamp of main wavelength of 365 nm (1.5 m W/cm^2 at the film surface) was used as the UV light source.

3 Results and discussion

Figure 1 shows the deposition rate of the films as a function of oxygen flow rate under a constant sputtering pressure (1 Pa). When the $[O_2/(Ar + O_2)]$ flow-rate from 0 increase to 10%, the TiO_2 films exhibited a steep decrease in the deposition rate, since the dissociation energy of the Ar was about 15.76 eV and O_2 was about 48.77 eV, Ar can more easily be dissociated than O_2. Then the deposition rate decreases slowly as the oxygen partial pressure further increases. Higher oxygen partial pressure would induce the surface oxidation of Ti target and result in lower deposition

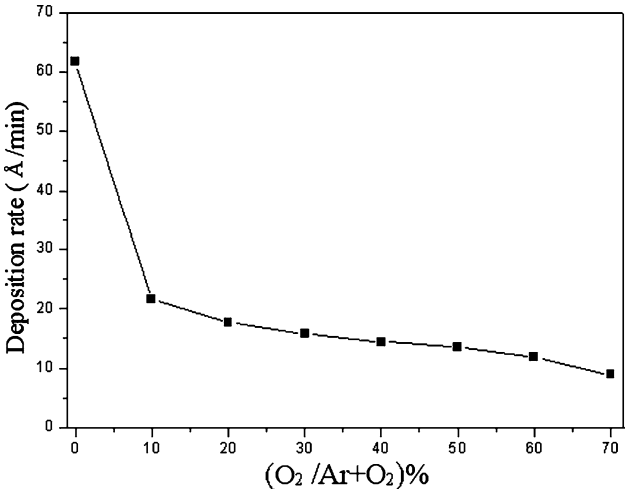

Fig. 1 Deposition rate of TiO_2 films under various [O2/(O2 + Ar)] flow-rate ratios with sputtering pressure of 1 Pa

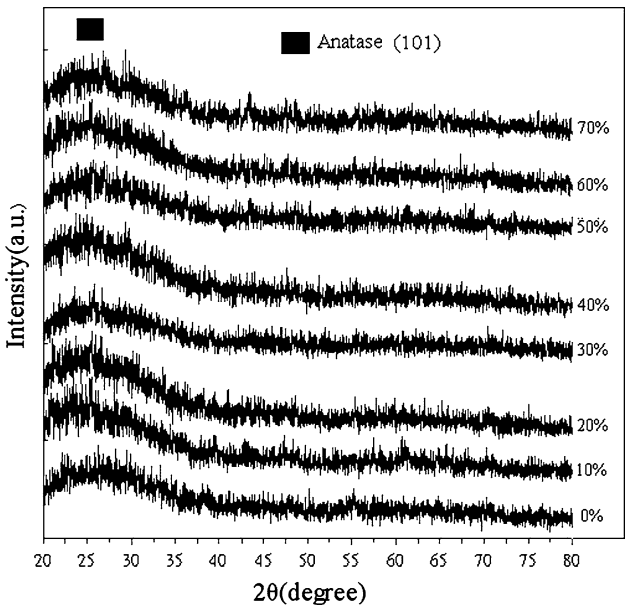

Fig. 2 XRD diffraction patterns of the TiO_2 films deposited at different [O2/(O2 + Ar)] flow-rate ratios

rate [15]. Increasing the oxygen flow rate leads to a target voltage decrease, this is probably related to an oxidation of the target surface, which will enhance the ion induced secondary electron emission from the target, and the surface oxidation of the target can explain the deposition rate of the films was decreased as the oxygen flow rate was increased [17].

X-ray diffraction patterns (XRD) of the TiO_2 films as a function of oxygen flow rate are shown in Fig. 2. For all films, there were no sharp diffraction lines and it is similar to the XRD pattern observed by Dhayal et al. [18] and Abdel-Aziz et al. [19]. In this study, the main peak of TiO_2 anatase structure appears at about 25°∼25.3°, the XRD patterns show a broad-hump shape indicating the amorphous structure of the film and glass substrate. However, it should be positioned at 25.3° for the TiO_2 anatase structure. The 2D atomic force microscopic measurements (AFM) images of the surface morphologies and roughness of the films deposited at various oxygen pressures are shown in Fig. 3. TiO_2 thin films exhibited uniform and smooth surfaces in this work. The films were mainly composed of small spherical particles. A slight decrease in surface roughness (from 6.84 to 4.34 nm) was observed as oxygen flow rate is increased from 0 to 50%. However, the

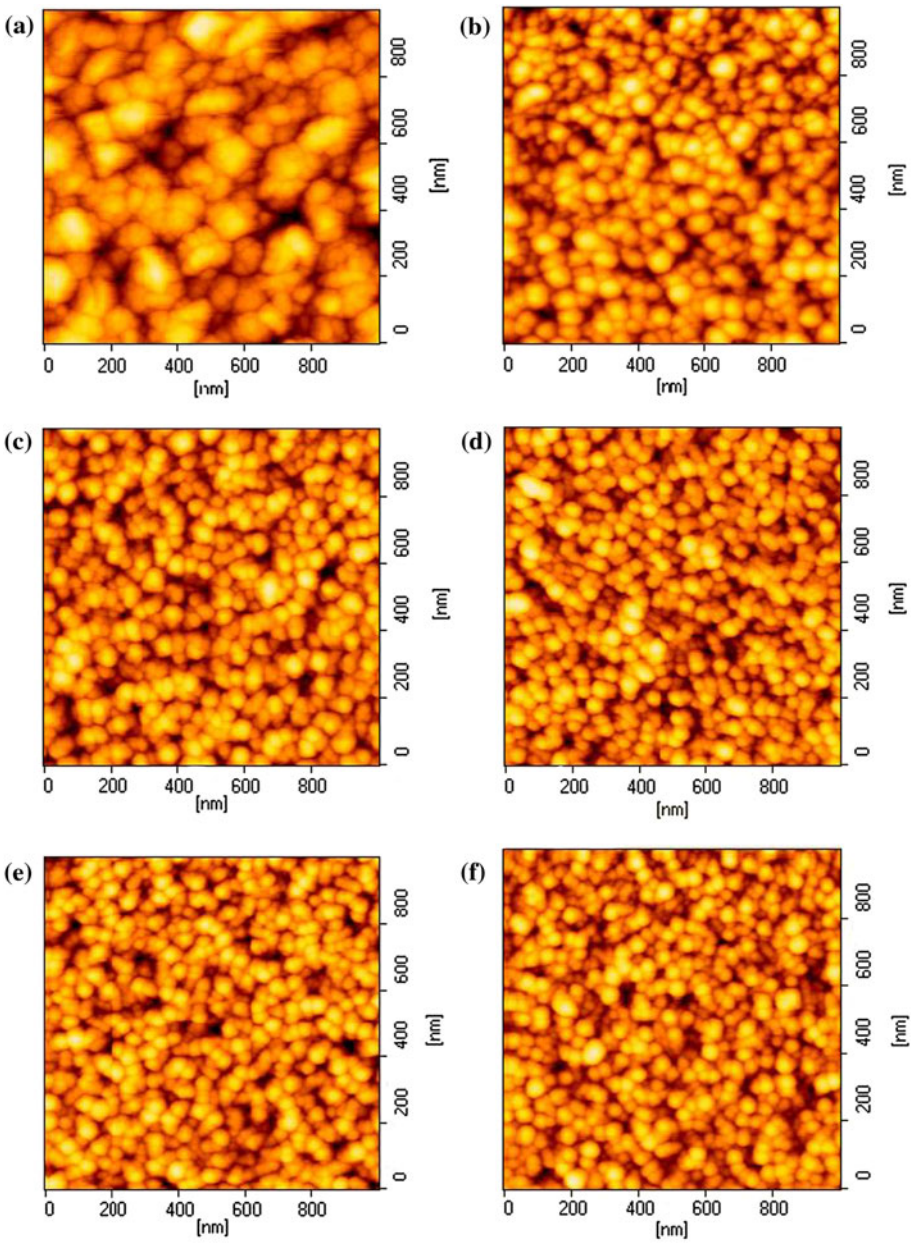

Fig. 3 AFM images of the films. (**a**) $[O_2/(O_2 + Ar)]$ of 0%, Ra = 6.84 nm, (**b**) $[O_2/(O_2 + Ar)]$ of 10%, Ra = 5.73 nm, (**c**) $[O_2/(O_2 + Ar)]$ of 30%, Ra = 5.21 nm, (**d**) $[O_2/(O_2 + Ar)]$ of 50%, Ra = 4.34 nm, (**e**) $[O_2/(O_2 + Ar)]$ of 60%, Ra = 4.87 nm, (**f**) $[O_2/(O_2 + Ar)]$ of 70%, Ra = 5.07 nm

roughness increased as the oxygen pressure increased further. This is also similar to the result of Xu et al. [8].

The cross-section of the films was observed by SEM shown in Fig. 4. The films are very compacted, homogeneous, and perfectly adherent to the glass substrate for all deposition condition. Figure 5 shows the schematic diagram for the pull-off adhesion test between the glass substrate and the TiO_2 thin film, which is similar to an engineering tensile strength test [20]. In this study, the direct tensile test method, rather than interfacial shear through bending, or lap-shear, was used to measure the adhesion strength. A steel bar, of diameter 5 mm, was used for the test. Adhesive epoxy (3 M Scotch-Weld, Epoxy adhesives DP-460) was applied between the steel bar and the TiO_2 thin film. The pulling test was done at room temperature and atmospheric pressure, using a motor crosshead speed of 1 mm/min. For TiO_2 films deposited on glass substrates under various $[O_2/(O_2 + Ar)]$ flow-rate ratios, the peel off stresses were about between 17.35 and 25.31 MPa. The TiO_2 thin films deposited on glass substrates showed very good adherence, and no cracking or peel-off was observed after deposition.

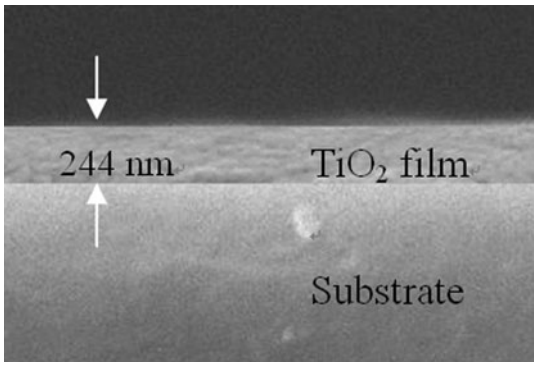

Fig. 4 SEM cross-section image of an as-grown TiO_2 film deposited on a glass substrate, deposited at $[O_2/(O_2 + Ar)]$ flow-rate of 50%

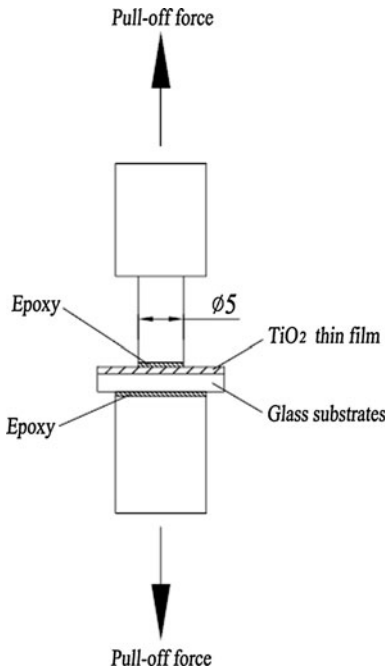

Fig. 5 Schematic diagram of pull-off adhesion test

The photo-induced hydrophilicity of the TiO_2 films was evaluated by measuring the changes in the contact angles for pure water. The contact angle was measured as a function of UV irradiation time for the TiO_2 films produced at different values of oxygen partial pressure (fixed substrate temperature of 400 °C and total gas pressure of 1 Pa), and shown in Fig. 6. The contact angle of glass substrate was not decreased after the UV irradiation for 180 min, indicated the glass substrate has no hydrophilic characteristics (not shown). Compared with the contact angle of the film deposited at argon flow rate of 0% was decreased from 39.7 to 36.2 after UV irradiation for 9 min, shows that the surface of the film was less hydrophilic. The initial water contact angle of the films deposited at oxygen partial pressure of 50% was approximately 7.9°, which was smaller than the initial contact angle of the film deposited at other oxygen partial pressure (20° ~ 11.2°). When the film surface was irradiated by UV light, the contact angles started to decrease, the water contact angles of the films deposited under various oxygen partial pressure after the 9 min UV irradiation in air were approximately 6.3° ~ 4.5°, shown the film surface was ultra-hydrophilicity.

Photocatalytic activities of the TiO_2 films were estimated by photocomposition of MB with the concentration of 12 mol/L in aqueous solution by UV light irradiation.

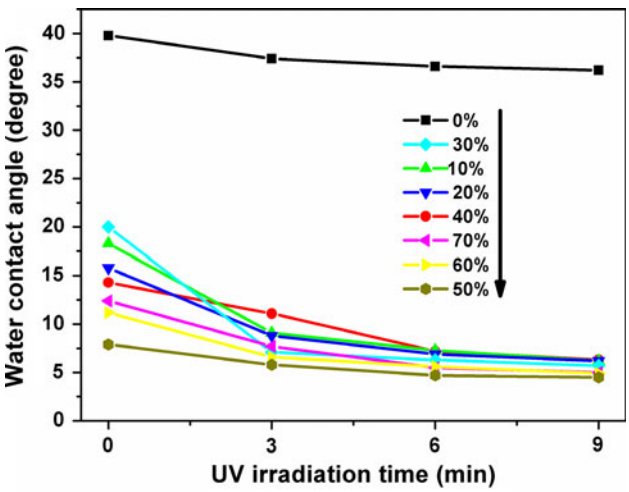

Fig. 6 Water droplet contact angle of the TiO_2 films as a function of UV irradiation time under different $[O_2/(Ar + O_2)]$ flow-rates

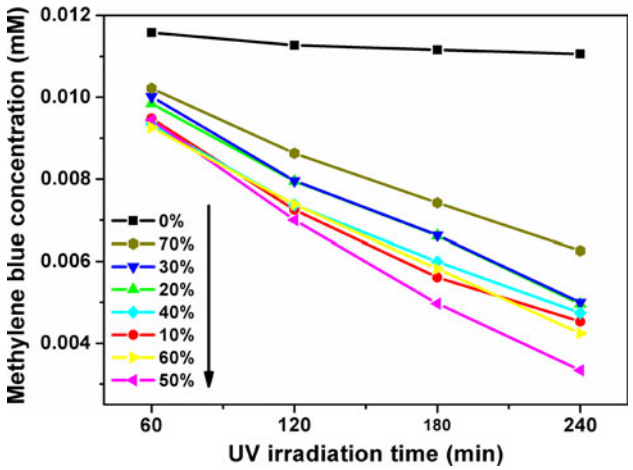

Fig. 7 Photocatalytic activities of the TiO_2 films deposited at different oxygen pressure

Figure 7 shows the change in concentration of MB as a function of UV irradiation time. The figures indicate the MB concentration decreases continuously concomitant with the UV irradiation. As can be seen, the film deposited at the oxygen pressure of 0% showed did not have photocatalytic decomposition ability of MB as it was nearly amorphous in nature. The TiO_2 films deposited at $[O_2/(Ar + O_2)]$ flow rate of 50%, showed the high photoinduced decomposition of MB (MB decomposition from 12 to 3.34 μ mol/L after 240 min-irradiation), which indicated that 50% oxygen pressure more anatase phase than those deposited at other oxygen pressure, the crystalline structure is one of the most significant factors to determine the photocatalytic activity. In addition, 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, the TiO_2 film deposited at $[O_2/(Ar + O_2)]$ flow rate of 50% had the small grain size, which may be another reason for the observed high photocatalytic activity [8]. In the nanoparticles, the exciton energy can be estimated by using the Brus equation, i.e., the effective mass model (EMM) [21–23]:

$$\Delta E_g = \frac{h^2}{8R^2\mu} - \frac{1.8e^2}{\varepsilon R} \quad (1)$$

where ΔE_g is the band gap shift, R is the radius of the particle size, μ is the reduced mass of the exciton and ε is the dielectric constant. The band gap of ultra-fine semiconductor particle increases with the decrease in particle size when it is smaller than the band gap minimum. The result corresponds to the experimental result of Lin et al. [24], that is, the smaller the particle size, the faster the degradation rate.

4 Conclusions

TiO_2 thin films having anatase (1 0 1) crystal structure were fabricated on non-alkali glass substrates by rf magnetron sputtering under various oxygen partial pressures at a fixed substrate temperature of 400 °C and total gas pressure of 1 Pa after 3 h of deposition. The X-ray diffraction patterns (XRD) of the TiO_2 films shows there were no sharp diffractions. The main peak of TiO_2 anatase structure appears at about 25° ~ 25.3°, revealing a broad-hump shape which indicates the amorphous structure of the film and glass substrate. The TiO_2 thin films exhibited uniform and smooth surfaces in this work. The films were mainly composed of small spherical particles. A slight decrease in surface roughness (from 6.84 to 4.34 nm) was observed as oxygen flow rate was increased from 0 to 50%. The TiO_2 films deposited at a $[O_2/(Ar + O_2)]$ flow rate of 50% showed MB with high photoinduced decomposition and had small grain size, which may be another reason for the high photocatalytic activity observed.

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