Research Article

Photocatalytic Properties of Columnar Nanostructured TiO₂ Films Fabricated by Sputtering Ti and Subsequent Annealing

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Columnar nanostructured TiO₂ films were prepared by sputtering Ti target in pure argon with glancing angle deposition (GLAD) and subsequent annealing at 400°C for different hours in air. Compared with sputtering TiO₂ target directly, sputtering Ti target can be carried out under much lower base pressure, which contributes to obtaining discrete columnar nanostructures. In the present study, TiO₂ films obtained by annealing Ti films for different hours all kept discrete columnar structures as the Ti films deposited in GLAD regime. The longer the annealing time was, the better the phase transition accomplished from Ti to TiO₂ (a mixture of rutile and anatase), and the better it crystallized. In addition, those TiO₂ films performed photocatalytic decolorization effectively and showed a law changing over annealing time under UV light irradiation towards methyl orange, which demonstrated the potential applications for treatment of effluent.

1. Introduction

With the development of agriculture and industry, the global environmental problems are becoming more and more serious and have drawn more and more attention [1, 2]. The increasing environmental problems create a great demand for stable and environmentally friendly materials, which can perform efficient photocatalytic decomposition of hazardous substances before their emission to the environment. Photocatalytic degradation technique plays an important role to solve the organic pollution problems because it combines with solar energy and in perfect agreement with the requirement of sustainable processes development [3–5]. This technique can degrade organic pollutants into harmless inorganic substances such as CO₂ and H₂O under moderate conditions.

As an efficient photocatalyst, extensive research has been performed on titanium dioxide (TiO₂) along with its photocatalytic applications for effluent [6, 7]. Titanium dioxide (TiO₂) is nontoxic, chemically stable and possesses a unique combination of optical and photochemical properties [8–10]. The mechanism of TiO₂ photocatalytic oxidation is to offer a highly reactive, nonspecific oxidant, namely hydroxyl

radical ($\cdot\text{OH}$) which is capable of destroying, wide range of organic pollutants nonselectively and quickly in wastewater [11–13].

A great amount of literature published for TiO₂ photocatalytic oxidation indicates the use of TiO₂ powders [14], but the TiO₂ powders have some practical problems such as immobilization and recycling which requires costly separation procedures after used. The columnar nanostructured TiO₂ film by GLAD [15, 16] in this paper has no problem with immobilization and recycling and has a relatively larger surface area compared with flat film which contributes to the photocatalytic efficiency.

This study investigated columnar nanostructured TiO₂ films annealed for different hours to get the law how the morphology, crystal structure, and photocatalytic properties change over annealing time at 400°C in air.

2. Experimental

Ti columnar structure was obtained by GLAD using magnetron sputtering and subsequently annealed under appropriate conditions to achieve TiO₂ columnar structure. And

FIGURE 1: Schematic diagram of the GLAD technique in the magnetron sputtering system.

(a)

(b)

FIGURE 2: Cross-section and surface morphology of columnar nanostructured Ti film by GLAD.

FIGURE 3: XRD spectra for columnar nanostructured Ti film by GLAD.

then some performance tests were carried out to get the morphology, crystal structure, and photocatalytic properties.

The main technology used in this paper to acquire columnar structure is glancing angle deposition (GLAD). The columnar microstructure exhibiting a high degree of porosity was obtained as a result of the shadow effect [17–20]. The schematic diagram of GLAD in the magnetron sputtering system is showed in Figure 1.

The sputtering of Ti in pure Ar was performed at low pressure (about 0.11 Pa). The distance between the Ti target and the Si substrate centers was about 11 cm. The purity of the Ti target was 99.99% (diameter of 60 mm and thickness of 3 mm). The Si substrates were 3-inches monocrystalline ([100]) wafers with low resistivity (0.02 Ωcm). The deposition angle between the substrate normal and the incident flux was fixed at 80° ($\theta_1 = 25^\circ$ and $\theta_2 = 55^\circ$) for all depositions in the GLAD regime and was held constant in each experiment. Ar gas flow was kept 10 sccm during the deposition process which continued 90 minutes with a deposition power of 201.6 W.

Four groups of samples (columnar nanostructured Ti films) with size of 13 mm × 10 mm were annealed at 400°C in air for 1, 2, 3, and 4 hours, respectively, in quartz tube furnace to be oxidized and crystallized. Then columnar nanostructured films of a mixture of rutile and anatase were obtained.

Characterization was conducted using XRD, SEM, and UV-vis spectrophotometer.

XRD measurements were performed for structural characterization. The parameters of a diffractometer ($U = 45$ kV, $I = 200$ mA) were the same for all samples. The surface morphologies of the nanostructured films were observed by SEM. The photocatalytic activities of TiO₂ nanostructures were characterized by photocatalytic decomposition of methyl orange under UV light irradiation.

FIGURE 4: Cross-sections and surface morphologies of columnar nanostructured TiO₂ films after annealed at 400°C for (a) 1 hour, (b) 2 hours, (c) 3 hours and (d) 4 hours.

FIGURE 5: XRD spectra for columnar nanostructured TiO₂ films after annealed at 400°C for 1–4 hours.

FIGURE 6: Transmittance spectra of methyl orange with sample annealed for (a) 4 hours, (b) 3 hours, (c) 2 hours, (d) 1 hour after 2-hour UV radiation, (e) without sample after 2-hour UV radiation and (f) without sample and no UV radiation.

FIGURE 7: Degradation rates of methyl orange with TiO_2 sample annealed for different hours (1, 2, 3, and 4).

3. Results and Discussion

As shown in Figure 2, the Ti film by GLAD in the experiment has oblique aligned columnar nanostructure with a high degree of porosity and large surface area. XRD spectra in Figure 3 demonstrate that there is nothing else but Ti [20].

SEM images of the TiO_2 films annealed for 1, 2, 3, and 4 hours, respectively, are presented in Figure 4 (cross-sections and surface morphologies). There are almost no differences in discrete columnar morphologies between them [18, 21]. They all keep discrete columnar structures as the Ti films deposited by GLAD.

The diffraction patterns of the TiO_2 films show that peaks correspond to the known diffraction maxima of the anatase and rutile phase as marked in Figure 5. The columnar

structure accomplished the phase transition from Ti to a mixture of rutile and anatase while keeping its discreteness [12]. XRD shows that the longer the annealing time is, the better it crystallizes. The average crystallite size D of rutile was calculated by Scherrer's equation using the full width at half-maximum of the XRD peaks of R (110). The sizes of the rutile grains in the TiO_2 films annealed for different hours are all about 10 nm.

Each TiO_2 sample was placed in the center of a small beaker with 5 mL diluted methyl orange (about $10 \mu\text{mol/L}$) in it, and one beaker without TiO_2 sample but methyl orange was prepared for comparison. The photocatalytic degradation was performed under 500 W UV lamp for two hours. The concentration change of aqueous methyl orange is obtained from transmittance spectrum measured by a UV-vis spectrophotometer as shown in Figure 6.

Transmittances of methyl orange at 465 nm (a) with sample annealed for 4 hours after 2-hour UV radiation, (b) with sample annealed for 3 hours after 2-hour UV radiation, (c) with sample annealed for 2 hours after 2-hour UV radiation, (d) with sample annealed for 1 hour after 2-hour UV radiation, (e) without sample after 2-hour UV radiation, and (f) without sample and no UV radiation (origin methyl orange) are 71.0%, 68.3%, 66.0%, 64.0%, 61.0%, and 55.5%, respectively. According to Beer-Lambert law, absorbance and concentration of an absorbing species have a linear relationship, and the relation between A (absorbance) and T (transmittance) is $A = -\log T$; the degradation rates of methyl orange (a), (b), (c), (d), and (e) are 41.9%, 35.2%, 29.4%, 24.3%, and 16.0%, respectively [12]. The degradation rate increases from 16.0% to 41.9% due to the photocatalytic activity of TiO_2 nanostructures [13]. Furthermore, the degradation rate increases over annealing time as showed in Figure 7.

4. Conclusions

The columnar structure accomplished the phase transition from Ti to a mixture of rutile and anatase while keeping its discreteness after annealed at 400°C in air. The longer the annealing time is, the better the phase transition accomplishes from Ti to TiO_2 (a mixture of rutile and anatase), and the better it crystallizes. Those TiO_2 films all perform photocatalytic decolorization effectively and reusable under UV light irradiation towards methyl orange. The degradation rate increases with increasing annealing time and increases from 16.0% to 41.9% due to the photocatalytic activity of the obtained TiO_2 nanostructures.

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