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Influence of sputtering power on structure and photocatalyst properties of DC magnetron sputtered TiO_2 thin film

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Abstract

TiO_2 thin films were deposited by DC reactive magnetron sputtering technique on silicon wafer and glass slide at sputtering power of 210 W and 230 W. A pure metallic titanium target was sputtered in a mixture of argon and oxygen gases. The distance of Ti-target to substrate holder (d_{s-t}) was 120 mm. The films were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. The photocatalytic activity was evaluated by the measurement of the decomposition of methylene blue after UV irradiation. It was found that the crystalline structure of TiO_2 thin films strongly depended on the sputtering power. The mixed phase of anatas/rutile TiO_2 thin films were successfully obtained with the sputtering power of 230 W. While anatase TiO_2 thin films were obtained with sputtering power of 210 W. The TiO_2 thin film with anatase structure exhibited the best photocatalytic activity.

1. Introduction

Titanium dioxide (TiO_2) is one of the most widely studied photocatalysts for environmental applications due to its nontoxic nature, chemical stability, commercial availability at a low cost and robust, general reactivity [1]. In recent years, functional TiO_2 coatings are expected to use in medicine, architecture, automobile manufacture, antibacterial, deodorizing and self cleaning effects. In addition,

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these properties make it suitable for applications such as antireflective and protective layers for optical coating, UV filters, gas sensors and photocatalysts for the air oxidation of organic compounds [2-3].

TiO_2 films prepared by various method, such as DC or RF sputtering, evaporation method, ion beam technique, ionized cluster beam (ICB) and chemical vapour deposition, result in the amorphous or anatase phase unless the films are deposition at a temperature than 300 °C. Titanium dioxides are three kinds of crystalline phase, anatase, rutile and brukite [4]. Titanium dioxide is a wide band gap oxide. Undoped anatase is an anisotropic, tetragonal insulator (a = 0.3785 nm, c = 0.9514 nm) with a band gap of 3.2 eV, while the band gap of undoped rutile tetragonal with a = 0.4594 nm, c = 0.2958 nm) is 3.0 eV. Brookite (orthorhombic with a = 0.9184 nm, b = 0.5447 nm, c = 0.5145 nm) is formed in thin films only under special condition [5]. Each crystalline form is convenient for a different purpose. While rutile desirable for optical applications, anatase has more efficient photocatalytic properties [6-7].

In this work, TiO_2 thin films were deposited by reactive DC magnetron sputtering on unheated substrate under various sputtering power of cathode in order to study the effect of the conditions on structure, surface morphology and the relation of phase structure on photocatalytics property.

2. Materials and methods

2.1. Preparation of the films

TiO_2 thin films were deposited on silicon wafer (100) by reactive DC sputtering using Ti metal target was sputtered in a mixture of argon and oxygen gases. The vacuum chamber has a diameter of 310 mm and height of 370 mm. A pure titanium disk (99.97%) of 5.4 mm in diameter was used as a sputter target (Fig. 1). The DC powers were generated to vary at 210 W and 230 W, respectively.

The deposition processes were performed on unheated substrate. The distance between the substrate holder and titanium target ($d_{s\text{-}t}$) was fixed at 120 mm (Fig. 1) and used a mixture of Ar (pure 99.999%) and O_2 (99.999%) were kept constant values of 1 sccm and 4 sccm, respectively. The flow rate of Ar and O_2 gases were controlled by mass flow controller. The base pressure and total pressure of the sputtering chamber were 5.0×10^{-5} mbar and 5.0×10^{-3} mbar, respectively. When the deposition time was fix at 3 hours.

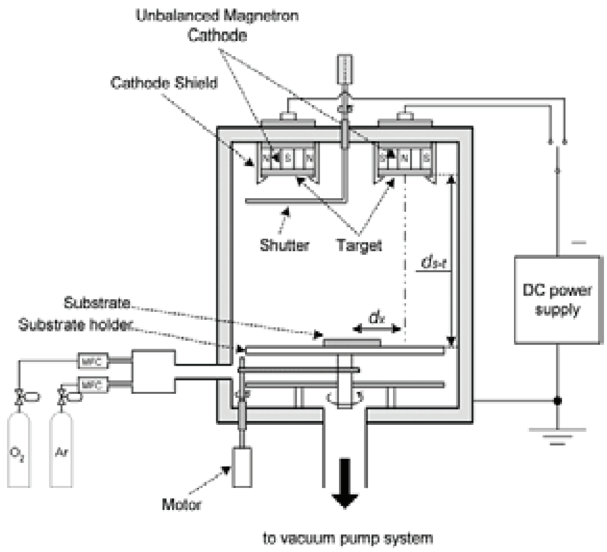


Fig. 1. Schematic diagram of the DC magnetron sputtering apparatus

2.2. Characterization

The crystal structure of the titanium dioxide thin films was characterized by X-ray diffractometer (Rint 2000, Rigaku Corporation) with Cu K_α radiation; the surface morphology and thickness were evaluated by an atomic force microscope (Nanoscope IV, Veeco Instrument Inc.). The photocatalytic property of the films was determined by the decomposition of dry methylene blue ($C_{16}H_{18}N_3S$ Cl $3H_2O$) on the films surface. During the measurement of the photocatalytic activity, the titanium dioxide surface covered with methylene blue film was irradiated with ultraviolet light (Phillips CLEO COMPACT 15 W) for 1 hr and each hour the transmittance of 650 nm light was measured. Using the value of transmittance before the irradiation T_0 and the measured transmittance T_i at each hour, the absorbance (ΔABS) characterizing the decomposition of methylene blue was calculated by $\Delta ABS = \ln(T_i/T_0)$ [6].

3. Result and discussion

3.1. Structure of titanium dioxide thin films

The XRD pattern of TiO_2 thin films deposited with various sputtering power are shown in Fig. 2. The results show that all the films characteristic peaks mixed of anatase/rutile and anatase structure, suggesting. The films as deposited on the power of 230 W have mixed phase of polycrystalline anatase (101) and rutile (110) structure which diffractive angles (2θ) of the films were 25.3°, 27.5°, respectively.

In addition, anatase structure has similar intensity with rutile structure as shown in Fig. 2(a) and found that the pure anatase (101) at 25.3° which sputtering power of 210 W as shown in Fig. 2(b). In case of short substrate-target distance and high power, the collision is strong and the excess thermal energy is transmitted to the substrate. There for the prepared thin film has rutile structure since the substrate temperature during deposition is higher than 300 °C. In the case of long distance or low power, the thin film has anatase structure since the thermal energy is reduced before reaching the substrate [7].

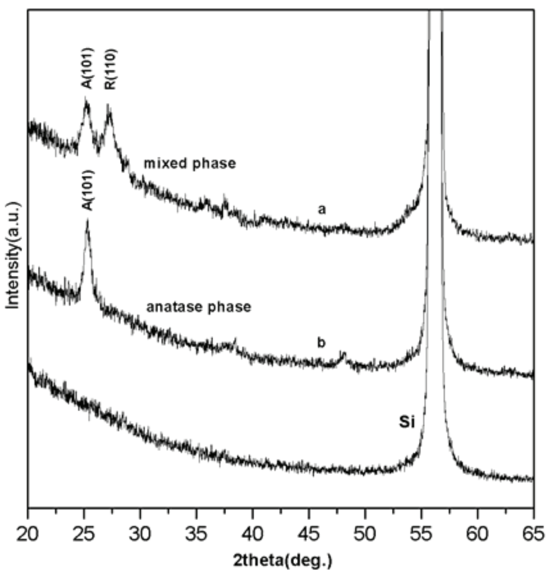
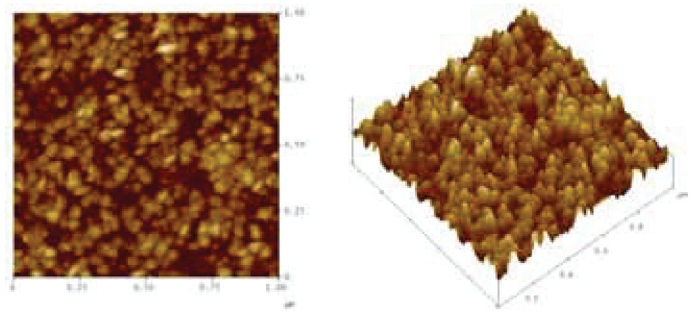


Fig. 2. The XRD patterns of TiO_2 thin films deposited at different cathode power. (a) 230 W; (b) 210 W

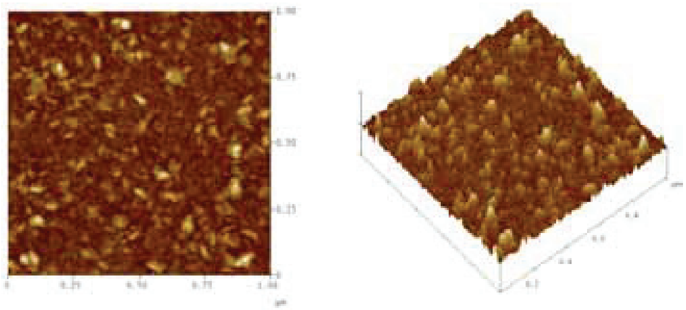
3.2. Morphologies of the films

The surface morphologies of the deposited TiO_2 thin films deposited at various sputtering power are shown in Fig. 3. The surface morphology of the film deposited at sputtering power of 230 W as shown in Fig. 3(a). The film was composed of different grain size; the most of grain size were big. In addition, it was found that the films deposited at sputtering power of 210 W were small and some grain was sharp as shown in Fig. 3(b). From AFM images, it was found that, the grain size of TiO_2 thin films becomes small when decreasing the sputtering power during deposited processes form 230 W to 210 W. When the sputtering power decreasing, the energy of sputter atoms in the deposition process decrease, it was obviously seen that the surface structure depended on the deposition power, which could be described in the theory of charge cluster (TCC), the size of cluster was related to the agglomeration and charging processes in gas phase. With sputtering power increasing, electron increased, so probability of cluster being charged was increased [8]. In the Fig. 3 shows the AFM 2, 3-dimensional images from the two TiO_2 thin films.

The TiO_2 thin films were composed of different grain size. We found that, the grain size of TiO_2 anatase thin film in Fig. 3(b) was small than the films were shown in Fig. 3(a) consistent of titanium dioxide thin films anatase/rutile structure. These high energy particles undergo gas scattering due to the collision processes between the target and the substrate before reaching the substrate surface. The surface roughness of the rutile titanium dioxide thin film is larger than that of anatase titanium dioxide thin film as shown in the Fig. 3(a)-3(b) [7]. Roughness of the anatase/rutile structure was similar to the range of 3.67 - 3.35 nm (Fig. 3(a), 3(b)). Thickness of the films was similar to the range of 133- 123 nm.



(a)



(b)

Fig. 3. Surface morphologies of TiO_2 thin films deposited with different the sputtering power. (a) 230 W; (b) 210 W

3.3. Photocatalytic properties

The photocatalytic property of the titanium dioxide thin films deposited under different of sputtering power as shown in Fig. 4. We found that all films showed photocatalytic property after UV irradiation. From the figure we revealed the relation between the photocatalytic activities which the ability to decompose methylene blue cover films surface under UV irradiation in each hour for 6 hours. When the films were irradiated by UV light, the absorbance of mathylen blue will decrease which indicate that the films performed photocatalytic property. We were seen the photocatalytic property changing when the structure of the TiO_2 thin films to changed, It was found that, the protocatalytic property of TiO_2 strongly depended on the crystalline structure of the thin films. In this work, the titanium dioxide thin films with anatase phase (Fig. 4b) which deposited with sputtering power of 210 W clearly exhibited the best significant photocatalytic activity more than the mixed phase anatase/rutile (Fig. 4a) which deposited with sputtering power of 230 W. The anatase structure with high energy band gap (3.2 eV), which high degree of recombination more than retile structure. When the electron-hole pairs migrate from the inside of the photocatalyst to the surface, the high degree of recombination between photo-induced electron-hole pairs is a major factor controlling the photocatalytic activity of the films when expose to the UV light [9].

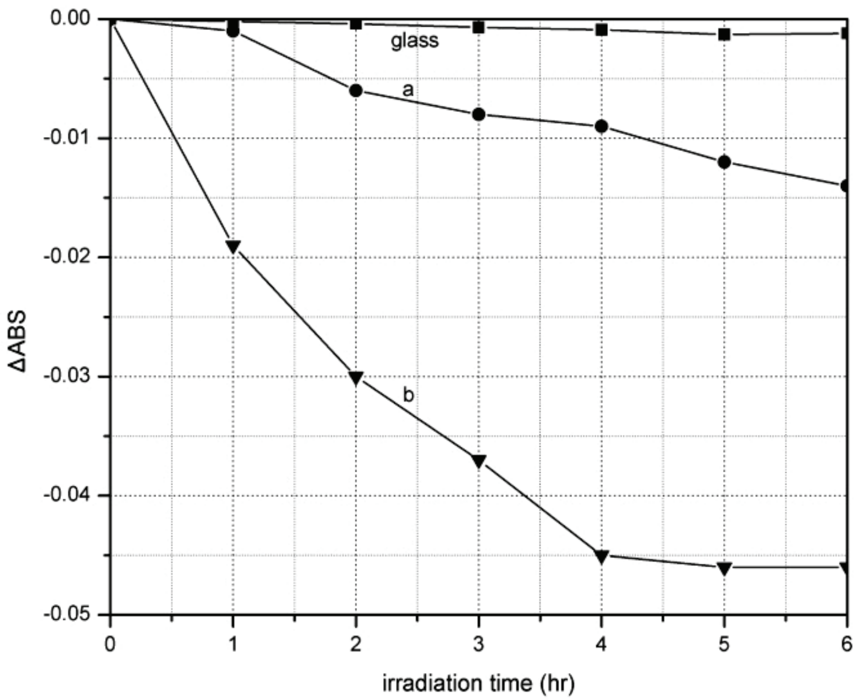


Fig. 4. Absorbance of methylene blue after UV irradiation of TiO_2 thin films deposited with different sputtering power. (a) 230 W; (b) 210 W

4. Conclusions

In this work, we successfully deposited TiO_2 thin films were by reactive DC magnetron sputtering technique on unheated substrate to study the effect of sputtering power on the photocatalytic property. The results show that the structure of titanium dioxide thin films were changed from anatase structure to mixed of anatas/rutile structure when increased sputtering power of cathode. We found that the grain size of mixed phase bigger than grains size of anatase phase. While surface roughness increasing when grain sizes of the films become larger. The thickness of thin films within the range of 133- 123 nm. In case of photocatalytic property, all films perform photocatalytic property when expose to the UV light. In addition, it was found that the TiO_2 thin film with anatase phase exhibited the best photocatalytic activity more than mixed phase of anatas/rutile. We were concluded the structure of titanium dioxide thin films strongly on photocatalytic property.

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