

## Effect of substrate temperature on structural properties and photocatalytic activity of TiO<sub>2</sub> thin films

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Received 17 April 2006; accepted 15 April 2007

**Abstract:** Titanium dioxide (TiO<sub>2</sub>) films with anatase structure were prepared on quartz glass substrates by pulse laser ablating titanium (99.99%) target under oxygen pressure of 10 Pa at substrate temperature of 500–800 °C. The structural properties of the films were characterized by X-ray diffractometry(XRD), X-ray photoelectron spectroscopy(XPS) and field emission scan electron microscopy(FESEM). The results show that, as the substrate temperature is increased from 600 °C to 800 °C, the anatase structure of the films changes from random growth to (211)-oriented growth. The absorption edge tested by UV-Vis Spectrometer has a blue shift. The photocatalytic activity of the films was tested on the degradation of methyl orange. It is found that the film with random growth structure exhibits better photo-degradation efficiency than that with (211)-oriented growth structure.

**Key words:** TiO<sub>2</sub> thin film; pulsed laser deposition; photocatalytic activity; orientation

### 1 Introduction

In recent years, TiO<sub>2</sub> thin film has attracted much attention because of its chemical, electrical and optical properties[1–2]. It is known that the TiO<sub>2</sub> crystal usually has three different crystallographic structures: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic)[3]. Two of them, rutile and anatase, are commonly used in photocatalysis and the TiO<sub>2</sub> with anatase structure shows a higher photocatalytic activity [4–6]. This unique photocatalytic property makes it suitable for the oxidation of organic pollutants and other contaminants from wastewater or drinking water supplies [7–9]. To grow high-quality TiO<sub>2</sub> films various deposition methods have been used, such as chemical vapor deposition[10], magnetron sputtering[11], reactive sputtering[12], sol-gel deposition[13] and pulse laser deposition(PLD)[14].

The main advantages of PLD are the ability to create high-energy source particles, permitting the growth of high quality film at low substrate temperature, simple experimental setups and operation in controlled gas environment and pressure[15–16]. The preparation of TiO<sub>2</sub> film using PLD had been studied[14, 17–18]. In

those papers, they have investigated the film crystallinity under various parameters such as ambient pressure, substrate temperature, and the density of target. However, the relationship between the structure of anatase TiO<sub>2</sub> films and its photocatalytic activity has less been studied deeply. In this paper, TiO<sub>2</sub> thin films were deposited on quartz glass substrates by pulse laser deposition(PLD) technique. The crystal structure and the surface morphology of the as-deposited TiO<sub>2</sub> films were investigated by X-ray diffractometry(XRD), X-ray photoelectron spectroscopy(XPS) and field emission scan electron microscopy(FESEM). The optical and photocatalytic properties of the TiO<sub>2</sub> thin films were measured with optical transmittance spectrum. The influences of the substrate temperature on the structural and optical properties were investigated.

### 2 Experimental

TiO<sub>2</sub> thin films were deposited by using the pulsed laser deposition technique. The chamber was evacuated by using a turbo-molecular pump to a base pressure of  $5 \times 10^{-4}$  Pa and then filled with oxygen (99.99% purity) at a working pressure of 10 Pa. Pulsed Nd: YAG laser with a wavelength of 1 064 nm was used. The repetition

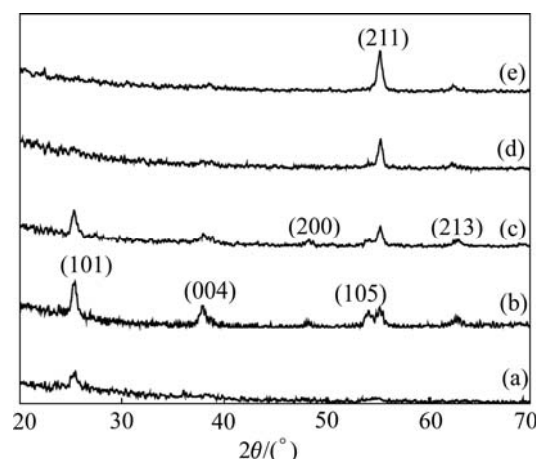
rate is 20 Hz and the fluency on target was set at 60 J/cm<sup>2</sup> for all samples. TiO<sub>2</sub> films were grown on 2.5 cm × 2.5 cm quartz glass substrates. A target of Ti (99.9% purity) was used to provide titanium for oxidation. The distance between the target and the substrate was kept at 2.5 cm. The deposition time of 90 min was maintained for all specimens. TiO<sub>2</sub> thin films were deposited at various substrate temperatures ranging from 500 °C to 800 °C. After deposition, the crystallographic structure of the films was investigated by X-ray diffractometry (XRD, Rigaku Dymax) with a Cu target and a mono-chromator at 50 kV and 300 mA. Tangent Profilometer (Dektak 16000.Veeco.USA) was used to measure the thickness of the films. XPS spectra of the films were acquired with an ESCALAB Mk II (Vacuum Generators) spectrometer using unmonochromatized Al K<sub>α</sub> X-rays (240 W). Cycles of XPS measurements were performed in a high-vacuum chamber with a base pressure of 1.33 μPa. FESEM (JSM-6700F) was used to characterize the surface morphology of the films. The optical properties of the TiO<sub>2</sub> thin films were characterized with UV-visible spectrophotometer (725PC).

The photo-degradation of aqueous methyl orange was used to estimate the photocatalytic efficiency of the deposited TiO<sub>2</sub> films. The visual light source is a 500 W high-pressure mercury lamp (100 mm long), which is surrounded by a circulating water jacket to cool the lamp. Typically, the films were put in the reactor containing 30 mL of 20 mg/L aqueous methyl orange, which was stirred through piping air into the beaker at a flux of 50 mL/min. The reaction mixture was exposed to the high-pressure mercury lamp perpendicularly. The distance between the lamp and the reactor was kept at 20 cm for all specimens. All operations were conducted at ambient temperature. After irradiation the methyl orange was analyzed by using UV-visible (UV-Vis) Spectroscopy. Following the exposure to light, the decolorization of methyl orange at its absorption maximum (449 nm) was recorded as a function of time.

### 3 Results and discussion

#### 3.1 Structural properties

Fig.1 shows the XRD patterns obtained from TiO<sub>2</sub> films grown at substrate temperatures of 500, 600, 700, 750 and 800 °C, respectively, in an oxygen pressure of 10 Pa. All specimens show the anatase structure with crystallographic parameter of  $a=3.785 \text{ \AA}$ ,  $c=9.513 \text{ \AA}$ . As the temperature increased, the textures of the films were changed; when the temperature increased to 750 °C and 800 °C (211)-oriented TiO<sub>2</sub> anatase structure was obtained. The degree of crystal-axis orientation can be estimated using the Lotgering orientation factor  $f$  [19] taking into account of the following diffraction peaks:

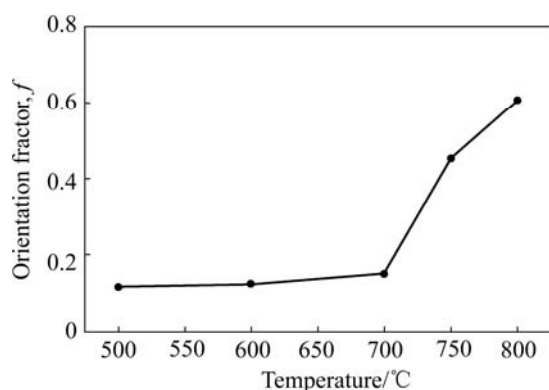


**Fig.1** XRD patterns of TiO<sub>2</sub> thin films on quartz glass substrate at different growth temperatures: (a) 500 °C; (b) 600 °C; (c) 700 °C; (d) 750 °C; (e) 800 °C

(101)=25.3°, (004)=37.8°, (200)=48.0°, (105)=53.9°, (211)=55.1°, (213)=62.1°, (204)=62.7°, (116)=75.0°.

$$f = P_{hkl} - P_{hkl}^0 - P_{hkl}^0 \quad (1)$$

where  $P_{hkl}$  is peak intensity ratio of the oriented ( $hkl$ ) direction to the sum of all diffraction directions for oriented sample and  $P_{hkl}^0$  is the corresponding value for the standard sample (from JADE card). When orientation factor  $f$  equals 1, the degree of orientation for ( $hkl$ ) is complete; on the other end, complete random state is shown by  $f=0$  [20]. The value of  $f$  for (211) is calculated from the XRD peak intensity of the thin film prepared at various temperatures as shown in Fig.2. The value of  $f$  for (211) was very low (about 0.11) at the substrate temperature of 500–700°C, but it increases from 0.116 to 0.609 with increasing the substrate temperature from 700 °C to 800 °C. This clearly indicates that the preferred orientation growth along (211) plane occurs at high deposition temperature. It is considered that the increase of orientation to (211) plane is due to the increment of nucleation rate[20]. During PLD, the kinetics of atomic arrangement is mainly influenced by the substrate temperature and the kinetic energy of deposition atoms[21]. Therefore, at a relatively low temperature, because of the relatively low deposition rate, there should be enough time for adatoms to move on surface to look for the lowest energy sites before the adatoms are covered by the next layer of atoms. As a result, the homogeneous growth results in a random growth and smooth surface structure. However, at relatively high growth temperature (for example, 800 °C), the higher nucleation rate may induce the increase of the number of nucleus. As a result of increasing nuclei, anisotropic growth like the (211) plane for the TiO<sub>2</sub> film may be possible.

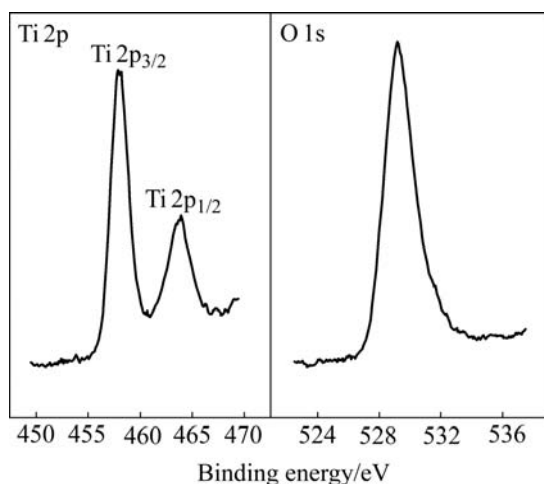


**Fig.2** *f* (degree of crystal-axis orientation factor) of anatase TiO<sub>2</sub> thin films deposited at different temperatures

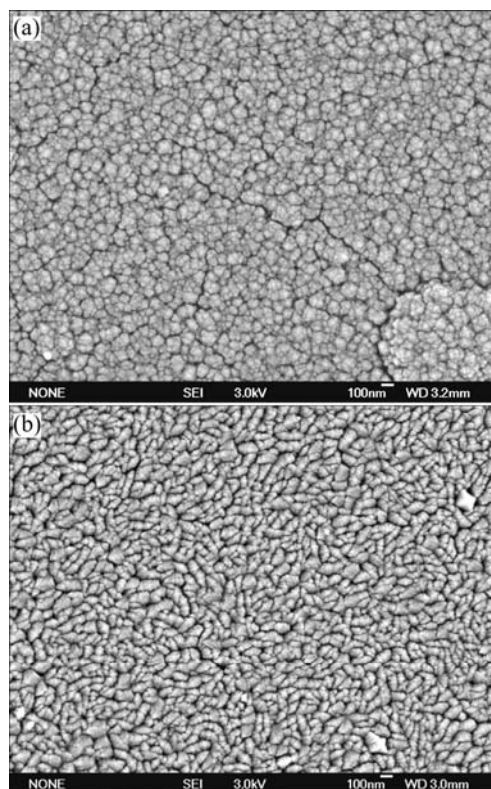
The thickness of the film has been measured to be 0.52, 0.54, 0.58 and 0.65 μm, corresponding to the substrate temperature of 500, 600, 700 and 800 °C, respectively. Because the increase of substrate temperature resulted in the increase of the deposition rate, the thickness of films increased with the increase of deposition temperature.

Figs.3(a) and (b) show XPS Ti 2p and O 1s core levels of the as-deposited TiO<sub>2</sub> film, respectively. From Fig.3(a), one can see that the core levels of Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> are at approximately 464.0 and 458.3 eV, respectively, which are assigned to the Ti<sup>4+</sup> (TiO<sub>2</sub>), with a peak separation of 5.7 eV between peaks. The core level of O 1s is at 529.2 eV, see Fig.3(b), which is attributed to titanium dioxide on the surface. The data are in agreement with the fact that the main peak of TiO<sub>2</sub> is located at 529.9 eV. There is no evident difference in XPS between the films deposited at different substrate temperatures. The XPS results are in agreement with the above XRD results.

Fig.4 shows the two typical FESEM images of the



**Fig.3** XPS Ti 2p and O 1s core levels of as-deposited TiO<sub>2</sub> film at 600 °C



**Fig.4** FESEM images of TiO<sub>2</sub> thin film grown on quartz glass substrate at deposition temperatures: (a) 600 °C; (b) 800 °C

films deposited at substrate temperatures of 600 and 800 °C, respectively. Surface morphologies were changed with the development of orientation with increasing deposition temperature. At 600 °C TiO<sub>2</sub> film showed random growth surface and equal-axial particles, with the average particle size of about 50 nm (Fig.4(a)). When the film was deposited at high substrate temperature of 800 °C, the shuttle-like particles can be observed (Fig.4(b)) with the average particle size of about 90 nm.

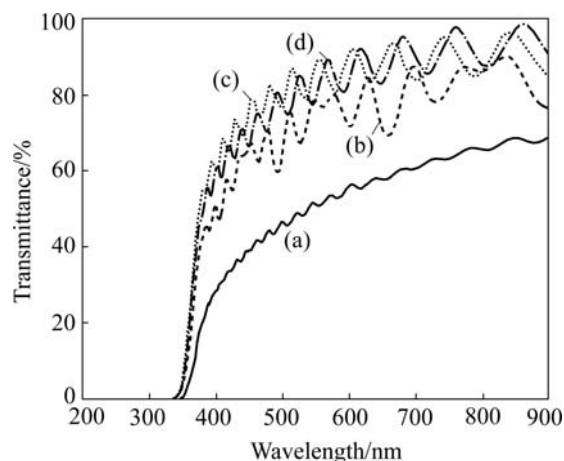
### 3.2 Optical and photocatalytic properties

Fig.5 shows the UV-visible spectroscopy of the TiO<sub>2</sub> thin films observed at room temperature. It can be seen that the absorption edge has a blue shift. The reason for the blue shift may be complex. However, as the particle size of the films is below 100 nm, quantum size effect can be used to explain the magnitude of the shift[4]. Quantum size effect can be expressed by the Brus equation[22]:

$$\Delta E = \frac{\eta^2 \pi^2}{2R^2} \left| \frac{1}{m_e} + \frac{1}{m_h} \right| - \frac{1.786e^2}{\epsilon R} - 0.248E_{Ry}^*$$

where  $\eta$  is the converting efficiency of quantum,  $R$  is the radius of the particle,  $m_e$  and  $m_h$  are the effective masses for the electrons and holes,  $\epsilon$  is the dielectric constant, and  $E_{Ry}^*$  is effective Rydberg energy. The first item is bondage energy, which is proportion to  $1/R^2$ ; the

second item is the coulomb attraction of electrons and holes, and the third item represents the space amendatory effect. As the particle size reduces, because the increase of bondage energy is more evident than the coulomb item that leads to the decrease of energy, so smaller grain size leads to larger shift of the absorption edge.

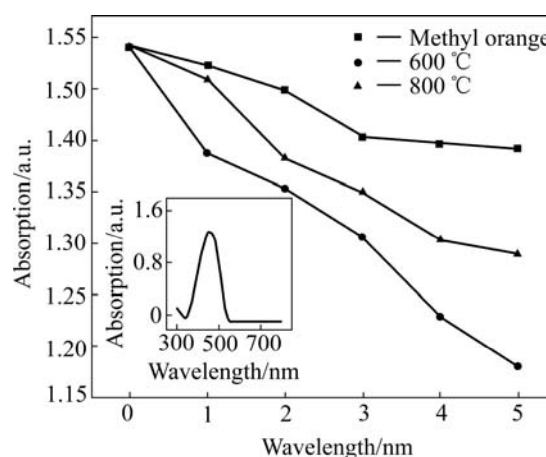


**Fig.5** UV-Vis transmittance spectra of TiO<sub>2</sub> showing blue shift with increase of deposition temperature: (a) 500 °C; (b) 600 °C; (c) 700 °C; (d) 800 °C.

Titanium is a typical semi-conductor oxide with measured optical band gap. It is known that when TiO<sub>2</sub> film is irradiated by UV-vis light with energies equal to or higher than the band-gap energy, the electron-hole pairs are generated and these excitations can migrate to the surface to initiate redox reactions with adsorbates. The ability of a semiconductor to obtain more electron-hole pairs to adsorbed species on its surface is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbates[4]. The band gap energy  $E_g$  can be determined from the absorption coefficient  $\alpha$  calculated as a function of  $ah\nu = B_i(h\nu - E_g)^2$  [23], where  $B_i$  is the absorption constant for an indirect transition. The absorption coefficient can also be expressed as:  $\alpha = -\ln(T)/d$ , where  $T$  and  $d$  are the transmittance and the film thickness, respectively. According to the above two functions, we got the band gap energies of the films deposited at different temperatures (500, 600, 700 and 800 °C). The band gap energies are 3.15, 3.19, 3.21 and 3.25 eV, respectively. Based on the band energy we speculated that the random anatase structure films that have lower band gap energy, would exhibit wider wavelength response range and lead to higher photo-degradation efficiency.

In order to test the photocatalytic efficiency of the films, they were tested them on the degradation process of methyl orange. The inset in Fig.6 shows the absorption spectrum of the aqueous methyl orange, it is seen that the solution shows largest absorption at wavelength of 449 nm. Therefore, the decolorization of

methyl orange at its maximum absorption wavelength (449 nm) was recorded. Fig.6 shows the degradation of methyl orange solution with TiO<sub>2</sub> films, deposited at two substrate temperatures: 600 and 800 °C, as photocatalysts. The degradation curve of the aqueous methyl orange without photocatalysts was also plotted for comparison. From these curves we can see that the TiO<sub>2</sub> film deposited at 600 °C shows the best photocatalytic activity. Compared with the (211)-oriented TiO<sub>2</sub> anatase structure film the random TiO<sub>2</sub> anatase structure film, has better photocatalytic activity.



**Fig.6** Degradation of methyl orange solution with TiO<sub>2</sub> photocatalyst films deposited at different substrate temperatures (The inset is optical transmittance spectrum of methyl orange solution)

## 4 Conclusions

1) The TiO<sub>2</sub> film deposited at relatively low temperatures (500–600 °C) shows random growth and has a smaller average nanometer particle size (about 50 nm); and the film deposited at relatively high temperatures (750–800 °C) tends to grow along (211) orientation.

2) The TiO<sub>2</sub> films with random anatase structure, which exhibit lower band gap energy, show higher photo-degradation efficiency than that with (211)-oriented growth structure.

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(Edited by HE Xue-feng)