

## Deposition of photocatalytic TiO<sub>2</sub> and N-doped TiO<sub>2</sub> films by arc ion plating

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**Abstract:** TiO<sub>2</sub> and N-doped TiO<sub>2</sub> films were deposited on the glass substrates by arc ion plating method. The results show that the deposition rate does not change with the increasing deposition time. The increase of mass flow rate of N<sub>2</sub> gives rise to the increase of deposition rate. All as-deposited TiO<sub>2</sub> and N-doped TiO<sub>2</sub> films are amorphous. The anatase TiO<sub>2</sub> phase with preferred orientation (101) is acquired by post-annealing at 400 °C for 2 h. The incorporation of N into the TiO<sub>2</sub> films and the heat treatment extensively shift the band edge to the visible light region.

**Key words:** arc ion plating; photocatalytic TiO<sub>2</sub>; N-doped TiO<sub>2</sub>; absorption edge

### 1 Introduction

Photocatalytic TiO<sub>2</sub> has been attracting more and more attention due to its high stability and activity, and can be used in many fields such as the decomposition of organic pollutant, splitting water and development of self-cleaning glass[1–3]. Since the band gap of TiO<sub>2</sub> is approximately 3.2 eV, only the UV light of wave length less than 380nm can be absorbed[4]. Recently, many studies have been performed to extend the available spectrum for TiO<sub>2</sub> from UV region to visible region. One approach in the development of such visible light-responsive catalysts was to develop various photosensitizing dyes adsorbed on TiO<sub>2</sub> films[4–5] and another approach was to dope transition metal such as V[6], Cr[7], Fe[8], Co[9] and Ni[10] or anion such as carbon[11], nitrogen[12–13] and sulfur[14] into TiO<sub>2</sub> films or particles. Photocatalytic TiO<sub>2</sub> films can be prepared by several methods such as sol-gel[15], CVD[16], magnetron sputtering[17] and arc ion plating[18]. Owing to the high deposition rate, convenient parameter control and excellent film quality, arc ion plating is one of the most prospective methods to deposit TiO<sub>2</sub> and anion-doped TiO<sub>2</sub>[19].

### 2 Experimental

The TiO<sub>2</sub> and N-doped TiO<sub>2</sub> films were deposited on microscope glass slides (with dimensions of 75.5 mm×25.5 mm×1.2 mm) by arc ion plating (AIP-1000–10 Coating System). The glass slides were prepared by ultrasonic cleaning in acetone and then being blown to dry. The disc target was titanium with a purity of 99.95% and the target dimensions were 100 mm in diameter and 45 mm in thickness. The base pressure in the chamber was  $2 \times 10^{-3}$  Pa and the substrate temperature was room temperature at the beginning of the deposition. The reactive gases O<sub>2</sub> (99.99%) and N<sub>2</sub> (99.999%) were controlled by mass flowmeter. The total pressure of O<sub>2</sub> and N<sub>2</sub> was kept at 1.2 Pa. When TiO<sub>2</sub> films were deposited, no N<sub>2</sub> was introduced and the mass flow rate of O<sub>2</sub> was 340 cm<sup>3</sup>/min. In order to get N-doped TiO<sub>2</sub> films with different N contents, the mass flow rate of N<sub>2</sub> was respectively set at 40, 80, 120, 160, 200, 240, 260 and 280 cm<sup>3</sup>/min. No bias voltage was applied to the substrates during the deposition of the films. The distance between target and substrate was 200 mm. The arc current was 40 A. Three kinds of TiO<sub>2</sub> films with different thickness were prepared by controlling

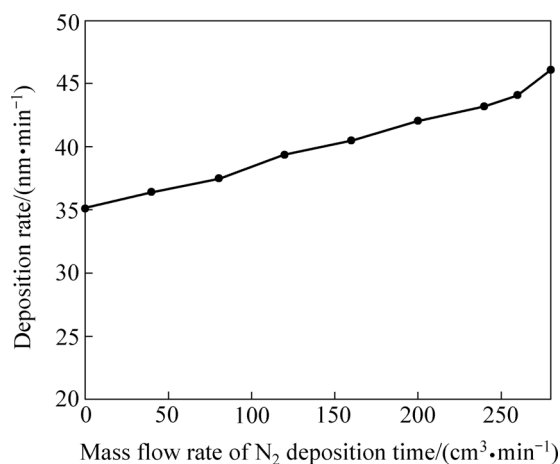
deposition time at 15, 30 and 45 min. The deposition time of all N-doped TiO<sub>2</sub> films was kept at 30 min. The film specimens were annealed at 400 °C for 2 h in a chamber-type electric furnace under atmospheric ambience.

The crystalline structure and crystallographic orientation of the films were measured by Bruker D8 ADVANCE X-ray diffractometer (XRD) using Cu K<sub>α</sub> radiation. The surface morphology of the films was examined using a field emission SEM. UV-Vis spectra of the films on glass substrate were measured in air at room temperature using UNICO UV/VIS 2802PCS spectrophotometer in the range from 190 nm to 1 100 nm. The film thickness was determined by fitting transmittance optical spectra using Scout software.

### 3 Results and discussion

#### 3.1 Deposition rate

The thickness of the as-deposited TiO<sub>2</sub> with deposition time of 15, 30 and 45 min is respectively 0.53, 1.05 and 1.57 μm. The deposition rate is about 35 nm/min for all these TiO<sub>2</sub> films and keeps constant with the increasing deposition time. Fig.1 shows the curves of deposition rate versus the mass flow rate of N<sub>2</sub>. The deposition rate increases with the increase of mass flow rate of N<sub>2</sub>. This change of the deposition rate is ascribed to the change of evaporation rate of the Ti target in different reactive atmosphere.



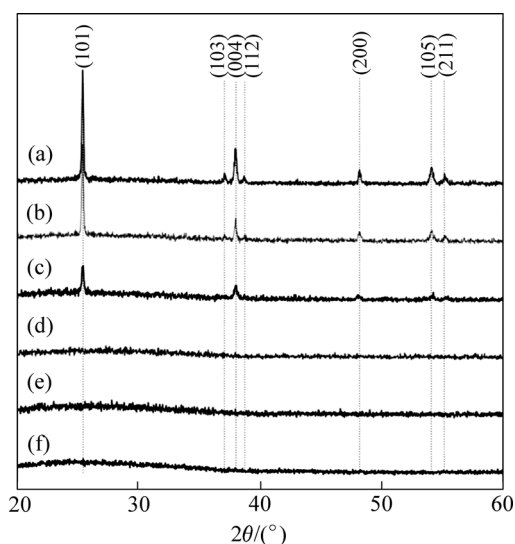
**Fig.1** Curves of deposition rate of TiO<sub>2</sub> films versus mass flow rate of N<sub>2</sub>

#### 3.2 Phase structure

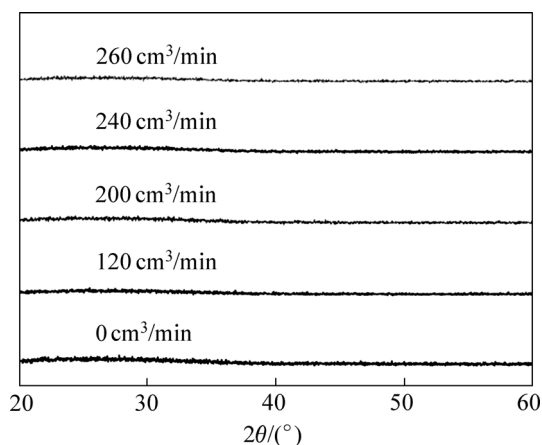
The XRD patterns of the as-deposited TiO<sub>2</sub> films and the post-annealed specimens after different deposition time are shown in Fig.2. No distinct diffraction peak is detected in the results of all the three kinds of as-deposited films, thus indicating that all the TiO<sub>2</sub> films are amorphous. Due to the high ionized rate and heating effect of plasma on the substrates, rutile

phase is apt to form during the deposition was process. In order to prevent the formation of rutile phase structure, in this experiment, the deposition was processed under room temperature, the arc current was controlled at 40 A, and no bias voltage was applied to the substrates. Under this condition of lower energy, neither rutile phase nor anatase one can be formed. Heat treatment at 400 °C in air for 2 h was applied to the as-deposited TiO<sub>2</sub> in order to get the complete anatase TiO<sub>2</sub> phase. For the post-annealed films, as our anticipation, only the diffraction peaks of anatase TiO<sub>2</sub> is found. (101) is the main preferential orientation. With the increasing thickness of the films, there exists an increasing intensity of the diffraction peaks for the post-annealed films.

Fig.3 shows the XRD patterns of the as-deposited N-doped TiO<sub>2</sub> films deposited under different mass flow rate of N<sub>2</sub>. All the as-deposited films were amorphous.

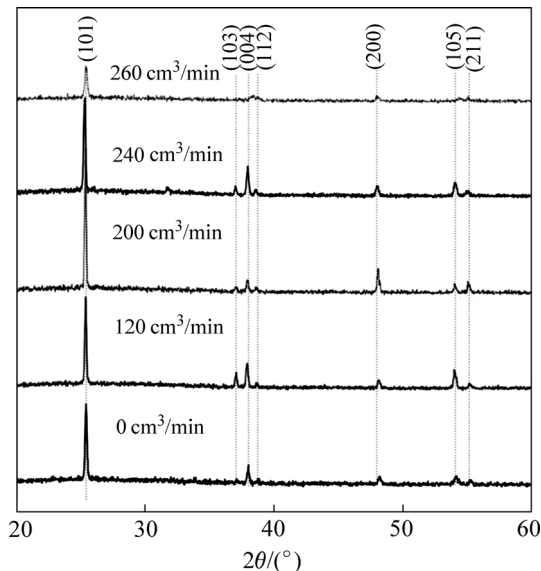


**Fig.2** XRD patterns of TiO<sub>2</sub> films: (a) Post-annealed film, 45 min deposition time; (b) Post-annealed film, 30 min deposition time; (c) Post-annealed film, 15 min deposition time; (d) As-deposited film, 45 min deposition time; (e) As-deposited film, 30 min deposition time; (f) As-deposited film, 15 min deposition time



**Fig.3** XRD patterns of as-deposited N-doped TiO<sub>2</sub> films under different mass flow rates of N<sub>2</sub>

The N-doped TiO<sub>2</sub> films were annealed at 400 °C in atmospheric ambience to acquire crystalline films. Fig.4 shows the XRD patterns of the post-annealed N-doped TiO<sub>2</sub> films. Unexceptionally, all the post-annealed films are anatase with a (101) preferential orientation.



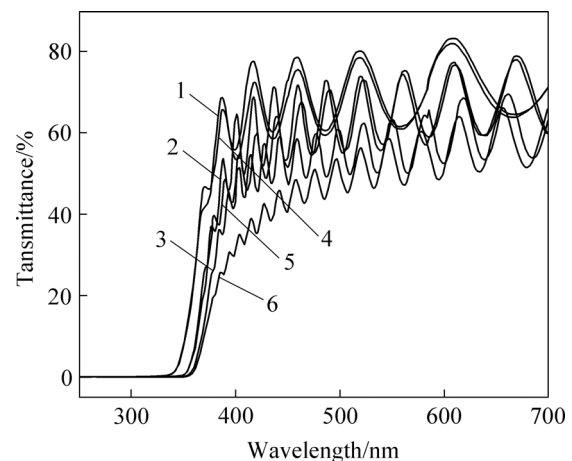
**Fig.4** XRD patterns of post-annealed N-doped TiO<sub>2</sub> films different flow rates of N<sub>2</sub>

### 3.3 Optical properties

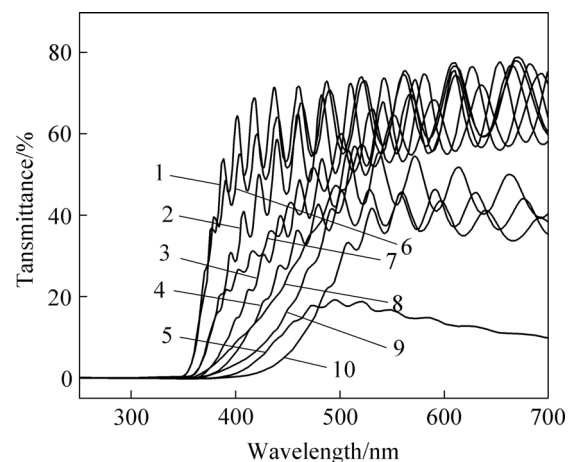
TiO<sub>2</sub> film deposited for 15 min or 30 min was colorless and transparent to visible light. While the film deposited for 45 min is not complete transparent to visible light. Fig.5 shows the UV-Vis spectra of the as-deposited and the post-annealed TiO<sub>2</sub> after different deposition time. The band edges of the deposited films shift towards the visible region obviously with the increasing deposition time. This shift of band edges is ascribed to the quantum size effect[20]. The transmittance of the as-deposited TiO<sub>2</sub> films decreases with increasing deposition time and this is due to the increase of the film thickness. Annealing treatment hardly changes the band edges of the film deposited for 15 min or 30 min, but the post-annealed film deposited for 45 min exhibits considerable absorption in wavelength regions longer than 400 nm. The transmittance of the films decreases to some extent owing to the post-annealing. With increasing thickness of the films, the transmittance decreases more significantly.

Fig.6 shows the UV-VIS spectra of the as-deposited and post-annealed N-doped TiO<sub>2</sub> films deposited under different mass flow rates of N<sub>2</sub>. For the as-deposited films, the introduction of N into the films gives rise to a distinct shift of band edges to visible region and a constant decrease of the transmittance. The

post-annealing further makes the band edges shift to longer wavelength. It is reported that most of N-doped TiO<sub>2</sub> exhibits visible light absorption as a shoulder in the wavelength range of 400–600 nm, which indicates that the isolated N 2p orbital are formed above the O 2p orbital due to the limited concentration of N that the substitute for O in TiO<sub>2</sub> lattice is lower than 2%[21]. But in this work, even the N-doped TiO<sub>2</sub>, whose band edge is close to 500 nm, does not show the visible light absorption as a shoulder. Compared with other deposition technique such as sol-gel and magnetron sputtering, arc ion plating method possesses high ionization rate, N can be easily introduced to the lattice of TiO<sub>2</sub>. The mixing of N 2p states with the O 2p states shifts the valence band edge upwards to narrow the band gap energy of TiO<sub>2</sub>.



**Fig.5** UV-vis transmission spectra of as-deposited and post-annealed TiO<sub>2</sub> films after different deposition time: 1—15 min, as-deposited; 2—30 min, as-deposited; 3—45 min, as-deposited; 4—15 min, post-annealed; 5—30 min, post-annealed; 6—45 min, post-annealed



**Fig.6** UV-vis transmission spectra of as-deposited and post-annealed N-doped TiO<sub>2</sub> films under different flow rates of N<sub>2</sub>: 1—0 cm<sup>3</sup>/min; 2—120 cm<sup>3</sup>/min; 3—200 cm<sup>3</sup>/min; 4—240 cm<sup>3</sup>/min; 5—260 cm<sup>3</sup>/min; 6—0 cm<sup>3</sup>/min, post-annealed; 7—120 cm<sup>3</sup>/min, post-annealed; 8—200 cm<sup>3</sup>/min, post-annealed; 9—240 cm<sup>3</sup>/min, post-annealed; 10—260 cm<sup>3</sup>/min, post-annealed

## 4 Conclusions

1) TiO<sub>2</sub> and N-doped TiO<sub>2</sub> films were deposited on glass substrates by arc ion plating technique. The thickness of the TiO<sub>2</sub> films is linear with the deposition time. The increase of mass flow rate of N<sub>2</sub> improves the deposition rate of the films. All as-deposited TiO<sub>2</sub> and N-doped TiO<sub>2</sub> films are amorphous.

2) After annealed at 400 °C for 2 h, the anatase TiO<sub>2</sub> phase with (101) preferred orientation is acquired. The introduction of N into the TiO<sub>2</sub> lattice narrows the band gap energy of TiO<sub>2</sub> and gives rise to a shift of the band edge to the visible light region. The post-annealing further makes the band edges shift to longer wavelength.

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