Nuclear Instruments and Methods in Physics Research B 307 (2013) 381–384

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Research of composition and photocatalytic property of carbon-doped Ti-O films prepared by R-MS using CO_2 gas resource

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ARTICLE INFO

Article history:
Received 27 September 2012
Received in revised form 17 November 2012
Accepted 19 November 2012
Available online 26 January 2013

Keywords:
Carbon-doped
Photocatalysis
Ti-O films
Magnetron sputtering
XPS

ABSTRACT

In this paper, carbon-doped Ti-O films were prepared on silicon wafer and stainless steel by reaction magnetron sputtering using CO_2 as carbon and oxygen source. By changing the ratio of CO_2/O_2, a series of films with different composition can be obtained. X-ray photoelectron spectroscopy (XPS) was employed to analyze composition of as-prepared films. The result proved that carbon was doped into titanium successfully. Ultraviolet–visible (UV–Vis) spectrophotometer in the wavelength range of 250–900 nm was used to record the absorbance of as-prepared film samples. The photocatalytic activities of as-prepared films were evaluated by measuring the decolorization rate of methyl orange under UV light irradiation. The results showed that as-prepared carbon-doped Ti-O films have fairly photocatalysis activity, which to be hoped to become candidate materials for photocatalyst.

1. Introduction

In recent years, the population growth with its increased needs has prompted many industrial developments and this has led to an increase in pollution. Especially textile industries use colored dyes such as methyl orange (MO), methylene blue, acid red 14, etc. Usage of these colored dyes becomes a major source of environmental contamination [1,2]. Heterogeneous photocatalysis by semiconductor materials has been extensively studied and widely applied to environmental purification both in gas and liquid phases [3].

Titanium dioxide (TiO_2) is the most suitable photocatalyst due to its high photocatalytic activity, good chemical and biological stability, high energy efficiency, minimum waste streams, relatively low cost and non-toxicity [4]. But photocatalytic activity of TiO_2 was only excitated by ultraviolet (UV) light due to its wide band gap (Eg = 3.2 eV). Thus, their use is limited to environments where sufficient UV light is in contact with TiO2 surface. Therefore, the development of these materials by inclusion of specific dopant, so that visible light may also be used to stimulate the photocatalytic activity represent an important target [5]. Furthermore, TiO_2 powder is difficult to recycle, easy to agglomerate, and causes a problem of separation from the solution [6], that is the problem of immobilization.

There were some reports about photocatalysis of carbon-doped TiO_2 [7–9]. But few paper was published that use CO_2 gas as carbon and oxygen source to prepare carbon-doped Ti-O films. In this paper, the carbon-doped Ti-O films were prepared on metal substrate by reaction magnetron sputtering (R-MS) using CO_2. Firstly, coating Ti-O films on the surface of metal is to solve the problem of immobilization. Secondly, doping carbon element into Ti-O lattice is to make the absorbance edge red shift and photoactivity improved.

2. Materials and methods

Carbon-doped Ti-O films were prepared on silicon, stainless steel and glass by R-MS using high purity titanium (99.99%) as titanium plasma source and CO_2 gas as C and O source under RT. Table 1 is the process parameters.

The composition of carbon-doped Ti-O film was studied by X-ray photoelectron spectroscopy (XPS, Type K-ALPHA, Thermo Electron Corporation, USA). Absorbance is a very important property for assessing photocatalysis. The absorbance of as-prepared films was measured by UV–Vis spectrophotometer (type TU-1810) in the wavelength range of 250–900 nm. Photocatalytic activity of synthesized carbon-doped Ti-O films were also evaluated by the degradation test of methyl orange (MO) under UV light irradiation. During the photo-degradation test, MO solution

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http://dx.doi.org/10.1016/j.nimb.2012.11.080

Table 1
The synthesized process parameters and thickness of carbon-doped Ti-O films.

Sample no.	Ar/sccm	CO_2/sccm	O_2/sccm	CO_2/O_2	Bias voltage/V	Times/min	Thickness/nm
1#		18	–	–			586.9
2#		18	12	3:2			344.2
3#	60	18	6	3:1	−150	15	574
4#		18	3	6:1			561.1
5#		36	3	12:1			432.6

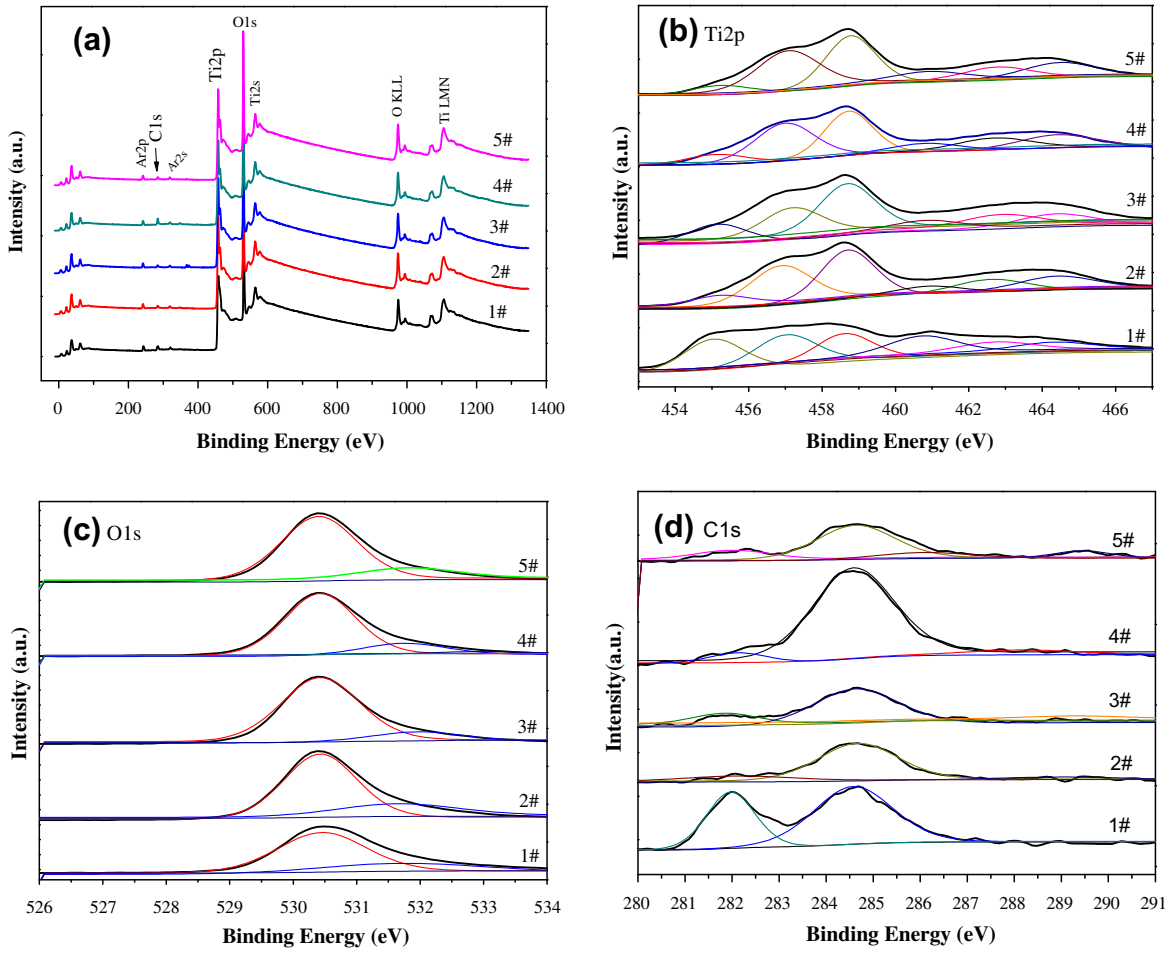

Fig. 1. (a) XPS full spectra, (b) Ti 2p spectra, (c) O1s spectra and (d) C1s spectra of as-prepared carbon-doped Ti-O films after etching 30 s.

(10 mg/L) was loaded in the dish and the as-prepared carbon-doped Ti-O films were placed into the MO solution. A 15 W bactericidal lamp was used as UV source. The lamp was placed at the top of the dish with the spacing between the light bulb and the surface of dish being 5 cm. The concentration of MO in solution was measured interval of time by monitoring the absorbance at 464 nm on a UV–vis spectrophotometer. Film thickness was measured by Alpha-Step R-500 surface profiler and listed in Table 1.

3. Results and discussions

XPS is quite sensitive to the characteristics of the film surface because the non-elastic scattering mean free path λm of emitted photoelectron is very short [10,11]. As-deposited Ti-O-C films deposited on the stainless steel were analyzed by XPS after etching 30 s. Fig. 1a showed the XPS full spectra. It can be seen from Fig. 1a that as-prepared films contained Ti, C and O elements. Fig. 1b–d showed the XPS spectra for Ti2p, C1s and O1s, which were fitted by Gaussian and by approximating the contribution of background by the smart mode using thermo advantage soft developed by Thermo Fisher Scientific Corporation. The chemical bonding state between Ti and C, Ti and O in the films were also analysized (seen in Fig. 1b–d).

The Ti2p spectrum can be decomposed into six peaks. The peak positions at about 464.2, 462.6 and 461.1 eV shown in Fig. 1(b) correspond to the core levels of $Ti^{4+}2p1/2$, $Ti^{3+}2p1/2$ and $Ti^{2+}2p1/2$, respectively, whereas about 458.2, 457.0 and 455.4 eV peaks can be attributed to $Ti^{4+}2p3/2$, $Ti^{3+}2p3/2$ and $Ti^{2+}2p3/2$. Oxygen was observed to exist in two chemical states due to the presence of two peaks at about 530 and 531.4 eV as shown in Fig. 1(c), which are attributed to O-Ti and C–O/C≡O bands, respectively. The asymmetric C1s spectrum, shown in Fig. 1d, can be mainly decomposed into two peaks centered at about 282.0, 284.6 eV, which are as-