Surface & Coatings Technology 303 (2016) 184–190

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Co-sputtered boron-doped titanium dioxide films as photocatalysts

Shi-Jie Shen [a], Tien-Syh Yang [b], Ming-Show Wong [a,*]

[a] Department of Materials Science and Engineering, National Dong Hwa University, Hualien, Taiwan, ROC
[b] General Educational Center, Tzu-Chi College of Technology, Hualien, Taiwan, ROC

ARTICLE INFO

Article history:
Received 23 October 2015
Revised 6 March 2016
Accepted in revised form 14 March 2016
Available online 16 March 2016

Keywords:
Titanium dioxide
Boron-doped titania
Photocatalyst
Sputtering
Nanoporous film

ABSTRACT

Boron-doped titanium dioxide (B-TiO_2) films were deposited by reactive magnetron co-sputtering from metallic titanium (Ti) and titanium diboride (TiB_2) targets in Ar/O_2 plasma. The films were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Ultraviolet–visible (UV–vis) spectroscopy. The photocatalytic activities of the samples were evaluated for degradation of methylene blue (MB) under UV and visible light irradiation. By changing the TiB_2 target power, various boron amount and species are formed in the as-deposited and the annealed films. Therein, the [BO_3] as well as [Ti_2BO_2] species would redshift the UV–visible absorption edge and improve the visible light activity of TiO_2. Most of the B-species could be oxidized into B_2O_3 phase and evaporated in the annealed films. This introduced porosity into the films and apparently promoted the UV-light photocatalytic activity. The remaining B_2O_3 phase itself has no direct effect on the photocatalytic activities, but in couple with TiO_2 they can reduce the recombination rate of the photogenerated carriers, and hence improve the photocatalytic activities of the annealed B-TiO_2 films.

1. Introduction

Titanium dioxide (TiO_2), for its functionality, low cost and chemical stability, has been used widely in various fields, such as solar cells, photocatalytic splitting of water for green-energy hydrogen (H_2) production, air and water purification by removal of organic and inorganic pollutants, superhydrophilicity for anti-fogging and self-cleaning, selective synthesis of organic compounds, and photo-killing of pathogenic bacteria [1–6]. However, TiO_2 as a photocatalyst has two major shortcomings — wide band gap (3.2 eV and 3.0 eV for anatase and rutile phases, respectively) and high recombination rate of the photogenerated electron–hole pairs, which hinder the sunlight-induced photocatalytic activity and causes the low quantum efficiency in photocatalytic reactions [7,8].

Non-metal doping has been exploited for over a decade as a prevailing way to change the photo-absorption properties of TiO_2 for harvesting solar light with applications including photocatalysis and photoelectrochemistry [9–13]. Recently, some studies have exploited boron-doped TiO_2 (B-TiO_2) [14–27], and co-doping with other non-metal elements (e.g., co-doping with B and N) [19,20]. However, the results and the interpretations on the role of B in TiO_2 are still not clear. Zhao et al. [14] reported that the B-1s XPS peak at 191.6 eV contributes to the redshifted absorption spectrum of B-TiO_2 to the visible region, but does not provide significant promotion of visible-light photocatalytic activity for degradation of TCP (trichlorophenol). However, it can be greatly enhanced by further co-loading with Ni_2O_3. The possible B-species in B-TiO_2 with the most stable state was the O substituted by B that was responsible for the band gap narrowing according to the authors' DFT calculations for three systems [14]. Geng et al. [15] employed the DFT-LDA-supercell calculations to show that the substitutional B to O species and interstitial B-species had comparable energy, both could occur in real materials, but only the substitutional B-species would lead to narrowing of the band gap that was observed for the samples obtained by Zhao et al. in [14]. In addition, the substitutional B-species proposed by Geng et al. [15] would proceed from the geometry optimization so that the B atom was strongly bonded to two O atoms and weakly to two Ti atoms (Ti_2BO_2). Afterwards, In et al. [19] showed that the B-1s XPS peak at 190.6 eV was also associated to the substitutional B to O species and contributed to the observed visible-light absorption and photocatalytic activity for MTBE (methyl tertiary butyl ether) conversion. On the other hand, Chen et al. [16] observed a B-XPS peak shifted from 191.1 to 192.2 eV with the increasing boron ratio, suggesting the successive increase of B—O bonds in B-TiO_2. The B-species blueshifted the UV–visible absorption of TiO_2 and increased the UV-induced photocatalytic activity for regeneration of NADH (nicotinamide adenine dinucleotide). In some cases in the literature, the XPS peaks attributed to the B-species may co-exist with other peaks with the BE from about 192.8 to 194 eV, indicating further B—O bonds formation like B_2O_3 micro-aggregates into the titania samples or onto their surfaces [19,21].

---

* Corresponding author.
E-mail address: mswong@ndhu.edu.tw (M.-S. Wong).

http://dx.doi.org/10.1016/j.surfcoat.2016.03.042

The two B species corresponding to the photocatalytic activities in the B—TiO_2 systems: the substitutional B to O species and the interstitial B species were interpreted with a detail calculation [13,24]. Finazzi et al. [24] reported that the B substitutional to O species resulted in a paramagnetic defect $[BTi_3]^\bullet$, which introduced new states in the mid-gap of TiO_2. The interstitial B species as diamagnetic species could be coordinated to three or four oxygen atoms with the $[BO_3]$ species more stable than $[BO_4]$ species. The position of the B atom in $[BO_3]$ differed from the position in boron oxide (B_2O_3) that indicated that the B atoms were not oxidized completely to the B^{3+} state [24]. Several authors have pointed out that the interstitial B atom in the lattice of anatase or rutile TiO_2, located near O atoms formed B—O bonds instead of B—Ti bonds such as O—B—O or Ti—B—O [16,20,25–27].

Some studies proposed that the B-TiO_2 samples redshifted the UV–visible absorption edge of TiO_2 [14,15,19,22,24–27] and promoted the visible-light photocatalytic activity [14,15,17–19,22,24–27]. Some samples showed blueshift [16,20,23], and therefore the UV-light-induced photocatalytic activities were increased [16], but some samples still showed enhanced visible-light-induced photocatalytic activity [20]. However, both blueshifts [16,20] were found to be due to the decrease of the TiO_2 crystal size (quantum size effect) by B-doping. On the other hand, Yang et al. [23] interpreted the experimentally observed reverse shifts conducted the calculation that the redshift was due to the substitutional B atoms and the blueshift was due to the interstitial B atoms by "band-filling mechanism". Therefore, the local chemical structure of the boron, the electronic nature of the dopant species and the origin of the photocatalytic activity improvement of the B-TiO_2 samples still need to be clarified.

The sol–gel and impregnation techniques represent the most commonly used methods to prepare B-TiO_2. Reactive magnetron sputtering deposition is one of the physical vapor deposition (PVD) methods and it is a powerful technique to prepare oxide films with controlled stoichiometry and structure by modifying the sputtering conditions such as gas pressure, substrate temperature, target materials and powers on the targets. We have used successfully the reactive magnetron sputtering to deposit N-TiO_2 [28] and C-TiO_2 [29–32] in our laboratory, and investigated in details the phase compositions of the TiO_2 samples, the chemical states of the dopant species, and the correlation between the properties and the improvement of the photocatalytic activity under UV or visible light irradiation. In the present study, we exploit the B-TiO_2 films deposited by the reactive magnetron co-sputtering, to shed light on the influence of boron in TiO_2 on the photocatalytic reactions under UV or visible light irradiation.

2. Experimental

2.1. Preparation of B-TiO_2 films

The B-TiO_2 films were prepared by a reactive magnetron sputtering system assembled by AJA International, Inc. (USA). The sputtering system allows independent control of several critical deposition parameters and the details of the system were described elsewhere [33]. The distance between the substrate holder and the targets was 100 mm. The chamber was evacuated with a mechanical pump (ALCATEL 2015SD) and a turbomolecular-pump (ALCATEL TMU261). The base pressure was 4.0×10^{-5} Pa or lower. The films were deposited at the substrate temperature of 100 °C by co-sputtering from two 99.99% titanium (SDIC) metal targets with the constant power on each target of 200 W and one 99.5% TiB_2 target with varying target powers of 30, 60, 90, 120, 150 and 180 W in the Ar/O_2 plasma. The gas flow rates were fixed at 20 sccm for Ar and 8 sccm for O_2 under the total pressure of around 4.0×10^{-1} Pa (3.0×10^{-3} Torr). In this study, the B-TiO_2 films were labeled as B-TiO_2-XXX for the as-deposited films, and B-TiO_2-XXXA for the annealed ones, therein XXX is the TiB_2 target power in watts.

The substrates used in the study were polished Si (100) wafers and glass or fused quartz slides, which were solvent-cleaned before placing inside the vacuum chamber and sputter-etched with argon plasma for 10 min prior to the film deposition to remove any residual pollutants on the surface. The thicknesses of the films were controlled to be around 300 nm.

2.2. Film characterization

The structure and crystallinity of the films were investigated by an X-ray diffractometer (XRD, Rigaku D/MAX-2500) operating with Cu-K_α radiation at 40 kV and 150 mA. The ultraviolet-visible (UV–Vis) absorption spectra of the films were recorded using a JASCO V-650 spectrophotometer. For conducting the optical measurements, the samples deposited on the quartz substrates were used in order to avoid the UV–Vis absorption by the Si substrate in the range from 300 to 800 nm. The surface composition of the samples and the bonding configuration in the films were detected by a K-Alpha™ + X-ray Photoelectron Spectrometer (XPS) using AlKα X-ray (1486.6 eV) at 12 kV and 72 W, with an energy resolution of 0.05 eV. The binding energy was referenced to the C1s line at 284.85 eV that was used for calibration.

The photocatalytic properties were evaluated by measuring the decomposition rate of methylene blue (MB), monitored by the absorption peak at around 664 nm in the UV–vis absorption spectra. The visible light illumination was carried out using a fluorescent lamp (Philips P-LF27W/865) with the wavelength distribution from around 400 to 750 nm and with the maximum intensity at 543 and 611 nm, producing an average power density of 4.2 mW/cm^2 at a distance of 8 cm between the visible-light source and the sample. The UV illumination was carried out using 8 W fluorescent light source (UVItech-LF104L) with the wavelength distribution from around 300 to 400 nm and with the maximum intensity at 370 nm. The distance between the UV light source and the sample was 10 cm, which induces an average power intensity of 3.2 mW/cm^2.

3. Results and discussion

The elemental compositions of the B-TiO_2 films were obtained from the XPS spectra. Fig. 1 shows the effect of the TiB_2 target power on the boron, titanium and oxygen contents in the as-deposited and the annealed B-TiO_2 films. The boron incorporation in the as-deposited B-TiO_2 films increased with increasing the TiB_2 target power, up to 16.3 at.% for B-TiO_2-180, while both the oxygen and titanium contents decreased. After annealing at 600 °C in air for 1 h, the remaining boron contents in the annealed films were 0.04 at.% for B-TiO_2-30A and 4.01 at.% for B-TiO_2-180A.

All the B-TiO_2 films deposited at 100 °C, regardless of the TiB_2 target power, were all amorphous without any observable XRD peaks (not shown). The annealed B-TiO_2 films had anatase TiO_2 structure with various amounts of rutile phase as shown by the XRD patterns in Fig. 2. The B-TiO_2-30A film was almost single phase anatase, while the B-TiO_2-60A film was mixed phase with more rutile than anatase content in it. With increasing the target power from 60 W to 180 W, the rutile content was decreased gradually. In our past study [31,34], the amorphous TiO_2 film deposited by the sputtering system was transformed to the anatase phase at 600 °C in air for 1 h, and for some samples there was some part of the rutile phase in them. When the annealing temperature was raised to 800 °C, the film was transformed to rutile phase almost completely with a little content of the anatase phase. The factors that affect the phase transformation and stability of TiO_2 have been reported to be the intrinsic parameters, such as the impurities and defect contents, grain size, and composition of the original sample, as well as extrinsic ones such as the annealing atmosphere and temperature [34,35]. Thus, the phase composition of the annealed doped titania is a complicated matter and it is hard to be precisely controlled experimentally.