Materials Research Bulletin 78 (2016) 179–185

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Wettability, structural and optical properties investigation of TiO_2 nanotubular arrays

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ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form 27 December 2015
Accepted 16 January 2016
Available online 19 January 2016

Keywords:
A. Ceramics
A. Thin films
B. Vapor deposition
C. X-ray diffraction
C. Electron microscopy

ABSTRACT

In this study, the effect of microstructural evolution of TiO_2 nanotubular arrays on wettability and optical properties was investigated. Pure titanium was deposited on silica glass by PVD magnetron sputtering technique. The Ti coated substrates were anodized in an electrolyte containing NH_4F/glycerol. The structures of the ordered anodic TiO_2 nanotubes (ATNs) as long as 175 nm were studied using field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The result shows a sharp peak in the optical absorbance spectra around the band gap energy, 3.49–3.42 eV for annealed and non-annealed respectively. The thermal process induced growth of the grain size, which influence on the density of particles and the index of refraction. Furthermore, the wettability tests' result displays that the contact angle of intact substrate ($\theta = 74.7^\circ$) was decreased to 31.4° and 17.4° after anodization for amorphous and heat treated (450 °C) ANTs coated substrate, respectively.

1. Introduction

Depletion of fossil fuel energy resources together with environmental contamination has long been a crucial global issue depending on the degree of industrialization. Research on photocatalysts shows the decomposition of organic contaminant using clean solar energy without yielding any harmful by-products [1,2]. In particular, photocatalytic TiO_2 exhibits higher activities in oxidation and reduction processes and stability to chemical reactions in comparison with SiO_2, ZnO, WO_3, CdS while maintaining a relatively low cost [3,4].

Since Patrick Hoyer in 1996 proved the possibility of growing ordered and self-organized titanium dioxide (TiO_2) nanotubes by using an electrochemical deposition method into an alumina template [5] there have been many attempts to improve the performance of these highly organized structures.

Titanium nanotube is considered a very imperative material for its favorable applications in various fields from energy harvesting to photocatalytic and sensors applications. Titanium is always bonded to other elements in nature, and it is broadly distributed and occurs primarily in the minerals anatase, ilmenite, brookite, rutile, titanite, perovskite, and in many iron ores [6]. From all the mentioned minerals, only anatase, brookite and rutile are pure titanium oxide compounds. In fact TiO_2 occurs in these three crystalline polymorphs: anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal), each containing its own similar, but different structural and optical properties [7].

Based on literatures, most of the reported studies have been done on Ti foil that confines the potential applications of ATNs. The opaque metal Ti has limitations for some optical-electric devices such as electrochromic devices or dye-sensitized solar cells in which a transparent metal oxide electrode is needed. The problem is owing to the inappropriate illumination from the cell's backside, where intensity of light loses significantly when it travels through the counter electrode, platinum coating and the redox mediator system [8]. Hence, it is vital to improve methods for construction of highly ordered TiO_2 nanotubes from titanium thin films on any substrate like glass [9] silicon [10] and conducting glass [11–14].

To provide a thin film of titanium many techniques are available such as physical vapor deposition (PVD) magnetron sputtering technique, thermal diffusion (TD), chemical vapor deposition (CVD) and pulsed laser deposition. Among these, PVD magnetron sputtering technique is quite well known method to obtain thin film of metals and other materials.

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http://dx.doi.org/10.1016/j.materresbull.2016.01.035
0025-5408/

TiO_2 nanotubes consider to be one of the best forms of titanium dioxides, because of its tubular structure that improve the functionally of titanium dioxide in many applications, namely water splitting and dye synthesized solar cell. The large surface area provided from the nanotube walls (inside and outside surfaces) in addition to the perfect porosity structure of the hallow nanotube facilitate light harvesting and allow for much larger reaction interface [15].

The thin TiO_2 coated layer would show the self-cleaning effect due to the hydrophilicity which reduces the wetting angle of water under the conditions of ultraviolet irradiation. Water with a low wetting angle can penetrate between the contaminant and substrate, and cleans the surface from rainfall [16,17].

There are different fabrication techniques to form titanium dioxide nanotubes such as template-directed method, hydrothermal, sol–gel, electro-spinning, and electrochemical anodization. The hydrothermal technique uses for a powder form of TiO_2 and required complex equipment and has the disadvantage of discontinuous processing, whereas the precipitation technique allows relatively easy fabrication but resulted in an inhomogeneous composition and agglomerations [18]. Anodic oxidization technique was used in this research work, since it makes the formation of the uniform and highly oriented nanotubes relatively easy.

The aim of this study was to investigate the effect of microstructural changes on wettability and optical properties of TiO_2 nanotubular arrays coated on fused silica glass. To achieve these, first, PVD magnetron sputtering technique was used to deposit pure titanium atop substrate. Second, anodization method was employed to fabricate TiO_2 nanotube arrays on titanium coated silica glass.

2. Materials and methods

2.1. Substrate preparation

Prior to the Ti coating, all substrates were sonicated in acetone for 10 min at 30 °C, washed three times with distilled water and dried at 100 °C for 1 h.

2.2. Deposition of titanium film on fused silica glass

Ti films were deposited by radio frequency (RF) magnetron sputtering on fused glass. A Ti target with purity of 99.9% was used. The deposition parameters are tabulated in Table 1.

The distance between the target and sample was 15 cm. To remove pinhole defects in the Ti film, the specimen was cleaned in an ultrasonic bath of acetone and deionized water for 10 min.

2.3. Preparation of TiO_2 nanotubes on fused silica glass

Anodic oxidation of the sputtered Ti films was performed in 0.5 wt% NH_4F/glycerol by a conventional anode (target sample)-cathode (graphite rod) system at room temperature with 30 V voltages and 6 min. The distance between the working and counter-electrodes was kept at 30 mm and the electrolyte was magnetically stirred during the process. After anodization, specimens were immediately rinsed in deionized water and then dried in air. Chemical etching with the aid of ultrasonic treatment in 0.05 wt% HF solution for 10 S was applied. Since the grown nanotubes are amorphous, annealing at 450 °C was performed in a standard laboratory furnace for 1 h in order to crystallize them and enhance their structural, wettability and optical properties.

Table 1
PVD coating parameters.

Parameters	Specification
Vacuum pressure	2×10^{-5}
Working pressure	3.5×10^{-3}
DC power	200 W
DC bias voltage	75 V
Deposition time	20 min
Temperature	150 °C
Ar flow rate	25 sccm

2.4. Characterization of TiO_2 nanotubular arrays

2.4.1. Microstructural characterization

The phase composition and purity of the samples were examined by powder X-ray diffraction (XRD) analysis using a PANalytical Empyrean X-ray diffractometer (Cu-Kα radiation) over a 2θ range from 20–80°. To clarify the phase structure, the XRD patterns were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS), namely JCPDS#005-0682 for Ti and JCPDS#01-071-1167 for TiO_2 (Anatase). The size and morphology of the anodized samples were characterized using a field emission scanning electron microscope (FESEM; SU8000, Hitachi, Japan) operated at an acceleration voltage of 1–2 kV.

2.4.2. Wettability

The surface hydrophilicity (wettability) of the TiO_2 coated specimens was examined by measuring contact angles using a sessile drop of deionized water deposited on each specimen surface. A video-based optical contact angle measuring system (OCA 15EC) was utilized to inspect the optical wettability. In this experiment, the liquid volume was kept constant (10 μl) for all contact angle assessments of the specimens. The wettability of the specimens was assessed using a drop velocity of 2 μl/sec at a temperature of 26 ± 1 °C.

2.4.3. Optical

Optical properties including absorbance, band gap, transmittance and refractive indexes of TiO_2 nanotubes thin film atop fused silica glass were evaluated by UV–visible spectroscopy PerkinElemer 750. The UV–vis absorption was performed in the range of 200–700 nm by scan rate about 240 nm/min

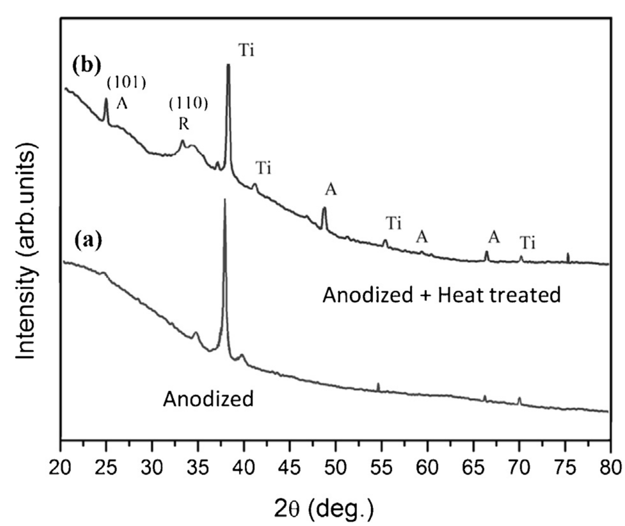

Fig. 1. XRD profile of the sample anodized at 30 V for 6 min in 0.5 wt% NH_4F/glycerol solution (a) before and (b) after annealing at 450 °C.