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High aspect-ratio transparent highly ordered titanium dioxide nanotube arrays and their performance in dye sensitized solar cells

Hong Wang, Hongyi Li *, Jinshu Wang *, Junshu Wu

Key Laboratory of Advanced Functional Materials, College of Materials and Engineering, Beijing University of Technology, Beijing 100124, PR China

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ABSTRACT

High aspect-ratio transparent titanium dioxide (TiO_2) nanotube arrays (TNAs) have been fabricated via anodizing titanium (Ti) thin films deposited by direct current magnetic sputtering at 400 °C. Anodization was conducted in glycol electrolyte containing 0.3 wt.% NH_4F and 2 vol.% deionized (DI) water, and the anodizing voltage was 60 V. High aspect-ratio TNAs with thickness of 12 μm were achieved after the Ti films were anodized for 5 h. The as-formed TNAs were amorphous and had been transferred into anatase after heat treatment at 500 °C for 2 h. The annealed transparent TNAs present an excellent transmittance property. The solar cells constructed by our transparent TNAs show excellent performance in dye sensitized solar cells and yield power conversion efficiency of 4.38% under AM 1.5.

1. Introduction

During the past decade, highly ordered TNAs, formed using anodization, have attracted lots of interest owing to their potential application in many fields [1–6], such as photocatalyst [1], biocompatibility [2], gas sensors [3] and dye sensitized solar cells [4]. Since TNAs are found to show excellent power conversion capability owing to large surface specific areas, vectorial charge transport routine and high dye adsorption capability, they have been largely used in dye sensitized solar cells (DSCs) [7,8]. TNA-based DSCs are classified into front-side illuminated and back-side illuminated according to the direction of incident light [9,10]. Park and co-workers removed 15 μm TNAs from Ti foils to a transparent conductive glass (FTO or ITO) to fabricate transparent photoelectrode based front-side illuminated DSCs, whose efficiency was 2.9%, higher than that of back-side illuminated DSCs [11]. Pang also found that the power conversion efficiency of TNAs/FTO glass-based DSCs was two times higher than that of the TNAs/Ti-substrate-based DSCs [12]. But a problem inherent to this technique is macro-/micro-crack formation in the nanotube films, resulting in some cases in the destruction of the nanotubes, when volatiles escape during heat treatment [13]. For the freestanding TNAs exploited from titanium foils, a thin layer between TNAs and FTO was inevitably formed after it was annealed. The layer limited the power conversion ability in two sides: 1) the layer reduces the light transmittance, 2) the layer retards the transportation of light-induced electron.

Preparation of TNAs directly on glass by anodization of Ti films deposited by radio-frequency (RF) or direct current (DC) magnetic sputtering can overcome these problems. To our knowledge, length of TNAs can rarely extend to microns [14,15] except Grimes and co-workers [13]. They had fabricated 20-μm-thick TNAs via 21−27 h anodizing the Ti films deposited by RF or DC magnetron and pointed out that the ability to fabricate such films has remained, until now, an unsolved technological challenge.

In the present study, we optimized the process as follows: 1) improving the substrate's temperature to 400 °C during sputtering, so as to increase the adhesion between FTO and Ti film; 2) adopting higher anodic voltage during anodization, in order to accelerate the formation of TNAs. Therefore, high-aspect ratio TNAs (~120 nm in diameter, ~24 nm in wall thickness, ~12 μm in length) have been easily formed on the transparent substrate.

2. Experimental

2.1. Preparation of Ti thin films

Ti films were deposited on FTO substrate by DC magnetic sputtering. The base chamber pressure was below 8.0×10^{-4} Pa, and the pressure remained ~1.0 Pa during deposition, which was performed under the conditions of argon with high purity of 99.999% and the target size is φ76 × 5 mm. Prior to all depositions, the substrates were ultrasonically cleaned for 10 min respectively in acetone, ethanol, and (DI) water. Targets were sputtering etched for 60 min in order to oxide and other impurities.

2.2. Preparation of TiO_2 nanotube arrays

The as-deposited Ti film was cut to snippets of 2×1.5 cm^2, then protected by colophony and paraffin. Anodization was conducted at

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* Corresponding authors. Tel./fax: +86 10 67391101.
E-mail addresses: lhy06@bjut.edu.cn (H. Li), wangjsh@bjut.edu.cn (J. Wang).

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60 V, for different times according to the real-time observed current–time curve, in glycol electrolyte, containing 0.3 wt.% NH_4F and 2 vol.% DI water. The anodized samples were immediately washed with DI water, followed by removing colophony and paraffin by completely dipping the samples in acetone for 1 min. After being washed in DI water, the samples were ultrasonically cleaned 30 s in DI water to remove surface debris, and subsequently dried in air. The anodized samples were annealed at 450 °C for 2 h (ramp 2 °C/min) to transfer the amorphous TiO_2 into anatase crystalline.

2.3. Assembly of DSCs

The cells were sealed by Surlyn films (60 μm in thickness), leaving a window with ~50 mm^2 in area. The DSCs were fabricated by soaking the nanotube array films in acetonitrile and ethanol complex solution (with volume ratio of 2:1) containing 0.35 mM N719 dye. The liquid solution of 0.3 M PMII, 0.05 M I_2, 0.5 M LiI, 0.3 M 4-TBP in acetonitrile served as electrolyte, and sputtered platinum layer (~5 nm thick) on FTO served as the counter electrode.

2.4. Characterization

The sample's morphologies were observed by Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S4800). The crystallinity was identified by X-ray diffraction (XRD) using a Bruker D8 advance diffractometer with Cu Kα radiation. The transmittance spectra of the nanotube arrays were recorded by a UV–visible spectrometer (Shimadzu, UV-2550). Solar cell current–voltage measurement was performed on Keithley 2400 power source under irradiation of 1.5 Sun.

3. Results and discussion

3.1. Titanium films on fluorine-doped tin oxide (FTO) glass

Films deposited at room temperature were found to have poor adhesion to the substrate, and peel off during anodization. Improving substrate temperature can make the particles diffused completely during sputtering because the particles' diffusion energy and migration rate increase with the temperature. Furthermore, weak adhesive atoms overflowed by the re-evaporation process and accordingly the deposited film tightly bonded to the substrate. Adhesion was not a problem for films deposited at 400 °C, under this temperature, and the compact crystalline columnar structure was obtained, which was favorable to yield well-defined tubular structure and couldn't be peeled off under high voltage anodizing. Therefore, the anodization can be performed at higher voltage and the growth rate of TiO_2 nanotube was improved. Fig. 1 illustrates top (a) and cross-sectional (b) morphology of 5.2-μm-thick titanium film deposited on FTO glass.

High optical reflectance of the metal film was found to be essential for obtaining distinct ordered nanotubes. Therefore, the metal film was expected to be dense and its surface roughness must be limited to nanometer range. The smooth titanium films with a mirror like finish were obtained, the length of the compacted column (i.e. the thickness of the films) was about 5.2 μm.

3.2. Transparent films of TNAs

TANs were formed by anodizing the titanium/FTO films in a two-electrode electrochemical cell at room temperature. Titanium films served as the anode and the graphite served as the cathode. The voltage remained 60 V during anodization. In the present work, anodization was performed until the titanium films were completely anodized to transparent TiO_2 nanotube array thin films. Real-time observation of the current enabled us to stop the anodization as soon as the film became transparent, at a point between P4 and P5 [11], as shown in Fig. 2c. 12-μm-thick TNAs were obtained after anodizing for 5 h at 60 V. FE-SEM morphologies were given in Fig. 2a and b. It was clear that the adhesion between the nanotube array and the substrate was excellent. The average pore size and wall thickness was 120 nm and 24 nm respectively. After annealing at 450 °C in atmosphere, amorphous titanium oxide was transferred into anatase, which was identified by XRD (Fig. 2d).

3.3. Optical and photovoltaic performance

The transmittance spectra of annealed TNAs film upon FTO and clean FTO was shown in Fig. 3a. The transmittance of FTO glass was about 80%, and the glass with 1-μm-thick nanotube arrays decreased slightly in visible range. For 12-μm-thick nanotube arrays, the transmittance was about 32% in the visible light range, over 26% at the wavelength around 530 nm, which was superior to reported work (about 15% for 10-μm-thick) [13], thus it would be appropriate for DSCs, as the absorption peak of N719 was around 534 nm [16]. Fig. 3b described the current–voltage characteristic of DSCs fabricated using different lengths of TiO_2 nanotubes. The 12-μm-thick nanotube films yielded a power conversion efficiency of 4.38% (with open-circuit voltage (V_{OC}) of 0.637 V, short-circuit current density (j_{SC}) of 12.39 mA/cm^2, and filling factors (FF) of 55.49%), 4 times of the 1 μm samples (1.11%) and 1.5 times of the 7.8 μm samples (3.11%).

4. Conclusions

Transparent highly ordered 12-μm-thick TNAs have been prepared by anodizing titanium thin films 5 h at 60 V in glycol electrolyte

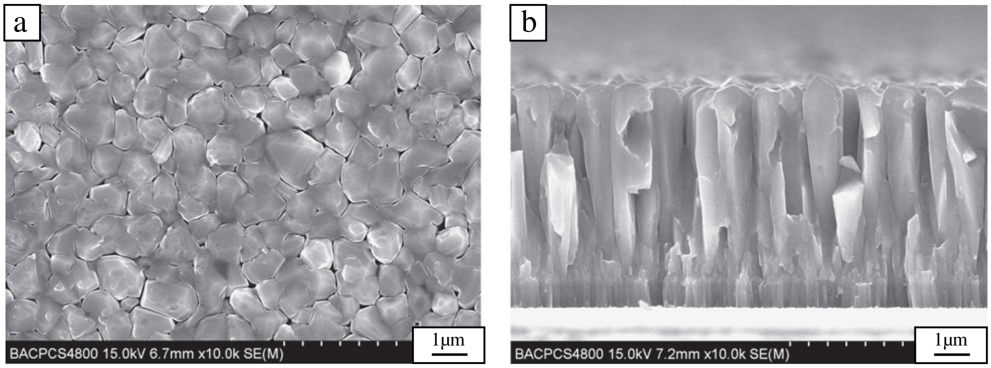

Fig. 1. Morphology of titanium films with crystalline columnar structure deposited on FTO: (a) top and (b) cross-section.