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Transparent conducting oxide glass grown with TiO_2-nanotube array for dye-sensitized solar cell

Chen-Hon Chen *, Keh-Chang Chen, Ju-Liang He

Department of Materials Science and Engineering, Feng Chia University, 100 Wen-Hwa Rd., Taichung 40724, Taiwan, ROC

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ABSTRACT

An arc ion plating (AIP) deposition system was employed to produce metal titanium layer on transparent conducting oxide glass, and followed by anodically oxidizing to form a TiO_2-nanotube array electrode. A dye-sensitized solar cell (DSC) was then assembled as ITO glass/[TiO_2-nanotube (N3 dye)]/I_2 + LiI electrolyte/Pt/ITO glass. Anodizing bath composition was varied, and post-annealing was carried out. Consequent changes in the TiO_2-nanotube array microstructure and photovoltaic efficiency of the assembled DSC device were revealed. Experimental results show that a 5-μm thick metal titanium layer can be obtained after 45 min AIP deposition. The metal titanium layer underwent complete conversion into XRD-amorphous TiO_2-nanotube array after anodic oxidation for 2 h. The tube can reach 10.7 μm long with tube inner diameter 92 nm. The ammonium fluoride in the anodizing bath accelerates the tube growth rate. Thermal annealing at temperatures over 250 °C works best on anatase crystallization of the TiO_2-nanotube. An ultimate photovoltaic efficiency 1.88% (active area 1 cm^2) of the assembled DSC device can be obtained for the TiO_2-nanotube grown ITO glass annealed at 350 °C.

1. Introduction

The rapid shortage of petrochemical energy has led to the great demand in developing clean and renewable energy sources; such as solar cells in these years. Recent development of solar cells in dye-sensitized type devices is one great step forward in the field. The dye-sensitized solar cells (DSCs) take advantages in simple fabrication technique and low production costs. With suitable dye absorption, the photovoltaic efficiency is reported to reach over 10% [1–3]. Mostly considered DSC under development is the titanium dioxide based device, where microstructure of the titanium dioxide electrode is essential to the photovoltaic efficiency of this kind. Large specific surface area provided by the mesoporous TiO_2 electrode is the key to the effective dye absorption [2]. Cost effective manufacturing [1,4] of the mesoporous TiO_2 electrode though, researchers suggested that one dimensional nano-structured TiO_2 such as nano-rod, nano-wire or nanotube is an alternative approach for higher photovoltaic efficiency [5–7] due to straightforward diffusion path of the free electron once being generated.

TiO_2-nanotube fabrication techniques so far being proposed include template replica process [7], sol–gel method [8], hydrothermal method [9] and anodic oxidation method [10–14]. Among which anodic oxidation is one promising route to prepare long and highly ordered TiO_2-nanotube array. This has been recently demonstrated by Shankar et al. who fabricated TiO_2-nanotube array on titanium foil with tube length up to 220 μm [14]. This technique may potentially be applied as a back-side illuminated DSC which should be predestined to sacrifice certain amount of incident light when traveling through electrolyte. On the other hand, direct growth of TiO_2-nanotube array on transparent conducting oxide (TCO) glass substrate for purpose of constructing front-side illuminated DSC is proposed by anodizing a pre-sputter deposited layer on TCO [12]. Lower deposition rate of the metal titanium pre-layer and poor film adhesion has limited TiO_2-nanotube length within 1 μm and unsatisfactory for practical application.

This study demonstrates the pre-deposition of metal titanium layer on indium tin oxide (ITO) glass by using arc ion plating (AIP) followed by anodic oxidation to produce TiO_2-nanotube array. Post-annealing of TiO_2-nanotube array prepared ITO glass samples were carried out and assembled as ITO glass/[TiO_2-nanotube (N3 dye)]/I_2 + LiI electrolyte/Pt/ITO glass to reveal the effectiveness of such a photovoltaic device. The advantage of AIP includes low deposition temperature, high deposition rate and strong film adhesion [13] and thus long and strongly adhered TiO_2-nanotube array is expected to be developed with high photovoltaic efficiency.

2. Experiments

ITO glass substrate with sheet resistance 20 Ω was cut into a dimension of 20 mm × 40 mm. AIP deposition was carried out in

* Corresponding author. Fax: +886 4 24519053.
E-mail address: jlhe@fcu.edu.tw (C.-H. Chen).

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Table 1
Metal titanium layer deposition parameter used in this study.

Deposition parameter	Value
Target material	Ti
Working pressure (Pa)	0.5
Arc current (A)	90
Flow gas	Argon
Deposition time (min)	45

Table 2
Three anodic oxidation electrolytes used in this study.

Electrolyte	Composition
A	1 L EG + 1.5 g NH_4F + 20 g H_2O
B	1 L EG + 2 g NH_4F + 20 g H_2O
C	1 L EG + 3 g NH_4F + 20 g H_2O

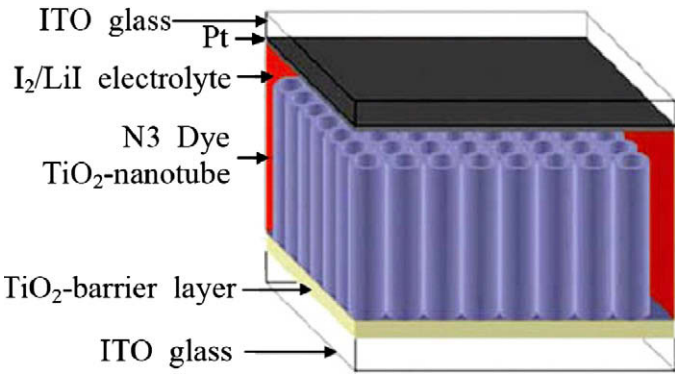

Fig. 1. Schematic diagram of the front-side illuminated DSC assembled in this study.

a common type system. Deposition parameters are listed in Table 1. The anodic oxidation bath contains ethylene glycol (EG), ammonium fluoride and H_2O as seen in Table 2. For TiO_2-nanotube growth, the titanium pre-deposited ITO glass was immersed in the bath and anodically applied with a voltage of 60 V for 2 h. After that, the samples were rinsed in deionized water and dried. Some of them were post-annealed at 150 °C, 250 °C, 350 °C and 450 °C for 2 h for comparison.

Surface and cross sectional morphology of the TiO_2-nanotube array was observed by using a field emission scanning electron microscope and crystal structure was characterized by an X-ray diffractometer. The surface area can be obtained by the calculation of the geometric roughness factor [14]. The TiO_2-nanotube array prepared ITO glass sample was assembled as a DSC device with its configuration schematically shown in Fig. 1. The device preparation procedures involve sample immersion in 3×10^{-4} M N3 dye (Ruthenium 535) for 24 h, then sandwiched with I_2(0.05 M) + LiI(0.5 M) + propylene carbonate electrolyte by another Pt coated ITO glass. The Pt coated ITO glass acts as the counter electrode where Pt coating can activate redox reaction of the iodine ion. Under the illumination from a xenon lamp (6 mW/cm^2), the photocurrent and photovoltage of the cells were measured with an active area of 1 cm^2 by using an EG&G 263A potentiostat. Open circuit voltage (V_{oc}) and short circuit current (J_{sc}) can be determined from the measured I–V curve.

3. Results and discussion

The AIP coating technique can be used to successfully deposit metal titanium layer on ITO glass and the anodic oxidization procedure can be used to successfully convert metal titanium layer into TiO_2-nanotube array. Fig. 2 shows cross sectional and surface images of the as-deposited metal titanium layer and the as-anodic oxidized TiO_2-nanotube array. With the AIP, it would be able to

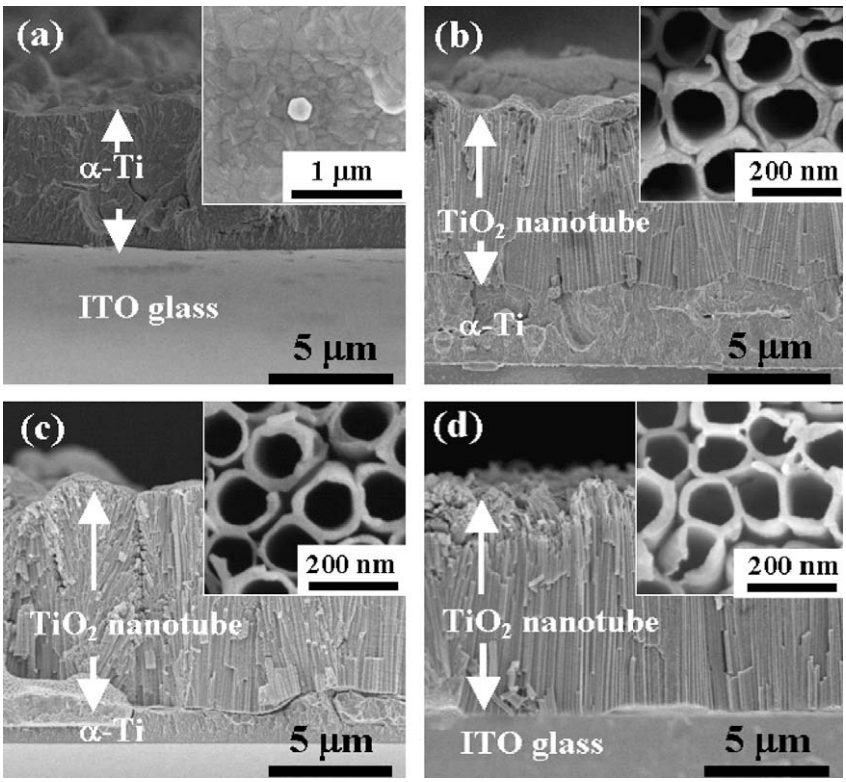

Fig. 2. Cross-sectional image of (a) AIP deposited titanium layer and TiO_2-nanotube as-anodic oxidizing in (b) electrolyte A, (c) electrolyte B and (d) electrolyte C. The inserted image presented with a top view image.