Optical Materials 36 (2014) 1430–1435

Contents lists available at ScienceDirect

Optical Materials

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

Preparation of double layer porous films of Titanium/Titanium oxide for photoelectrochemical cells application

Min-Gi Choi, Youl-Moon Sung *

Electrical Engineering, Kyungsung University, Busan 608-736, Republic of Korea

ARTICLE INFO

Article history:
Available online 1 February 2014

Keywords:
Double layer films
RF magnetron sputtering
Transparent conductive oxides
Nanoporous films

ABSTRACT

Double layer nanoporous films of Titanium (Ti)/Titanium oxide (TiO_2) were fabricated by a combined radio frequency sputtering and sol–gel combustion method and investigated with respect to its photo-anode properties of transparent conductive oxide-less dye-sensitized solar cells (TCO-less DSCs). The porous Ti layer can collect electrons from the TiO_2 layer and allows the ionic diffusion of iodide ion/triiodide ion (I^-/I_3^-) through the hole. The porous Ti layer with low sheet resistance (~2.7 Ω/sq.) can be prepared by substrate temperature 300 °C under RF power 300 W and Ar gas pressure 5 mTorr. The Ti/TiO_2 double layers prepared by combined RFS/SGC method show the good impedance characteristics. The efficiency (η) of prepared TCO-less DSCs sample is 5.73% [fill factor (*ff*): 0.76, open circuit voltage (V_{oc}): 0.71 V, short-circuit current density (J_{sc}): 10.61 mA/cm^2].

1. Introduction

The efficiency of dye-sensitized solar cells (DSCs) has been reported to show more than 10% photo-energy conversion efficiency, which is explained by efficient light-harvesting properties, charge-transfer properties, and electron-harvesting properties associated with nanoporous TiO_2 electrode [1–3]. The general DSCs system uses transparent conductive oxide (TCO) glass/TiO_2 porous layer attached with dye molecules/electrolyte/Pt sputtered TCO glass configuration. TCO layer is a necessary part in DSCs construction because of its low resistivity, high transparent ability [4]. As a TCO layer of DSCs, Fluorine-doped SnO_2 (FTO) has been mainly used due to the relatively high transparency and thermal stability at 500 °C [5–7]. However, the use of FTO coated glass for the two DSCs electrodes limits the cost-effectiveness of DSCs. Recently, the research efforts have been attempted for replacing the TCO glass, and thus the different types of Ti metal were applied for the photo-anode of DSCs [8,9].

In this work, Ti-metal film electrode was deposited by RF magnetron sputtering directly onto the nanoporous TiO_2 layer prepared by sol–gel hybrid combustion. As-deposited Ti film onto the underlying nanoporous TiO_2 layer also becomes nanoporous by directional deposition characteristic of plasma sputtering with poor step coverage. The porosity in Ti electrode is necessary since they allow the diffusion of iodide ion/triiodide ion (I^-/I_3^-) electrolyte to dye molecules enabling electron transfer. The photovoltaic performance of fabricated DSCs was investigated by analyzing the photo-conversion efficiency and electrochemical impedance measurements.

2. Experimental

Processing procedures of TCO-less DSCs photo-anode is schematically illustrated in Fig. 1. The photoanode of TCO-less DSCs sample is prepared in the following processes. A TiO_2 paste layer with a thickness of about 10 μm was deposited on the glass by doctor blade method [10], followed by a heat treatment at 450 °C for 30 min. Ti thin film in 2–2.5 μm thickness was then deposited on to the as-coated layer of TiO_2 nanoparticles by RF magnetron sputtering. The film deposition using RF magnetron sputter system can be briefly described as follows [11]. After pumping down to 1×10^{-6} Torr, the argon gas (purity: 99.99%) was introduced into the chamber through the mass flow controller. The target-substrate distance was kept at 70 mm and the sputtering power was 300 W. The operating pressure varied from 2 to 10 mTorr. The substrate temperatures were varied from room temperature (R.T.) to 500 °C. The sputtering time was 1 h.

In particular, the substrate was tilted by 30 degrees from the horizontal surface during deposition, which is to increase the step coverage of Ti film deposition at the one vertical side wall of the TiO_2 layer as shown in Fig. 2. This facilitates the secure connections between the working anode of Ti film and counter electrode. As-deposited and annealed layer of porous Ti/TiO_2 double layers was stained with N719 [Ru(II)L2(NCS)2:2TBA, where L = 2,2′-bipyridyl-4,4′-dicarboxylic acid] dye by immersing the films in an ethanolic solution of N719 dye (0.5 mM) for 24 h. The electrolyte is composed of 0.1 M I_2, 0.1 M Li I, 0.6 M

* Corresponding author. Tel.: +82 51 663 4777.
E-mail address: ymsung@ks.ac.kr (Y.-M. Sung).

0925-3467/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.optmat.2013.12.046

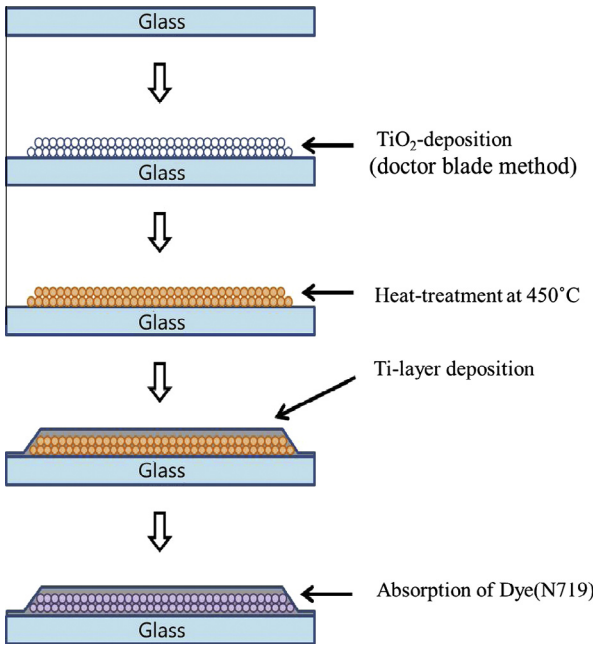

Fig. 1. Fabrication process of TCO-less DSC photo-anode.

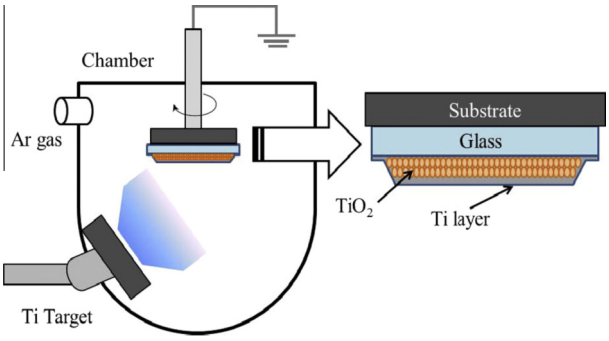

Fig. 2. Schematic diagram of RFS equipment.

1-hexyl-3-methylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in 3-methoxypropionitrile. Also a Ti sputtered FTO glass was used as a counter electrode. The microstructures of Ti films were characterized by field emission scanning electron microscope (FE-SEM). The conductivity of prepared Ti films was measured using four point probe method. Impedance distribution and conversion efficiency of the fabricated TCO-less DSCs sample were measured by electrochemical impedance analyzer (EIA; IM6, ZAHNER) and Solar-simulator (XES-301S+EL-100; SAN-EI ELECTRIC), respectively.

3. Results and discussion

3.1. Nanoporous Ti film

Firstly, TiO_2 paste prepared by sol–gel combustion method was coated with a thickness of 10 μm on a glass by doctor blade method, followed by a heat treatment at 450 °C for 30 min. The example of FE-SEM micrograph of nanoporous TiO_2 layer prepared by SGC method is displayed in Fig. 3. The TiO_2 layer has a "worm-hole" or "small-grain" structure with numerous small pores, this kind of texture was often reported for porous metal oxides. As shown

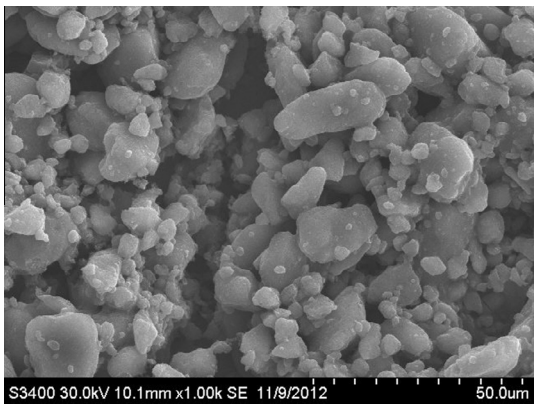

Fig. 3. FE-SEM micrograph of nanoporous TiO_2 layer prepared by SGC method.

in Fig. 3, the fabricated porous TiO_2 layer consists of uniform size cuboid particles of 10–30 nm size.

Fig. 4 shows the XRD patterns of the Ti films deposited by RFS at different substrate temperatures from R.T. to 500 °C under RF power of 300 W and Ar gas pressure of 5 mTorr. The crystalline peaks became pronounced at 300 °C. The intensities of the peaks at 37.5° (110) and 39.5 (110) increases along with a reduction in the peak half width at the substrate temperature of 300 °C. In addition, as is explained later, the lowest resistivity value was measured in the sample of 300 °C. Consequently, the Ti films of 300 °C were used for TCO-less cell application.

Fig. 5 shows the XRD patterns of the Ti films deposited by RFS at different Ar gas pressure from 2 to 10 mTorr under RF power of 300 W and substrate temperature of 300 °C. The XRD intensity change due to the increase in gas pressure causes the increase of (101) peak while the (002) peak decreased at a higher gas pressure. The higher gas pressure over 5 mTorr can facilitate the enhanced mobility of ad-atoms in the film surface and favored the formation of (101) peak of grains. The (002) peak appeared at 2 mTorr has transformed into (101) peak at 10 mTorr. It can be seen from Figs. 4 and 5 that the adhesion and surface energy between Ti particles and TiO_2 underlayer affecting the columnar structure of Ti film are dependent on the deposition parameters such as substrate temperature and gas pressure.

Effects of substrate temperature during deposition on the electrical properties of the electrode and DSCs efficiency were studied. It is obvious that the substrate heating during deposition may affect the Ti film microstructure resulting in the significant variation in electrical conductivity and pore morphology. Although the direct effects of deposition temperature on the film microstructures were not studied, they were indirectly compared by measuring the sheet resistance of the Ti films deposited at from R.T. to 500 °C. Fig. 6 shows sheet resistance versus substrate temperature of the Ti films deposited by RFS. The lowest sheet resistance of 2.7 Ω/sq. was prepared at the substrate temperature of 300 °C. The sheet resistance of the film decreases as the substrate temperature increases from R.T. to 300 °C, however it increases as the substrate temperature increases from 300 °C up to 500 °C. It is obvious that, as the substrate temperature increases, the defects density is reduced with increasing grain size resulting in low sheet resistance [12]. However, at higher substrate temperature, the diffusivity of ad atoms increases during deposition at very slow rate (the deposition rate was ~40 nm/min), which can result in decreasing film thickness and increasing step coverage of the Ti film on the nanoporous TiO_2 underlayer.

Fig. 7 shows sheet resistance versus Ar gas pressure of the Ti films deposited by RFS. The gas pressure is one of important parameters in controlling film thickness, whose variation certainly