Materials Science in Semiconductor Processing 24 (2014) 1–8

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Effect of seed layer on the growth of rutile TiO_2 nanorod arrays and their performance in dye-sensitized solar cells

M.Y. Liao, L. Fang *, C.L. Xu *, F. Wu, Q.L. Huang, M. Saleem

State Key Laboratory of Power Transmission Equipment & System Security and New Technology, College of Physics, Chongqing University, Chongqing 400044, PR China

ARTICLE INFO

Available online 20 March 2014

Keywords:
TiO_2
Nanorod arrays
Seed layers
Dye-sensitized solar cells

ABSTRACT

In order to improve the performance of TiO_2 photoanode-based dye sensitized solar cells (DSSCs), rutile TiO_2 nanorod arrays (NRAs) were grown on SnO_2:F (FTO) conductive glass coated with TiO_2 seed layer by a hydrothermal method. The TiO_2 seed layer was obtained by spin-coating titanium tetraisopropoxide (TTIP) isopropanol solution with concentration in the range of 0∼0.075 M. Then the effect of the thin TiO_2 seed layer on the crystal structure and surface morphology of TiO_2 NRAs and the photoelectric conversion properties of the corresponding DSSCs were investigated. It is found that TiO_2 NRAs are vertically oriented, about 1.7 μm long and the average diameter is about 35 nm for the samples derived from TTIP in the range of 0.005∼0.05 M, which are more uniform and better separated from each other than those without TiO_2 seed layer (average diameter 35∼85 nm). The photoelectric conversion efficiency of DSSCs based on TiO_2 NRAs with TiO_2 seed layer is larger than that without TiO_2 seed layer. Typically, the energy efficiency of DSSCs obtained from the seed solution of 0.025 M TTIP is 1.47%, about 1.8 times greater than that without TiO_2 seed layer. The performance improvement is attributed to the thinner, denser and better oriented NRAs grown on seeded-FTO substrate absorbing more dye and suppressing charge recombination at the FTO substrate/electrolyte interface.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been receiving considerable attention recently because they are cost-effective and environmentally friendly, ever since they were reported at the end of the past century [1]. The photoanode of DSSCs is mainly a mesoporous TiO_2 nanoparticles film on which a monolayer of sensitizing dyes is coated. The nanoparticle-based photoanode has numerous interparticle boundaries which easily trap the charge carriers and cause the decrease of carrier mobility and the carrier lifetime. In this regard, single crystalline semiconductor nanowire/nanorod arrays are very promising photoanode materials, since electron transport could be over two orders of magnitude faster in a nanowire array than in nanoparticle films [2–5]. Huang et al. reported that a rutile nanowire array was superior to an anatase nanoparticulate film of the same thickness for the generation of a short-circuit current and the energy conversion efficiency [6].

Up to now, a number of methods have been used to fabricate TiO_2 nanoarrays, such as chemical vapor deposition (CVD) [7], physical vapor deposition (PVD) [8,9], vapor–liquid–solid growth (VLS) [10], templated sol–gel method [11], and, mostly, hydrothermal reaction with an assistance of surfactant and copolymer [12–14]. Among these methods, hydrothermal/solvothermal synthesis of TiO_2 NRAs is a promising approach due to its simple

* Corresponding authors. Tel.: +86 23 65678369.
E-mail addresses: lfang@cqu.edu.cn (L. Fang), lingling19880210@126.com (C.L. Xu).

http://dx.doi.org/10.1016/j.mssp.2014.02.037
1369-8001

process, fast reaction velocity and low cost. In hydrothermal/solvothermal crystal growth, nucleation sites have a huge impact on the morphology and orientation of the TiO_2 NRAs, so it is of great importance to investigate the relationship between them. In recent two years, some groups have studied the effect of seed layer on the growth of TiO_2 NRAs and their performance in the dye-sensitized solar cells. Wang et al. reported that TiO_2 NRAs were grown on different substrates coated with a thin TiO_2 layer before hydrothermal synthesis. The DSSCs based on TiO_2 NRAs showed a power conversion efficiency ~1.10% [15]. Wei et al. presented various modifications of FTO glass substrate by coating titania particles (crystal seed). The corresponding DSSCs assembled with the as-prepared TiO_2 nanowire arrays as photoanode achieved an overall photoelectric conversion efficiency of 1.81% [16]. Very recently, Sun et al. employed the titanate nanosheet film as a seed layer for the hydrothermal growth of a single-crystalline rutile TiO_2 nanowire array on FTO conductive glass, and their DSSC got an overall solar energy conversion efficiency of over 3% [17].

By now, some groups [18,19] have reported that a compact TiO_2 blocking layer between FTO substrate and TiO_2 nanoparticles film can suppress the dark current and increase open circuit voltage. In addition, for hydrothermal crystal growing, nucleation sites have a great impact on the morphology of the nanorod arrays. Therefore, we observe the effect of TiO_2 seed layer with different concentrations on the morphology of TiO_2 NRAs and photoelectric properties of the corresponding DSSCs.

2. Experimental section

2.1. Materials and reagents

Titanium tetraisopropoxide (TTIP) was purchased from Alfa Aesar, and concentrated hydrochloric acid (HCl) was obtained from Sinopharm Chemical Co. Ltd., China. All of the solvents and chemicals in this study were of reagent grade. Conducting glass (fluorine-doped SnO_2, resistance 15 Ω/square, transmittance 90%) was received from Nippon Sheet Glass Co., Japan. Ethanol, Isopropyl alcohol and acetone were from Chongqing Chemical Reagent Co. Deionized water was used to prepare all the solutions. The redox electrolyte used in the DSSCs consisted of 0.1 M LiI, 0.05 M I_2, 0.6 M 1, 2-dimethyl-3-n-propylimidazolium iodide, and 0.1 M 4-tert-butylpyridine in acetonitrile. The sensitizer used here was cis-bis(isothiocyanato)bis(2,2'-bipyrridyl-4-4'-dicarboxylato)-ruthenium(II)-bis-tetrabutylammonium dye (N-719 as received from Solaronix).

2.2. Preparation of TiO_2 nanorod arrays

The seed layers were prepared by following the basic process described by Wang et al. [15]. Before hydrothermal synthesis, the substrates were spin-coated with TiO_2 seed layer using the solutions prepared by dissolving TTIP in isopropanol with different concentrations: 0.005 M, 0.025 M, 0.05 M and 0.075 M. Four pieces of FTO substrate were cleaned with ethyl alcohol and acetone for 30 min, respectively. One or two drops of the Ti^{4+} precursor with different concentrations were spread uniformly over the four pieces of FTO substrate surface and then quickly rinsed in absolute ethanol and dried in air; this process was repeated twice. Finally, the coated substrates were annealed in a box furnace at 500 °C for 2 h.

In a typical synthesis, the growth solutions were prepared by mixing TTIP, HCl (36–38%) and deionized water, with a volume ratio of 0.3:10:10. The above four pieces of seeded-FTO substrate and a bare FTO substrate for comparison were, respectively, placed against the wall of 25 mL Teflon-lined autoclave filled with 16 mL of the growth solution, and were heated at 160 °C for 8 h for the growth of TiO_2 NRAs. After the hydrothermal experiment, the as-prepared samples were rinsed with deionized water, and then dried in air.

2.3. Fabrication of DSSCs

For the fabrication of dye-sensitized solar cells, the TiO_2 NRAs photoanodes were limited to 0.25 cm^2 by removing extra NRAs with a blade, and immersed in a dry 1:1 acetonitrile/tert-butyl alcohol solution (0.5 mM) of N719 (Solaronix SA) at room temperature for 12 h to complete the dye adsorption. The DSSCs were fabricated by assembling the dye sensitized array film as the working electrode and Pt-coated FTO as the counter electrode, separated with a hot-melt surlyn film (25 μm), and sealed under heat. The redox electrolyte was introduced into the space between the working electrode and counter electrode through capillary. The two holes were then sealed using a surlyn film covered with a thin glass slide under heat.

2.4. Characterization

The crystal structure of the TiO_2 NRAs films was investigated by X-ray diffraction (XRD) with an MRD-Single Scan diffract-meter using the Cu Kα line ($\lambda = 1.5406$ °). The power of XRD was 1200 W and the scan was performed from 20° to 80° at a speed of 4°/min, with a step size of 0.02°. X-ray tube voltage and current were set at 36 kV and 20 mA, respectively. The surface morphologies of the as-prepared samples were examined with field emission scanning electron microscope (FE-SEM, Nova400). Transmission electron microscope (TEM; JEOL 2010F, Japan) images and selected-area electron diffraction patterns confirm that the TiO_2 are nanorods, as shown in Fig. 2. UV–vis absorption spectra were collected on a Perkin Elmer UV WinLab spectrophotometer. The photovoltaic performance of DSSC was tested by recording the *J–V* curves with a Keithley 2400 Source Meter under 100 mW/cm^2 AM 1.5 G simulated sunlight coming from a solar simulator (Oriel-91193) equipped with a 1000 W Xe lamp and an AM 1.5 filter. The light intensity was calibrated by using an Si solar cell (Oriel-91150). The active area of the solar cells was 0.25 cm^2.

3. Results and discussion

3.1. Morphological and structural characterization

Fig. 1 reveals the FE-SEM images of TiO_2 NRAs fabricated on bare FTO and seeded FTO substrates. These NRAs