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Effect of titanium dioxide blocking layer deposited by cathodic arc plasma on the energy conversion efficiency of dye-sensitized solar cells

S. Sansongsiri [a,*], T. Kaewmanee [a], D. Boonyawan [a], L.D. Yu [b], S. Thongtem [a,c]

[a] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[b] Thailand Center of Excellence in Physics, Chiang Mai University, Chiang Mai 50200, Thailand
[c] Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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ABSTRACT

TiO_2 blocking layers were deposited on commercial fluorine-doped tin oxide (FTO) glasses by cathodic vacuum arc technique for using as working electrodes of dye-sensitized solar cells (DSSCs). These blocking layers were produced between FTO and mesoporous TiO_2 layers to prevent electron-hole recombination. Photovoltaic performance of the DSSCs with and without TiO_2 blocking layer by different pulses was investigated. In this research, the film thicknesses with 500–2500 deposition pulses were 47–212 nm. The transmittance was in the range of 60–90% over the visible range with the absorption edge of 356 nm wavelength. The optical energy gaps were determined to be in the range of 3.23–3.34 eV. The deposition of TiO_2 blocking layer by 1000–2500 pulses was improved the photovoltaic performance. For the 2500 deposition pulses, the DSSC showed the highest energy conversion efficiency of 2.33% or 395% of that without blocking layer.
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1. Introduction

Dye-sensitized solar cells (DSSCs) are attractively studied due to their low production cost and simple fabrication [1–4]. A DSSC contains a dye-absorbed nanoporous TiO_2 layer on fluorine-doped tin oxide (FTO) coated glass as a working electrode. The other electrode is platinum (Pt) catalytic thin film coated on FTO glass as a counter electrode. Under the illumination with sun light, dye molecules were exited and photoexcited electrons were produced. The exited electrons were released to the conduction band of nanoporous TiO_2 layer and diffused to the external circuit. The dye generated electrons from redox reaction of the electrolyte, such as the iodide/triiodide couple. The iodide is generated by the reduction of triiodide at the platinum layer of the counter electrode [5–7]. The mesoporous TiO_2 layer of DSSC devices often contains small holes that allow direct contact between the electrolyte and the FTO conducting electrode, resulting in the charge leakage. In order to prevent the carriage leakage, a blocking layer is produced between the conducting electrode and the nanoporous TiO_2 layer [8–12]. The TiO_2 blocking layers with different cathodic arc deposition pulses were introduced between FTO substrates and mesoporous TiO_2 layers in order to enhance the performance of DSSCs. Different types of materials such as reduced graphene oxide and metal (Au, Ag) doped titania have been used as blocking layers by different techniques [13–20]. The modification layer can be directly coated on the conductive substrate by spray pyrolysis [21], chemical vapor deposition (CVD) [22], sputtering [23], sol-gel [24,25] and atomic layer deposition [26].

The cathodic vacuum arc is able to be used for metal component thin film deposition [27–31]. Metal ions are produced by arcing the metallic source cathode. Metal plasma directly diffuses and deposits on a substrate by applying a negative bias voltage. The film thickness and properties are controlled by the number of deposition pulse and bias voltage.

In this work, the TiO_2 thin film was produced and used as a blocking layer in DSSC devices. The TiO_2 thin film was deposited on an FTO glass by cathodic arc plasma deposition with varied deposition pulses. The film properties such as structure, surface morphology, optical transmission and optical band gap (E_g) were investigated by Raman spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and absorption spectroscopy. Over the deposited TiO_2 thin film, mesoporous TiO_2 layer was screened by a blade coating technique and assembled to the DSSC device for solar cell efficiency testing. The improvement of DSSC performance in terms of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and solar energy conversion efficiency (η) are reported.

2. Experimental details

The TiO_2 thin films were horizontally deposited on commercial FTO (sheet resistance of 7 Ω/cm^2) substrates by cathodic vacuum arc technique (Fig 1) operated in pulse mode with 1 ms pulse width at a

* Corresponding author.
E-mail address: sakonsa@gmail.com (S. Sansongsiri).

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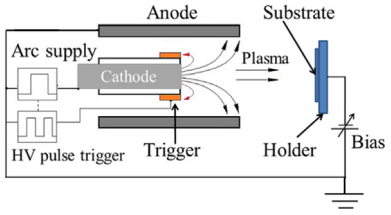

Fig 1. Schematic diagram of a cathodic vacuum arc horizontal system.

repetition rate of 1 pps and the arc current of 195 A. The cathodes used in this experiment were 99.9% pure Ti rod with 5.8 mm diameter. The FTO coated glass substrates of 2×1 cm^2 were ultrasonically cleaned with dishwashing liquid, wiped to dry and attached to the substrate holder. The attached substrate was drawn a line on the surface with a market pen that was removed when the film deposition was traced without film covering for film thickness surface profile measurement. The substrate was placed in a vacuum chamber at 10 cm away from the front of plasma source.

The chamber was evacuated to 2.3×10^{-3} mbar (limited by the rotary vacuum pump) and the oxygen gas (99.9% purity) was introduced into the chamber through a needle valve to attain a controlled working pressure of 5.0×10^{-3} mbar. There were four deposition pulses: 500, 1000, 2000 and 2500 pulses on all substrates biased with −50 DCV. The type of TiO_2 film was analyzed by Raman spectroscopy (HORIBA JOBIN YVON T6400 triple monochromator) of 532 nm solid state laser 100. The film thickness and roughness were measured by surface profile of AFM analysis (NanoScope IIIa, MMAFML N, Veeco) using a contact mode. The film morphology was investigated by SEM (JEOL JSM-6335F) and the optical transmission by UV-VIS spectroscopy (Lambda 25 Perkin Elmer). The transmission wavelength was taken between 300 and 800 nm used to determine an optical energy gap (E_g).

The mesoporous TiO_2 layer was coated using titanium (IV) oxide (anatase nanopowder, <25 nm particle size, 99.7% trace metal basis). The TiO_2 nanopowder paste was prepared by mixing with nitric acid, DI water and Triton™ X-100 surfactant to reduce surface tension. The TiO_2 porous film was prepared by a blade coating technique using the TiO_2 paste. The film was pre-dried at room temperature before annealing at 450 °C in ambient air for 30 min. The porous TiO_2 film as a DSSC working electrode was immersed in the dye (N719, Ruthenizer 353-bis TBM, solaronix) solution at room temperature for 21 h. To prepare the counter electrode, the platinum (Pt) catalyst (Platisol T, Solaronix) was coated on the FTO-coated glass by the blade coating technique and anneal at 450 °C for 30 min. The dye-covered TiO_2 electrode and Pt-counter electrode were assembled as a sandwich type cell and sealed with a suitable gasket. An Iodolyte HI-30 (Solaronix) electrolyte was dropped between the counter and working electrodes and pinched together for solar cell performance testing.

Photocurrent-voltage characteristics were measured by a computer-controlled system under a simulated solar radiation of 100 mW/cm^2. The performance parameters such as short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and photoelectronic conversion efficiency (η) were determined.

3. Results and discussion

The Raman shifts of TiO_2 thin films are presented in Fig 2. The dominant Raman peaks at 145, 200, 400, 520 and 640 cm^{-1} were detected and the TiO_2 films were specified as the anatase phase [32]. All the films show the peaks at the same wavenumber, and the intensity was reduced by the decreasing deposition pulse or film thickness. Possibly, amorphous phase was produced at low deposition pulse. The different vibrational modes were introduced by the disordering atoms. The higher degree of disordered atoms was produced, the lower vibration intensity was detected.

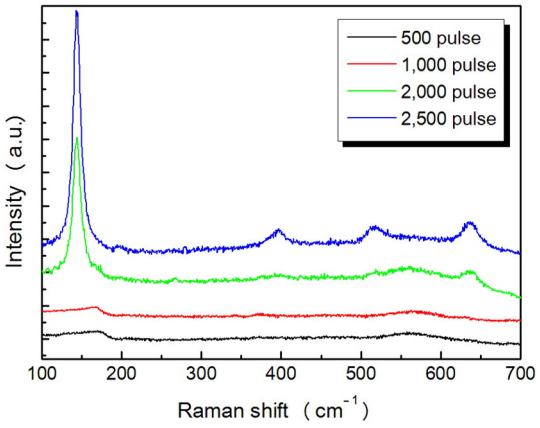

Fig 2. Raman shifts of TiO_2 layers produced by different cathodic arc deposition pulses at room temperature.

The surface morphology of thin films produced by different deposition pulses of 500, 1000, 2000 and 2500 pulses (Fig 3) was evaluated by AFM. All the film surfaces were rather rough with a number of irregular humps on top. The roughness was increased with the increase in the deposition pulses. The higher the deposition pulse rate was used, the more the roughness was obtained.

The thickness of thin films measured using surface step profile and the film roughness are shown in Fig 4. In this research, the film thickness was increased with the number of deposition pulses from 500 to 2500 pulses. At 500–2500 deposition pulses, the films were 47–212 nm thick. But for the film roughness, it was increased to the highest value of 8.2 nm at 2000 deposition pulses and decreased to 7.2 nm at 2500 pulses. These findings can be explained as follows. During the deposition process, Ti evaporated, was oxidized to TiO_2, diffused to the substrate, and randomly accumulated on top. The surface of the deposited film appeared as humps randomly distributed across the substrate. Upon increasing the number of pulses from 500 to 2000 pulses, the number of humps as well as the hump height was increased to the highest value (highest roughness of 8.2 nm). At this stage, a large difference in the hump height and the cavity depth (expressed as Y) was at the highest. When the deposition was 2500 pulses, TiO_2 was randomly deposited on the film with lowering in the film roughness to 7.2 nm because most of TiO_2 was deposited on the cavities to lower the Y value and to create new humps.

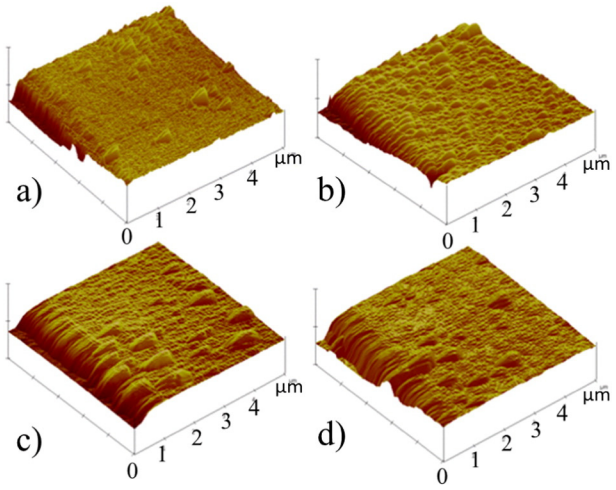

Fig 3. AFM images of TiO_2 thin films deposited by cathodic arc deposition pulses of (a–d) 500, 1000, 2000 and 2500 pulses, respectively.

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