

Fabrication of Porous Titanium Dioxide Thin Films by Electrostatic Spray Deposition and Their Application to Dye-sensitized Solar Cells

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The deposition of titanium dioxide thin films on a conductive glass (F-doped SnO₂-coated glass) substrate was studied using the Electrostatic Spray Deposition (ESD) technique. The precursor solution was prepared by dissolving the correct amount of titanium tetraisopropoxide into a mixture of ethanol and butyl carbitol. The effect of the process parameters, such as deposition temperature, composition of solvent and nozzle-to-substrate distance, on the surface morphology and microstructure of the films was examined with scanning electron microscopy (SEM). The titanium dioxide thin films with porous microstructure could be fabricated for various these parameters. The surface microstructure was strongly affected by both deposition temperature and composition of solvent. The as-prepared thin films were amorphous at the used deposition temperatures (200-270°C). Subsequently, the samples were annealed at 450°C for 2 h in air and studied using X-ray diffraction (XRD). As the result, the crystal structure of the samples transformed into the desired anatase phase. The dye-sensitized solar cells were fabricated with the as-prepared thin films, and then photovoltaic measurements of the cells were carried out. The effect of surface microstructure of as-prepared TiO₂ films on the conversion efficiency of the cells was also discussed.

Key words: Electrostatic spray deposition, Titanium dioxide, Porous thin films, Dye-sensitized solar cells

1. INTRODUCTION

Porous TiO₂ thin films are currently of intense interest as the electron conducting component in dye sensitized solar cells, as well as for applications in photocatalysis, electrochromics and biosensors. So far, a variety of physical and chemical approaches for thin film fabrication, such as magnetron sputtering[1], electron-beam evaporation[2], chemical vapor deposition[3], and spray pyrolysis[4], have been used to prepare TiO₂ thin films. In general, the physical approaches usually lead to highly dense and smooth films containing few structural flaws at very slow growth rates, whereas the chemical approaches may produce both relatively dense and porous films with proper manipulation of deposition or coating conditions. In the past few years, a novel fabrication technique for porous thin films of metal oxides, i.e. Electrostatic Spray Deposition (ESD) techniques, has been developed in the inorganic chemistry laboratory, TU Delft[5-7]. This technique has many advantages over several conventional deposition techniques, such as a simple set-up, inexpensive and non-toxic precursors, high deposition efficiency, and, in particular, easy control of the surface morphology of the deposited films. In our previous works [8-10], porous cathode thin films of SOFCs and lithium ion batteries have been prepared by ESD technique. The present study demonstrates the

feasibility to deposit porous TiO₂ thin films using ESD technique and presents the optimized process conditions to prepare porous TiO₂ thin films. The dye-sensitized solar cells have been made with the as-prepared TiO₂ films, and then photovoltaic measurements of the cells have been carried out. The effect of surface microstructure of as-prepared TiO₂ films on the conversion efficiency of the cells has been also discussed.

2. EXPERIMENTAL ASPECT

The schematics of the ESD set-up are presented in Figure 1. The ESD set-up consists mainly of an electrostatic spray unit, a liquid-precursor feed unit, and a temperature control unit. The electrostatic spray unit comprises a high DC voltage power supply (Matsusada Precision, HER-10R3), a stainless steel nozzle, and a grounded substrate holder. The liquid-precursor feed unit consists of a flexible tube and a syringe pump (Hurue Science, JP-V). The temperature control unit includes a heating element and a temperature controller connected to a thermocouple. A positive high voltage is applied to the stainless steel nozzle from which positively charged droplets are then generated and directed to the grounded substrate. Here, the droplets deposit and evaporation of solvent, crystallization, drying, and thermal decomposition of solute take place

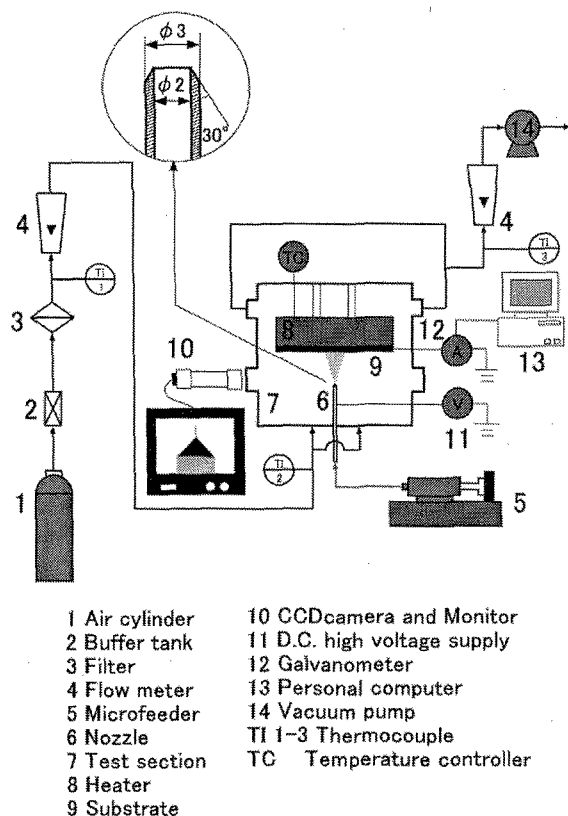


Fig. 1 Schematic diagram for the experimental apparatus used for electrostatic spray deposition (ESD).

at or near the substrate. Optically transparent F-doped SnO_2 -coated glass plates (Asahi Glass, A110U80, 20 mm x 20 mm x 1.1 mm in size) were used as the substrate.

TiO_2 thin films were prepared by using titanium tetraisopropoxide (TTIP, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) as a starting material. It was dissolved in a mixture of ethanol ($\text{C}_2\text{H}_5\text{OH}$) and butyl carbitol ($\text{C}_4\text{H}_9\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$) to obtain the precursor solution. The composition of ethanol ranges from 60 to 90 vol.% in the mixture. The concentration of TTIP was 0.05 mol/dm^3 . Typical deposition time was 2 hours in air atmosphere and the liquid flow rate of precursor solution was 0.5 ml/h. A positive high voltage was varied from 5.6 to 6.7 kV and applied to the nozzle. The distance between the tip of the nozzle and the substrate was ranged from 10 to 25 mm and the deposition temperature from 200 to 270°C. In the present study, the deposition of TiO_2 films was carried out on the cone-jet mode by ESD [10].

The surface morphologies and cross-sectional structure of as-prepared thin films were analyzed using field-emission scanning electron microscopy (FE-SEM, Hitachi S-800). The crystalline phase of the as-prepared films was identified using X-ray diffraction (XRD, Phillips PW1700).

Each TiO_2 thin film was cut in the size of 5 mm x 5 mm to standardize the area of cells, and then these films were immersed for more than 12 h in an ethanol solution of *cis*-(NCS)₂bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II)

($\text{Ru}(\text{bipy})_2(\text{SCN})_2$ (Kojima Chemical Co., Ltd.) at a $\text{Ru}(\text{bipy})_2(\text{SCN})_2$ concentration of $3 \times 10^{-4} \text{ mol/dm}^3$. The immersed films were rinsed with ethanol and then dried in Ar atmosphere. The electrolyte solution with an iodide ion – triiodide ion redox couple of I^-/I_3^- was a 3-methoxypropionitrile solution of 4-*tert*-butylpyridine (Aldrich Co., Ltd.), lithium iodide (Wako Pure Chemical Industries, Ltd.), iodine (Kanto Kagaku Co., Ltd.), and dimethylpropylimidazolium iodide (Solaronix Co., Ltd.). Each as-prepared film was placed on a counter electrode. The counter electrode was produced by sputtering platinum onto a glass substrate. The electrolyte solution was injected between the two substrates, which were sealed by using epoxy resin. The photovoltaic measurements were done under a halogen lamp. The intensity of the lamp is 140 mW/cm^2 .

3. RESULTS AND DISCUSSION

3.1 Preparation of TiO_2 thin films by ESD

Figure 2 shows the difference in surface morphology of thin films deposited at 0.5 ml/h for various deposition temperatures ranging from 200 to 270°C. The thin films deposited at 250°C are quite porous microstructure, however the surface morphology gradually changes from the porous microstructure to a smooth surface structure with decreasing deposition temperature down to 200°C. A lower deposition temperature leads to an incomplete solvent evaporation. Thus the particles

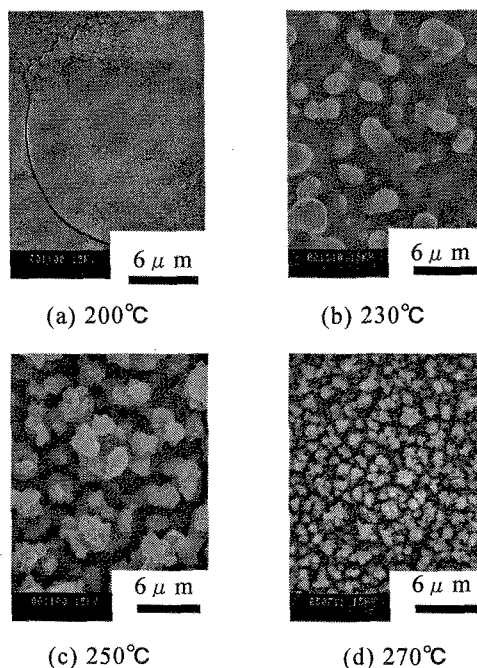


Fig. 2 SEM photographs of TiO_2 films deposited on conductive glass at 0.5 ml/h and 80 vol.% ethanol with various deposition temperatures. Nozzle-to-substrate distance: 15 mm.

landing on the substrate are still wet, and then widely spread on the substrate. Finally, the dense thin films may be formed with smooth surface (Fig. 2 (a)). However, a higher deposition temperature leads to a complete solvent evaporation. Thus, the porous thin films may be formed by the agglomeration of deposited solid particles (Fig. 2 (d)).

Figure 3 shows the difference in surface morphology of thin films deposited at 250°C for various ethanol composition in the solvent. The boiling point of butyl carbitol is 231°C, while that of ethanol is only 78°C. The increase of ethanol composition in the solvent promotes an evaporation of solvent from the sprayed drops. Thus, at the high composition of ethanol (90 vol.%), the particles landing on the substrate may be perfectly dry and subsequently deposit on it. A very porous thin film made of fractal agglomerates of tiny particles is formed, as shown in Fig. 3 (a). With decrease of the composition of ethanol in solvent, the particles landing on the substrate may be semidry or wet, and then spread on the substrate. Finally, a reticular thin film is formed, as shown in Fig. 3(c) or (d).

The effect of the distance between the tip of nozzle and the substrate on the surface morphology of thin films deposited at 250°C is shown in Fig. 4. It can be clearly seen that the structure of film changes from a dense film to the very porous one with increase of the distance. The flight time of sprayed drops increases with the distance. Therefore, this fact may indicate that the morphology strongly depends on the particle situation when the sprayed droplets deposit on the substrate.

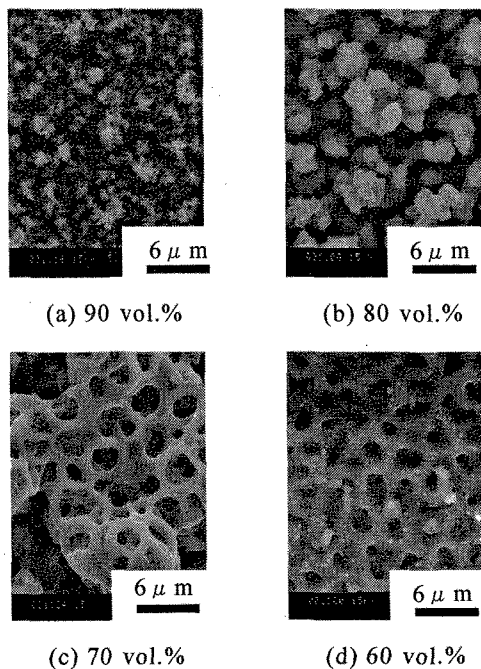


Fig. 3 SEM photographs of TiO₂ films deposited on conductive glass at 0.5 ml/h and 250°C with various compositions of solvent. Nozzle-to-substrate distance: 15 mm.

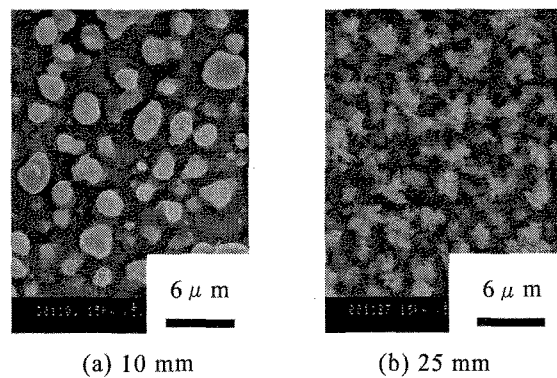


Fig. 4 SEM photographs of TiO₂ films deposited on conductive glass at 0.5 ml/h and 250°C with various nozzle-to-substrate distances. Composition of ethanol in solvent: 80 vol.%

Figure 5 shows the cross-section of TiO₂ films deposited at 250°C for 2 h. From the SEM picture, the thickness of film was about 7.3 μm. Assuming that the deposited thin film is pure anatase TiO₂ of theoretical density 3.89 g/cm³, the relative density of this film is on the average 40%, or its porosity 60% from the simple calculation. This indicates the highly porous structure of the deposited thin film.

Figure 6 shows the X-ray diffraction patterns of the thin film deposited at 250°C before and after annealing at 450°C in air atmosphere. Obviously, the as-deposited thin film is amorphous, however the crystal structure transforms into the desired anatase phase after the sample is annealed at 450°C for 1 hour. We also investigated the morphology and weight loss of deposited thin films before and after annealing. The maximum weight loss was 5% and there was no morphology change after annealing.

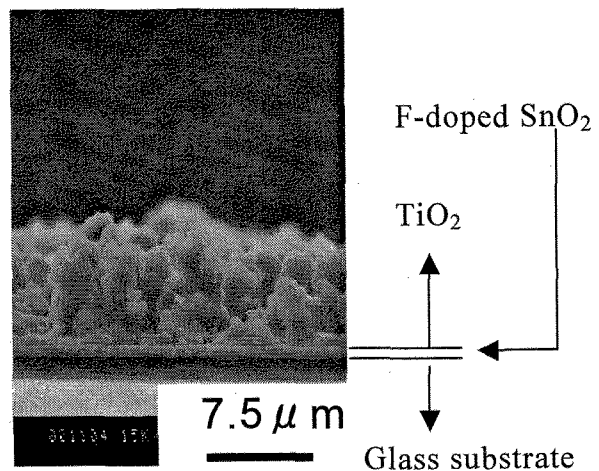


Fig. 5 SEM photographs of the cross-section of TiO₂ deposited at 250°C for 2 h. Composition of ethanol in solvent: 80 vol.%. Nozzle-to-substrate distance: 15 mm.

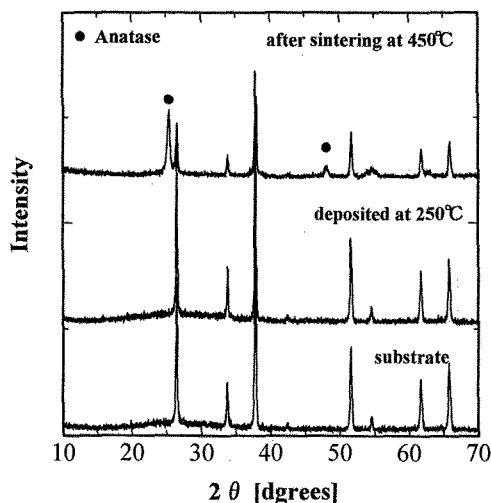


Fig. 6 XRD spectrum of TiO₂ thin films deposited at 250°C for 2 h. Composition of ethanol in solvent: 80 vol.%. Nozzle-to-substrate distance: 15 mm.

3.2 Photovoltaic properties of TiO₂ thin films prepared by ESD

Figure 7 shows the current-voltage curves measured for the dye sensitized solar cells fabricated with the TiO₂ films deposited on the conductive glass by ESD for various deposition temperatures. The nozzle-to-substrate distance was 15 mm and the composition of ethanol 80 vol.% in the deposition of TiO₂ by ESD.

The photovoltaic properties, such as solar cell efficiency (η), open circuit voltage (V_{oc}), short circuit current (I_{sc}) and fill factor (FF), of the cells are summarized in Table I. The open circuit voltages and the fill factors of the cells are around 0.7 V and 0.6 respectively, which is the typical value of dye-sensitized solar cells. Generally speaking, the photocurrent is almost proportional to the amount of a dye adsorbed on the TiO₂ surface. Thus, the small short circuit currents are ascribed to the fact that the amount of a dye adsorbed on TiO₂ is not enough to produce high photocurrent, and it depends on surface morphology of TiO₂ films. The maximum cell efficiency was 1.72 in the present study.

4. CONCLUSIONS

Porous TiO₂ thin films were deposited on conductive glass substrate by using the ESD technique for various deposition temperatures, composition of solvent and nozzle-to-substrate distance. The surface morphology of TiO₂ thin film was affected by these process parameters. The as-deposited thin films were amorphous, however the crystal structure transformed into the desired anatase phase after the samples were annealed at 450°C for 1 hour.

Dye-sensitized solar cells were fabricated with these films. The conversion efficiency was affected by the surface microstructure of TiO₂ thin films. The TiO₂ thin films prepared at deposition temperature 250°C and composition of ethanol 80 vol.% showed a maximum conversion efficiency in the present study, and it was

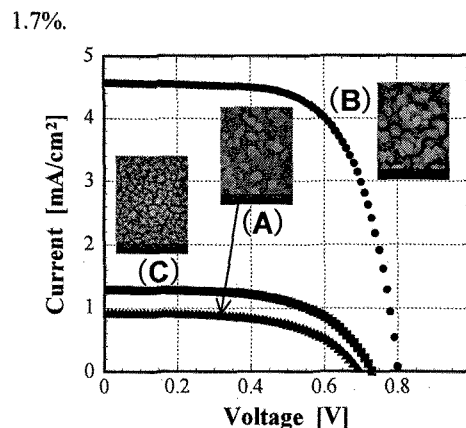


Fig. 7 Current-voltage characteristics of the dye sensitized solar cells fabricated with the TiO₂ films deposited on the conductive glass by ESD. (A) Deposition temperature: 230 °C. (B) Deposition temperature: 250°C. (C) Deposition temperature: 270°C.

Table I Photovoltaic properties of dye-sensitized solar cells fabricated with the TiO₂ films deposited on conductive glass by ESD.

Morphology	V_{oc} [V]	I_{sc} [mA/cm ²]	FF [-]	η [-]
A	0.69	0.92	0.59	0.27
B	0.8	4.57	0.66	1.72
C	0.73	1.29	0.6	0.40

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