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Fabrication of dye-sensitized solar cells by spray pyrolysis deposition (SPD) technique

Masayuki Okuya*, Koji Nakade, Daisuke Osa, Takafumi Nakano, G.R. Asoka Kumara, Shoji Kaneko

Department of Materials Science and Technology, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8561, Japan

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Abstract

Porous TiO_2 films were successfully synthesized in air from a commercial TiO_2-sol by spray pyrolysis deposition (SPD) technique. The film consisted of fine TiO_2 particles, approximately 30–50 nm in size, and showed the roughness factor as high as 1000. A dye-sensitized solar cell was constructed by SPD technique. In this technique, porous TiO_2/dense TiO_2/SnO_2:F junction was prepared within 10–15 min, which drastically shortened the fabrication period of working electrodes. The photovoltaic conversion efficiency was enhanced up to 5.1% under the quasi-sunlight of AM-1.5 and 100 mW/cm^2 by optimizing the porosity of TiO_2 film. The result leads to an industrial production of dye-sensitized solar cells in the near future.

Keywords: Spray pyrolysis deposition; Titanium dioxide; Thin film; Dye-sensitized solar cell

1. Introduction

Photovoltaic power is a hot topic among the recent clean energy sources. Although silicon solar cell is the most popular, it has to overcome many problems for a practical use, such as the stability, scaling up and cost. On the other hand, a dye-sensitized solar cell is one of the most promising candidates for a high-performance solar cell in the next generation, since it is fabricated by a simple manufacture process at relatively low cost [1]. As this photovoltaic system divides the area of the light harvesting and carrier separation, the carrier recombination due to a scattering is not so serious. Additionally, the system does not require pure and expensive materials, such as single crystalline silicon in the conventional p–n junction. A high vacuum and/or high temperature manufacturing process is no longer necessary to produce dye-sensitized solar cells, which is quite attractive to the low cost production.

In order to fabricate the solar cell for a practical use, an industrial procedure to prepare films on a large scale should be developed. Among many thin film processing techniques, a spray pyrolysis deposition (SPD) is one of the most promising ones, since the film formation is carried out in air by a simple apparatus. The SPD is essentially the same film processing technique as so-called pyrosol technique, in which a source solution is sprayed on a heated substrate to be deposited as films. In other words, when a source solution is atomized, small droplets splash and vaporize on the substrate, and leave dry precipitates in which thermal decomposition occurs [2]. Organometallic compounds and inorganic salts are used as source materials, which are dissolved in water, ethanol or other solvents to prepare source solutions. Since the source materials dissolve in a solvent as an ion, oligomer, cluster or sol, depending on their chemical properties, the surface morphology of deposited films is easily controlled by choosing species of the source materials [3–6]. SPD technique has fist been developed to deposit SnO_2:F and ITO transparent conducting film on a glass substrate, and is now applicable to prepare variety of compounds such as oxides, chalcogenides, and noble or base metals [7,8]. We have developed SPD technique into a quick film processing method by employing compressed air for the atomization and intermittent spraying, and reported various film syntheses, such as SnO_2 [9–11], SnS [12,13], Sn_2OS [12,13], Cu_2O [14], $CuInS_2$ [15,16], $NiFe_2O_4$ [17], and (Ni,Zn)Fe_2O_4 [18]. In addition, we recently applied this technique to TiO_2 film synthesis to fabricate dye-sensitized solar cells [3–6].

In this paper, we report TiO_2 film formation from a commercial TiO_2-sol by SPD technique. The porosity of films

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* Corresponding author. Tel.: +81-53-478-1155; fax: +81-53-478-1155.
E-mail address: tcmokuy@ipc.shizuoka.ac.jp (M. Okuya).

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was successfully controlled by adding a small amount of titanium tetra-*iso*-propoxide to the source solution. We propose a new industrial continuous procedure for constructing working electrodes of dye-sensitized solar cells by combining SPD technique into a conventional electrode production process.

2. Experimental

The schematic representation of SPD apparatus is shown in Fig. 1. Transparent conducting SnO_2:F films were prepared from 0.1 M of di-*n*-butyltin(IV) diacetate (Tokyo Kasei Kogyo Co. Ltd., Japan), abbreviated as DBTDA, ethanol solution with an additive of ammonium fluoride, NH_4F, (Wako Pure Chemical Industries Co. Ltd., Japan) with the molar ratio of $[NH_4F]/[DBTDA] = 1.6$ [9–11]. The source solution was sprayed by a nozzle (Lumina STA-6R-1 mmϕ, Fuso Seiki Co. Ltd., Japan) with compressed air onto a heated glass substrate (Corning 1737; 25 mm × 25 mm × 1 mm in size). The mist was pyrolyzed on the substrate at the substrate temperature of 500 °C to form SnO_2:F film in air. Since the mist cooled down the substrate, the spray was not carried out continuously but intermittently. During the film formation, each spray and waiting time was kept 0.5 and 5.0 s, respectively. This procedure was repeated 60 times to produce SnO_2:F conducting film with high quality, the sheet resistance $<10\ \Omega/\square$ and the average transmittance >80% in the visible light region.

Dense TiO_2 film was deposited on the SnO_2:F film in almost the same way that mentioned above from 0.1 M of titanium(IV)oxy acetylacetonate (Tokyo Kasei Kogyo Co. Ltd., Japan), abbreviated as TOA, ethanol solution [5]. Finally, 0.1 M of aqueous TiO_2-sol (STS-01; Ishihara Sangyo Co. Ltd., Japan) with an additive of titanium tetra-*iso*-propoxide (Wako Pure Chemical Industries Co. Ltd., Japan), abbreviated as TPT, was further sprayed on the dense TiO_2 film to fabricate porous TiO_2/dense TiO_2/SnO_2:F stacking layer.

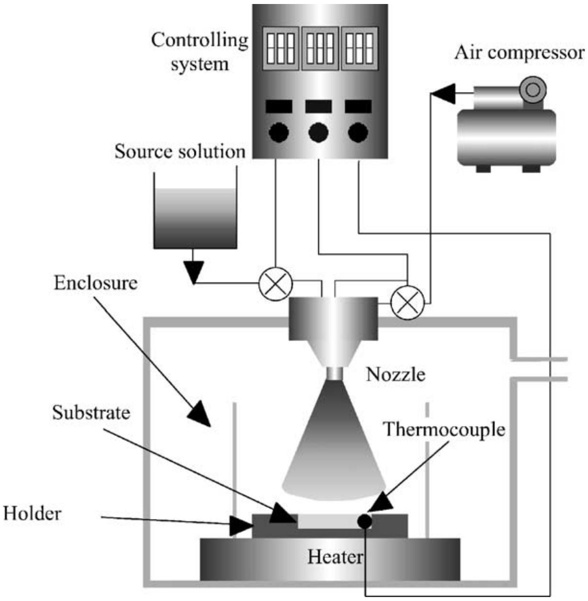

Fig. 1. Schematic representations of SPD apparatus.

Ruthenium(II) *cis*-(di-thiocyano)bis(2,2′-bipyridil-4,4′-dicarboxylic acid) dye was adsorbed on the surface of porous TiO_2 film by refluxing the electrode in 1×10^{-4} M of ethanol solution at 80 °C for 2 h. The amount of the dye adsorbed on the electrode was evaluated by colorimetry (UV-1200, Shimadzu Co. Ltd., Japan).

A counter electrode was prepared by sputtering platinum onto a glass substrate. A mixture of ethylene carbonate and propylene carbonate, 80/20 in volume, containing 0.5 M of tetrapropyl ammonium iodide (Wako Pure Chemical Industries Co. Ltd., Japan) and 0.04 M of iodine (Kanto Kagaku Industries Co. Ltd., Japan) was employed as an electrolyte. The electrolyte was sandwiched between the working and counter electrode to fabricate a dye-sensitized solar cell. The photovoltaic measurement was done under the quasi-sunlight of AM-1.5 and 100 mW/cm^2 irradiated directly on the cell.

3. Results and discussion

3.1. TiO_2 film formation by SPD technique

When aqueous TiO_2-sol was sprayed on a heated substrate, the film obtained here was powdery and cleaved easily from the substrate. The problem is easily solved by adding TPT to the source solutions. Fig. 2(a)–(d) show the surface morphology of porous TiO_2 films prepared from the source solution at molar ratios $[TPT]/[TiO_2\text{-sol}] = 0.3$–$8.0$. The films were composed of fine TiO_2 particles, the size of which increases with increasing $[TPT]/[TiO_2\text{-sol}]$ ratio from 10 to 80 nm at $[TPT]/[TiO_2\text{-sol}] = 0.3$ and 0.8, respectively. Since the original average TiO_2 particle size is 7 nm in the source solution, TPT is supposed to take in the particles to grow into secondary particles while pyrolyzing on the substrate, and then form necks between them. On the other hand, at $[TPT]/[TiO_2\text{-sol}] = 8.0$, the surface morphology of the film became smooth due to a significant neck growth, corresponding to a low porosity. We found that the grain size and porosity of TiO_2 films were easily controlled by changing $[TPT]/[TiO_2\text{-sol}]$ ratio in the source solution.

Fig. 3 shows the amount of a dye adsorbed on porous TiO_2 films with the thickness of 20 μm prepared from source solutions with various $[TPT]/[TiO_2\text{-sol}]$ ratios. At $[TPT]/[TiO_2\text{-sol}] = 0.3$, the amount reached the maximum as high as $9 \times 10^{-8}\ \text{mol/cm}^2$, corresponding to the roughness factor of 1000 according to the literature [19,20], which is a desirable value to produce high conversion efficiency in dye-sensitized solar cells. By utilizing this porous TiO_2 film, a dye-sensitized solar cell that shows high performance comparable to those prepared by a conventional technique will be fabricated.

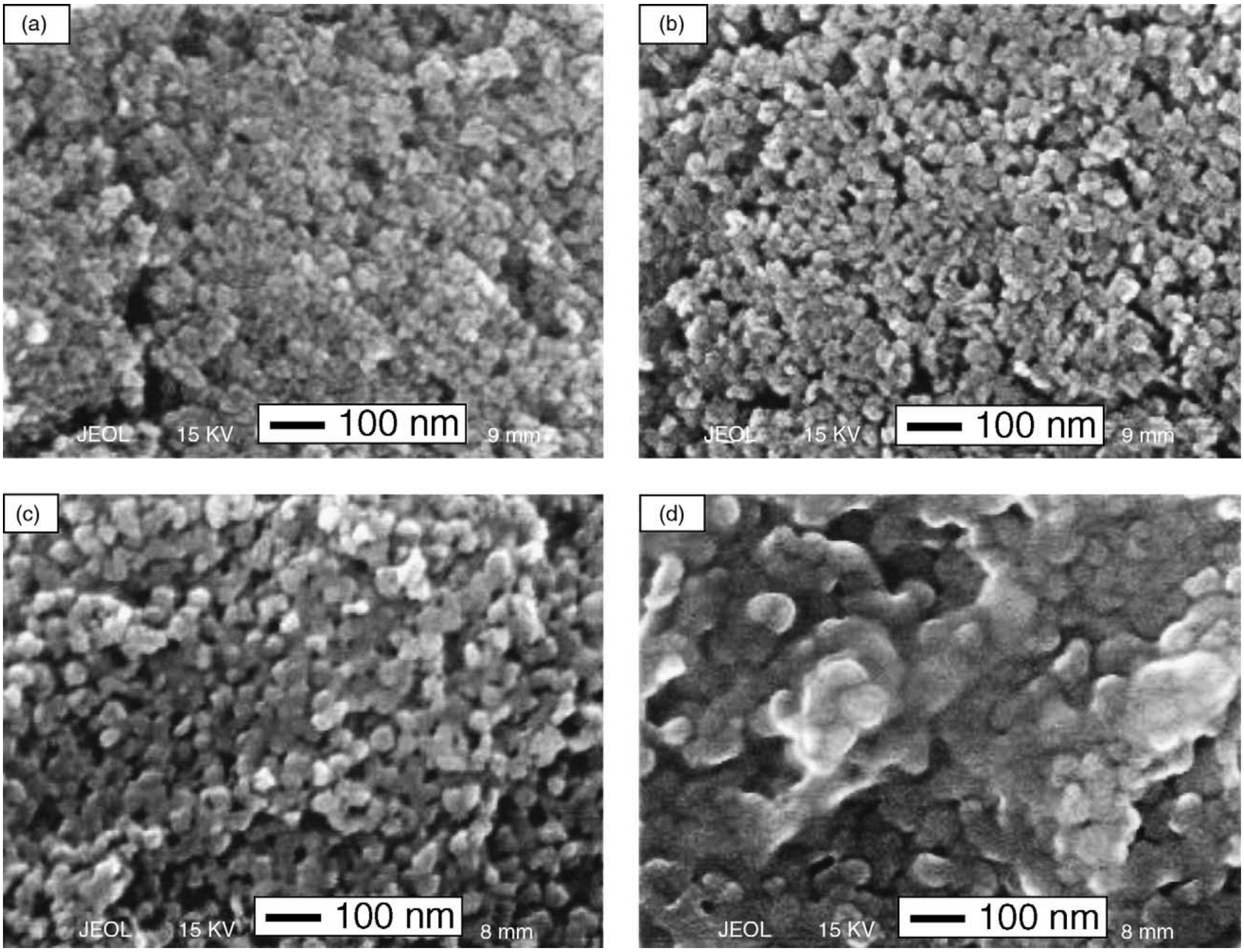

Fig. 2. Surface morphology of porous TiO_2 films prepared by SPD technique from the source solution with various [TPT]/[TiO_2-sol] ratios; (a) 0.3, (b) 0.5, (c) 0.8, and (d) 8.0. All films were deposited in air at the substrate temperature of 500 °C.

In the conventional TiO_2 film preparation from aqueous sols, such as dip coating and spin coating, after repeating the procedure of dipping, drying, and pre-sintering for several times, the film is sintered at 500 °C to promote necking between particles by an atomic diffusion. In this case, more than 1 h of sintering is required so that enough film strength due to the neck growth is achieved. This is the reason why several hours are required to form 10 μm-thick TiO_2 film in the conventional technique. By adding a little amount of TPT to the TiO_2-sol source solution, we succeeded in establishing a quick film formation procedure by SPD. The mechanism of TiO_2 film formation from aqueous sols in spin coating and SPD is shown in Fig. 4(a) and (b), respectively. From a viewpoint of the thermodynamics in sintering, a neck growth in the conventional technique is based on an atomic diffusion attributed to a mass transportation. Since an atomic diffusion rate in the solid is much slower than that in the liquid or gas, more than 1 h is required to grow enough necks between particles. On the other hand, SPD technique does not require an atomic diffusion within particles. TPT in the source solution is pyrolyzed easily on the heated substrate to form crystallized TiO_2 necks between particles within a few seconds. This mechanism enables SPD technique to drastically shorten TiO_2 film formation period.

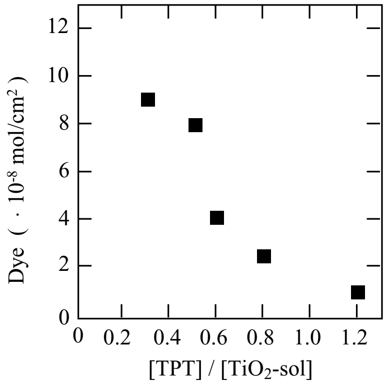

Fig. 3. The amount of a dye adsorbed on TiO_2 films with the thickness of 20 μm prepared from the source solution with various [TPT]/[TiO_2-sol] ratios.

In SPD technique, it is possible to control the film thickness by varying spray frequency. Fig. 5 shows TiO_2 film thickness as a function of spray frequency. The films were prepared from the source solution of [TPT]/[TiO_2-sol] = 0.6

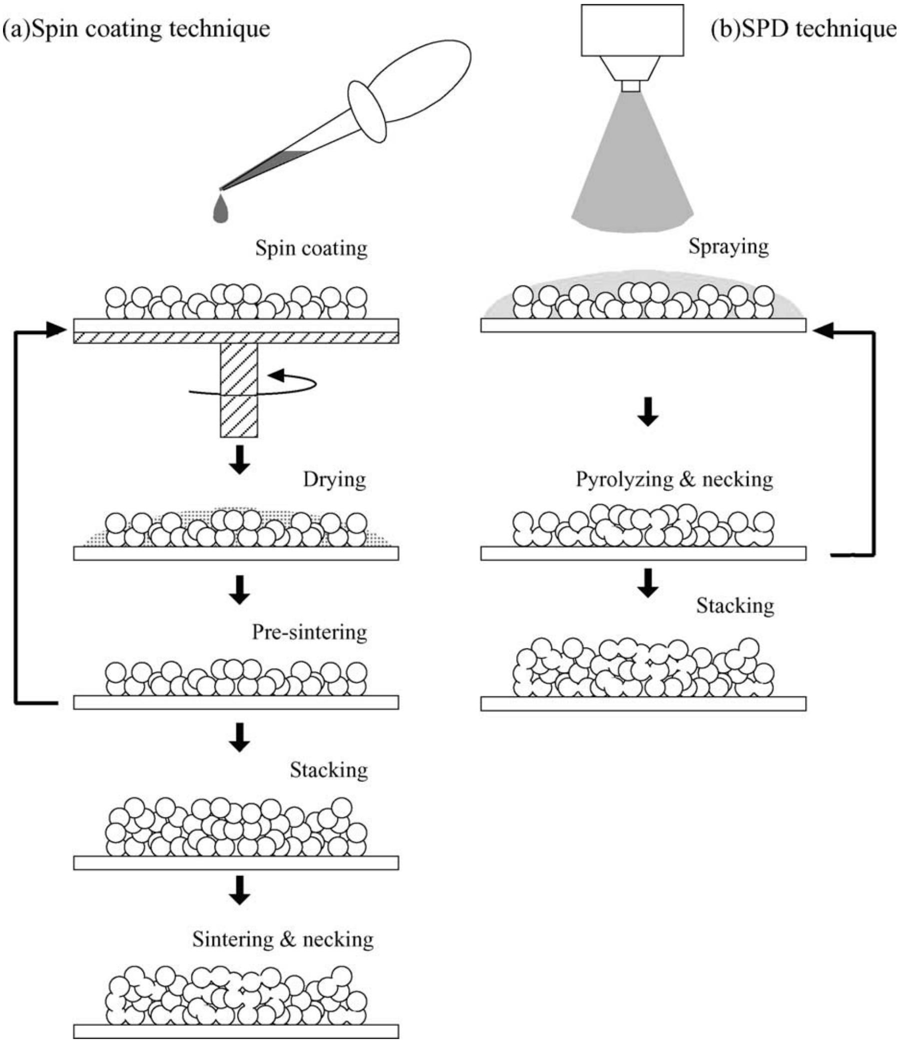

Fig. 4. The mechanism of TiO_2 film formation from an aqueous TiO_2-sol in (a) spin coating and (b) SPD technique.

by SPD technique. Since the film thickness is almost proportional to the spray frequency, we can easily control the film thickness. A dye-sensitized solar cell generally requires porous TiO_2 film with 10–20 μm in thickness to produce high efficiency, corresponding to repeat 50–70 times of each SPD cycle; 0.5 s of spraying followed by 3.0 s of waiting for the recovery of substrate temperature. In other words, the total processing period to prepare 10–20 μm-thick TiO_2 films is drastically shortened to 4–6 min.

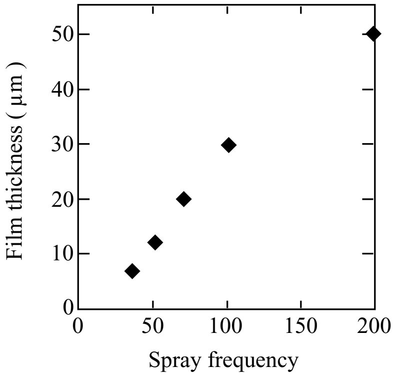

Fig. 5. TiO_2 film thickness as a function of spraying frequency prepared in air from the solution with [TPT]/[TiO_2-sol] $= 0.6$ at the substrate temperature of 500 °C by SPD technique.

3.2. Photovoltaic properties

Figs. 6 and 7 show the procedure to prepare working electrodes for dye-sensitized solar cells and the typical cross-section of a working electrode prepared by SPD technique, respectively. The porous TiO_2/dense TiO_2/SnO_2:F junction was fabricated within 10–15 min on a bare glass substrate by the successive SnO_2:F and TiO_2 film formation processes by SPD technique.

Fig. 8(a)–(e) show the photovoltaic properties of dye-sensitized solar cells fabricated with TiO_2 films with the thickness of 20 μm prepared from the source solutions with various [TPT]/[TiO_2-sol] ratios. In Fig. 8(a), the open circuit voltage, V_{OC}, was independent on [TPT]/[TiO_2-sol]

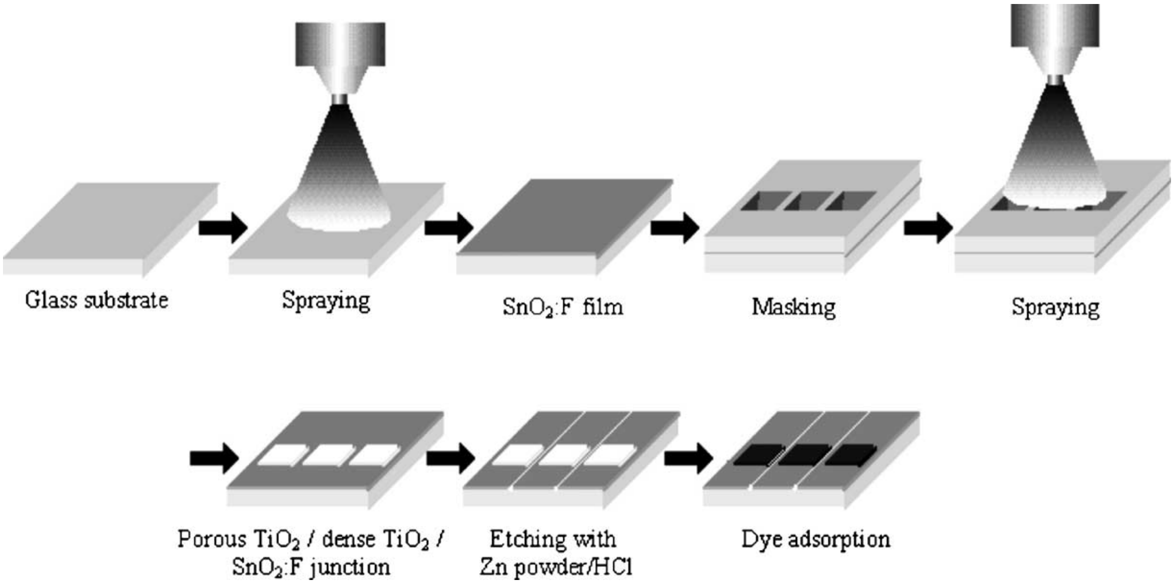

Fig. 6. The procedure to prepare a working electrode by SPD technique.

ratio and almost constant, approximately 0.7–0.8 V, which is a typical value of dye-sensitized solar cells. Since the open circuit voltage depends on the valance between the photo and dark current, the open circuit voltage is enhanced when the route for the dark current is cut off. In the conventional dye-sensitized solar cell, TiO_2 film with high porosity is employed as a working electrode, into which an electrolyte immerses to reach SnO_2:F film, which causes partial short circuits to reduce the open circuit voltage. In the dye-sensitized solar cell prepared by SPD technique, a dense TiO_2 buffer film prepared from TOA solution was inserted between SnO_2:F and porous TiO_2 film as shown in Fig. 7. Without this dense layer, a porous TiO_2 film does not attach firmly on the substrate enough to adopt it to dye-sensitized solar cells. The high open circuit voltage seems to be attributed to cutting off dark current routes by the dense TiO_2 film. We found that the buffer TiO_2 film played an important role to enhance the open circuit voltage as well as improved the adhesion between porous TiO_2 and SnO_2:F film.

The short circuit current, I_{SC}, increased up to 12 mA/cm^2 with increasing [TPT]/[TiO_2-sol] ratio in the source solution, while remained constant above [TPT]/[TiO_2-sol] $= 0.6$ as indicated in Fig. 8(b). Since the amount of a dye adsorbed on TiO_2 film decreased with increasing [TPT]/[TiO_2-sol] ratio in the source solution as shown in Fig. 3, the short circuit current is supposed to decrease in general, which is, however, contrary to our result. This is explained by considering the mechanism of neck growth between particles in porous TiO_2 film. As [TPT]/[TiO_2-sol] ratio in the source solution increases, the porosity of a film is lowered, which is ascribed to the fast neck growth rate, and the amount of a

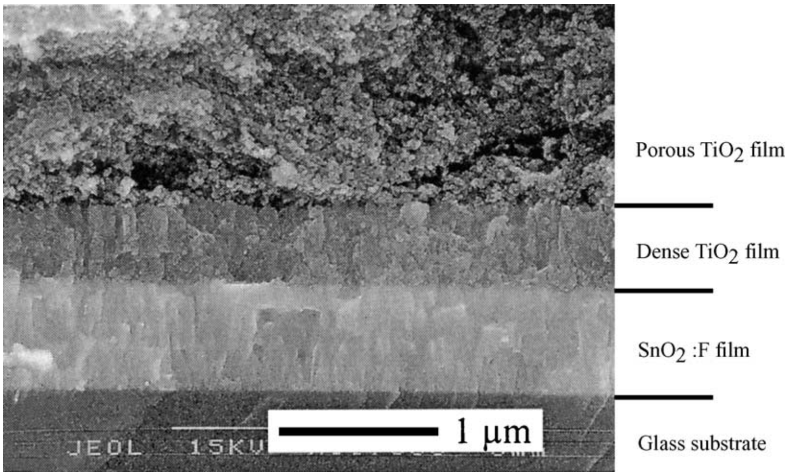

Fig. 7. The SEM image of the cross-section of a working electrode prepared by SPD technique. The porous TiO_2/dense TiO_2/SnO_2:F junction was deposited on a bare glass substrate by SPD technique within 15 min in air.

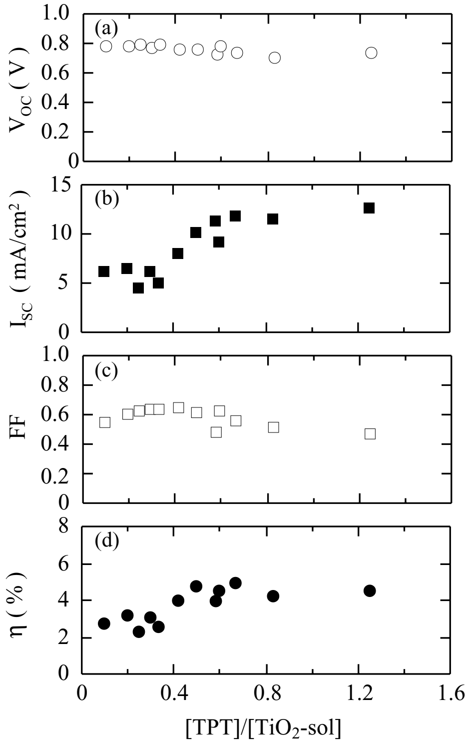

Fig. 8. Photovoltaic properties of dye-sensitized solar cells fabricated with TiO_2 films prepared at the substrate temperature of 500 °C from the source solution with various [TPT]/[TiO_2-sol] ratios by SPD technique; (a) open circuit voltage, (b) short circuit current, (c) fill factor, and (d) conversion efficiency. The measurement was done under the quasi-sunlight of AM-1.5 and 100 mW/cm^2 irradiated directly to the cell.

dye adsorbed on the film decreases as well to produce less photoelectrons. However, in the TiO_2 film prepared from the source solution below [TPT]/[TiO_2-sol] = 0.4, the neck growth between particles is poor and is not sufficient for mechanical and electrical contacts. The photoelectrons produced here will soon disappear due to the recombination. This is the main reason why the short circuit current is lower than that expected from the amount of a dye adsorbed on TiO_2 film. On the other hand, the abrupt increase in the short circuit current at [TPT]/[TiO_2-sol] = 0.4 seems to be attributed to the low recombination derived from large and sufficient necks between TiO_2 particles.

The fill factor (FF) is slowly declined from 0.7 to 0.5 with increasing [TPT]/[TiO_2-sol] ratios as shown in Fig. 8(c). The fill factor is known to be sensitive to the internal resistance and leakage current in the cell. In this study, since the fill factor is declined with increasing [TPT]/[TiO_2-sol] ratios, the relatively lower fill factor is due to residuals originated from TPT within the film, an interminglement of rutile phase with poor photovoltaic property, and a local contact between the counter and working electrode in the cell.

Fig. 8(d) shows the conversion efficiency, η, as a function of [TPT]/[TiO_2-sol] ratios in the source solution. The conversion efficiency is enhanced with increasing [TPT]/[TiO_2-sol] ratio and reached the maximum value as high as 5.1%. This result is similar to that of the short circuit current as indicated in Fig. 8(b). However, the conversion efficiency is declined above [TPT]/[TiO_2-sol] = 0.6 due to the decrease of the fill factor. In order to achieve higher conversion efficiency, the fill factor should be increased by improving a crystallinity of TiO_2 film to decrease an internal resistance and by reducing the film thickness down to 10 μm to enhance the light harvesting efficiency.

4. Summary

Deposition of porous TiO_2 films by SPD technique and their application to dye-sensitized solar cells are reported. By using SPD technique, the continuous procedure to deposit transparent conducting SnO_2:F film and the following TiO_2 deposition drastically shorten the fabrication period of working electrodes in dye-sensitized solar cells. The light-to-current conversion efficiency reached as high as 5.1% by optimizing [TPT]/[TiO_2-sol] ratios in the source solution. Although the conversion efficiency is relatively low, the possibility of an industrial production of dye-sensitized solar cells by SPD technique is shown here.

References

[1] B. O'Regan, M. Grätzel, Nature 353 (1991) 737.
[2] J.C. Viguié, J. Spitz, J. Electrochem. Soc. 122 (1975) 583.
[3] M. Okuya, N.A. Prokudina, K. Mushika, S. Kaneko, J. Eur. Ceram. Soc. 19 (1999) 903.
[4] M. Okuya, S. Kaneko, N.A. Prokudina, T. Fujiwara, K. Murakami, Ceram. Trans. 109 (2000) 473.
[5] M. Okuya, K. Nakade, S. Kaneko, Sol. Energy Mater. Sol. Cells 70 (2002) 473.
[6] M. Okuya, D. Osa, S. Kaneko, Key Eng. Mater. 228–229 (2002) 247.
[7] R.R. Chamberlin, J.S. Skarman, J. Electrochem. Soc. 113 (1966) 86.
[8] J.B. Mooney, S.B. Radding, Ann. Rev. Mater. Soc. 12 (1982) 81.
[9] K. Murakami, I. Yagi, S. Kaneko, J. Am. Ceram. Soc. 79 (1996) 2557.
[10] S. Kaneko, K. Nakajima, T. Kosugi, K. Murakami, Ceram. Trans. 100 (1999) 165.
[11] M. Okuya, S. Kaneko, K. Hiroshima, I. Yagi, K. Murakami, J. Eur. Ceram. Soc. 21 (2001) 2099.
[12] T. Kosugi, N. Kamiya, I. Yagi, K. Murakami, S. Kaneko, Trans. Mater. Res. Soc. Jpn. 20 (1996) 530.
[13] T. Kosugi, K. Murakami, S. Kaneko, Mater. Res. Symp. Proc. 485 (1998) 273.
[14] T. Kosugi, S. Kaneko, J. Am. Ceram. Soc. 81 (1998) 3117.
[15] S. Kaneko, T. Kosugi, T. Fujiwara, M. Okuya, Electrochem. Soc. Proc. 99/11 (1999) 118.
[16] T. Fujiwara, M. Okuya, S. Kaneko, J. Ceram. Soc. Jpn. 110 (2002) 81.
[17] Z. Wu, M. Okuya, S. Kaneko, Thin Solid Films 385 (2001) 109.
[18] A. Takayama, K. Kondo, M. Okuya, S. Kaneko, J. Ceram. Soc. Jpn. 110 (2002) 912.
[19] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
[20] K. Sayama, K. Hara, H. Arakawa, N. Mori, M. Satsuki, S. Suga, S. Tsukagoshi, Y. Abe, H. Sugihara, J. Chem. Soc. Chem. Commun. (2000) 1173.