

FTO/ITO double-layered transparent conductive oxide for dye-sensitized solar cells

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Abstract

New transparent conductive oxide (TCO) films, fluorine-doped tin oxide (FTO) films coated on indium–tin oxide (ITO) films, were developed for dye-sensitized solar cells (DSC). These transparent conductive films were prepared by a spray pyrolysis deposition (SPD) method at a substrate temperature of 350 °C in ITO and 400 °C in FTO. For ITO deposition, an ethanol solution of indium(III) chloride, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, and tin(II) chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{Sn}/(\text{In} + \text{Sn})$, 5 at.%) was sprayed on a TEMPAX #8330 glass substrate ($100 \times 100 \times 1.1 \text{ mm}^3$). After the deposition of ITO, FTO films were consecutively deposited for protecting oxidation of ITO films. FTO deposition was carried out by an ethanol solution of tin(IV) chloride, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ within the saturated water solution of NH_4F . These films achieved the lowest resistivity of $1.4 \times 10^{-4} \Omega \text{ cm}$ and the optical transmittance of more than 80% in the visible range of the spectrum. The electrical resistance of these films increased by less than 10% even though exposed to high temperatures of 300–600 °C for 1 h in the air. The DSC composed of the films were fabricated to confirm their availability. The films were of large size, $100 \times 100 \text{ mm}^2$. The DSC were made by conventional method. As a result, energy conversion efficiency of $\eta = 3.7\%$ was obtained.

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1. Introduction

Indium–tin oxide (ITO) thin films are widely used as a transparent electrode in opto-electronics devices, including liquid crystal displays, plasma display panels, and solar cells. Although ITO films show high transparency and electrical conductivity at room temperature, the latter property is severely spoiled under high temperature. When ITO films are exposed to high temperature of 300 °C or higher, their electrical resistance increases more than three times. The reason for this behavior has been thought that oxygen from the atmosphere bonds to a portion of the oxygen-vacant structures within the ITO films when it is heated, and accordingly reduces the oxygen vacancies, which functions as an electron supplier.

When these types of transparent conductive films are used to make a dye-sensitized solar cell (DSC) [1,2], the paste

of fine oxide powder such as titanium oxide is coated on the surface of the ITO films. Then, the paste is calcinated at the temperature range of 400–600 °C to form porous oxide semiconductor films. Unfortunately, as the conductivity of the ITO films decreases markedly during this process, the photoelectric conversion efficiency of the DSC also decreases.

The object of this development is to provide transparent conductive films with the ITO films, used for example as the DSC; the electrical resistance does not increase even when it is exposed to high temperature of 300 °C or higher.

In this work, the new transparent conductive films, in which fluorine-doped tin oxide (FTO) films are covered on ITO films (FTO/ITO films), were developed for DSC. The reason of developing this double-layered structure is because the heat resistance in more than 300 °C of FTO films is better than that of ITO films. FTO/ITO films were prepared by the spray pyrolysis deposition (SPD) method [3,4], which makes it possible for both ITO and FTO films to form on a glass substrate [5–9]. Characteristics of the films were investigated. Then, DSC were fabricated using these heat-resisting films. Moreover, energy conversion efficiency was measured.

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2. Experimental section

2.1. Film formation

All preparations and depositions were carried out in the air. $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (purity 99.5%), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (purity 98.0%), NH_4F (purity 99.9%), and ethanol (purity 99.5%) were purchased from Kanto Chemical Co. Inc. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (purity 97.0%) was purchased from Junsei Chemical Co. Ltd. All chemicals used were reagent grade.

Preparation of raw material compound solution for ITO and FTO films was as follows: $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (5.58 g) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.23 g) were dissolved in ethanol (100 ml). $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (1.40 g) was dissolved in ethanol (20 ml), and a saturated aqueous solution of NH_4F (0.24 g) was added. The mixture was placed in an ultrasonic washer for approximately 20 min to achieve complete dissolution.

Deposition of FTO/ITO films was as follows: the raw material compound solution was atomized by compressed air at 0.06 MPa in pressure. The atomized solution was transported onto a heated TEMPAX #8330 glass substrate ($100 \times 100 \times 1.1 \text{ mm}^3$). The substrate temperature was 350°C in ITO and 400°C in FTO. FTO deposition was consecutively conducted to avoid an oxidation of ITO films. The solution feed rate was 5 ml/min, and the nozzle–substrate distance was fixed to be 600 mm. The schematic representation of SPD apparatus is shown in Fig. 1.

Through the above processes, double-layered films were formed on a glass substrate: ITO films of approximately 720 nm in thickness in the first layer and FTO films of approximately 100 nm in thickness in the second layer.

For purposes of comparison, the same processes were used to form only the ITO films of approximately 720 nm in thickness, and only the FTO films of approximately 100 nm in thickness.

2.2. Film characterization

Film thickness was measured by a stylocontact method using a Slone Dectak 3030 after etching the film [10]. The measurement of the concentration depth profile was

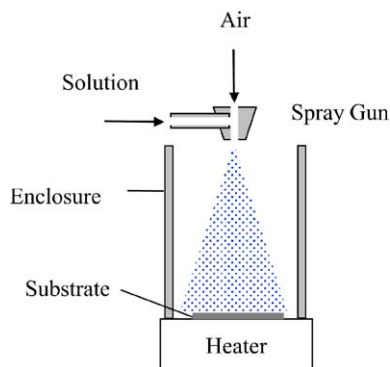


Fig. 1. Schematic representation of spray pyrolysis deposition apparatus.

also conducted by sequentially applying Auger electron spectroscopy (AES) with ion beam sputtering. The AES data were obtained using primary electron beam energy of 5 keV, which condition was the etching rate of 10 nm/min. The surface morphology and cross-section of the present films were observed with a field-emission-type scanning electron microscope (FE-SEM) (HITACHI S-5200). Acceleration voltage was 5 kV. The transmittance in the 200–2500-nm regions was measured with a JASCO V-570 spectrophotometer. The crystal structure of the films was determined by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (RIGAKU RAD-1C diffractometer). Sheet resistance of the films was measured by MITSUBISHI KAGAKU MCP-T600 four-probe-type resistance meter.

2.3. Solar cell fabrication

TiO_2 colloidal printing paste (Ti nanoxide-T, Solaronix SA) was coated on the FTO/ITO films ($100 \times 100 \text{ mm}^2$) using a doctor-blading technique. After drying the nanoporous electrode films on the FTO/ITO films, the films were sintering at 450°C in the air for 1 h. The FTO/ITO films with TiO_2 layer were immersed in 50 wt.% butanol and 50 wt.% acetonitrile mixed solution of 0.3 mM ruthenium(II) (2, 2'-bipyridyl-4,4'-dicarboxylate) $_2$ (NCS) $_2$ dye (calling as N3 Dye) for 18 h at room temperature. A counter electrode was prepared with platinum sputtering deposition on a TCO (FTO films; $8 \Omega/\text{square}$). Thickness of platinum thin film was approximately $4.0 \mu\text{m}$. Solar cells were made by placing the counter electrode on the dye-sensitized TiO_2 electrode, and then the gap of the two glass substrates was filled with electrolyte of the following composition: 0.1 M LiI, 0.05 M I_2 , 0.5 M tertbutylpyridine (TBP) and 0.3 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII) in methoxyacetonitrile as solvent.

For purposes of comparison, the same processes were used to make solar cells using the ITO films ($100 \times 100 \text{ mm}^2$).

2.4. I–V characterization

I–V characteristics of the solar cells (I_{sc} , V_{oc} , FF and η) were derived with a Schlumberger SI 1286. The solar cells under test were illuminated under a xenon lamp (YAMASHITA DENSO YSS-150A solar simulator, $100 \text{ mW}/\text{cm}^2$ at room temperature). The YSS-150A solar simulator was set to AM 1.5 conditions.

3. Results and discussion

The measurements of concentration depth profiles were performed by sequentially applying AES with ion beam sputtering (Fig. 2). The change of the existence ratio of tin and indium was observed at the thickness of approximately

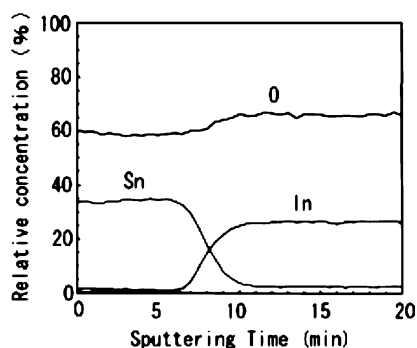


Fig. 2. Depth profiles of Sn, In and O concentration in FTO/ITO films.

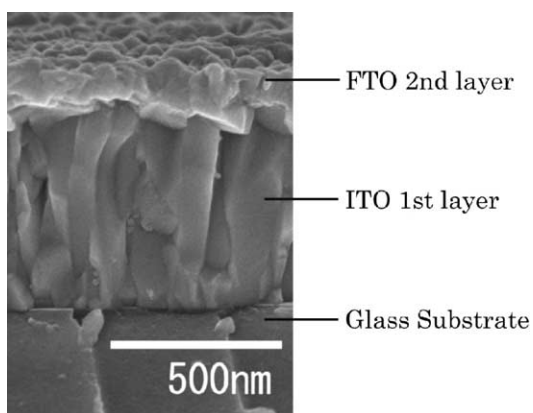


Fig. 3. Cross-sectional FE-SEM image of the double-layered film composed of ITO 1st layer and FTO 2nd layer.

100 nm; therefore, the thickness of FTO films in the FTO/ITO films was confirmed as approximately 100 nm.

Cross-sectional FE-SEM image of the FTO/ITO films is reproduced in Fig. 3. The double-layered films were observed to consist of the ITO in the first layer (thickness

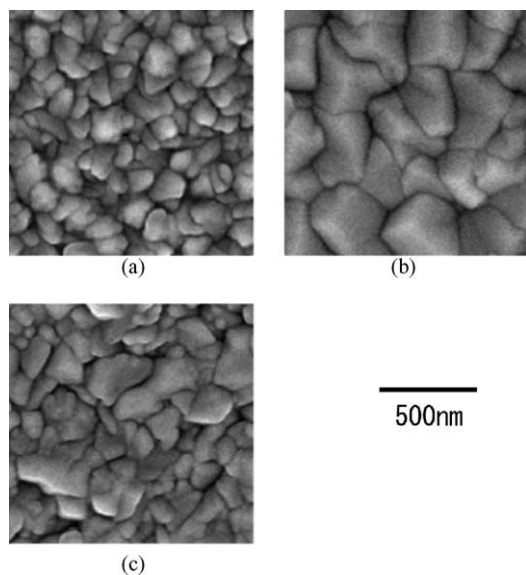


Fig. 4. FE-SEM images showing the surface morphology of (a) FTO, (b) ITO and (c) FTO/ITO films.

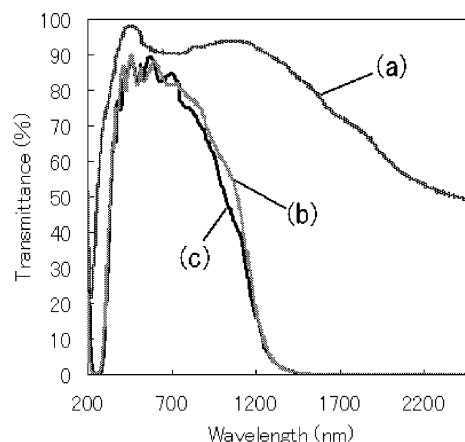


Fig. 5. Optical transmittance of (a) FTO, (b) ITO and (c) FTO/ITO films.

of 720 nm) and the FTO in the second layer (thickness of 100 nm). The surface morphologies of the FTO, ITO and FTO/ITO films are shown in Fig. 4. The average grain sizes of FTO and ITO films were approximately 50 and 150 nm, respectively. As for the FTO films on the ITO films, the

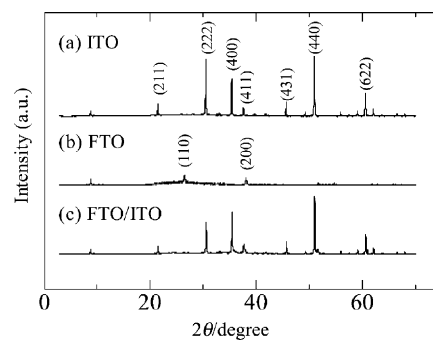


Fig. 6. X-Ray diffraction patterns of (a) ITO, (b) FTO and (c) FTO/ITO films.

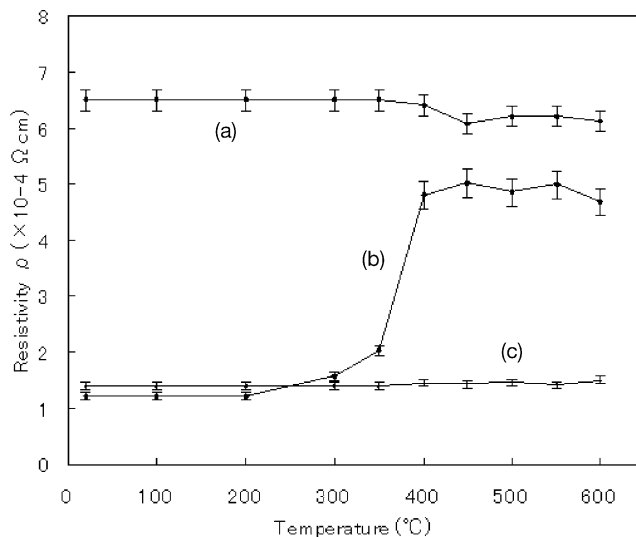


Fig. 7. Dependence of resistivities on annealing temperature for 1 h in the air. (a) FTO, (b) ITO and (c) FTO/ITO films.

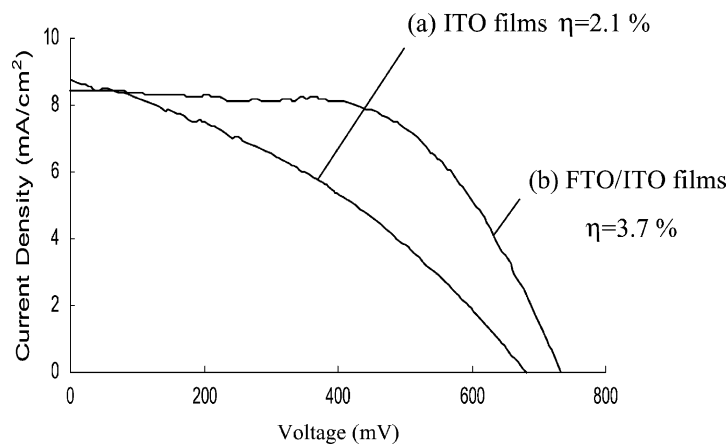


Fig. 8. I - V characteristics of $100 \times 100 \text{ mm}^2$ sized cells using (a) ITO and (b) FTO/ITO films.

grain size was observed about the same that of FTO films. The grain size of the FTO films was not influenced by the grain size of the ITO films.

Fig. 5 shows the transmittance spectra of the FTO, ITO and FTO/ITO films in comparison with the transmittance of the uncoated glass. The transmittance in the visible region was approximately 80%. In the FTO/ITO films, the similar result of the ITO films was obtained in the transmittance spectra.

Fig. 6a shows the XRD spectra of the ITO films. All peaks were assigned to In_2O_3 . Fig. 6b shows the XRD spectra of the FTO films. Diffraction peaks from the (110) and (200) planes of the FTO films were clearly observed. The XRD spectra of the FTO/ITO films are shown in Fig. 6c. Although the diffraction peaks of the In_2O_3 in the FTO/ITO films, those of the SnO_2 were hardly observed. This reason was that FTO films were remarkably thin in comparison with ITO films.

The resistivities of the ITO, FTO and FTO/ITO films are indicated in Fig. 7 as a function of temperature (annealing for 1 h in the air). Before annealing, the resistivities of the ITO, FTO and FTO/ITO films were 1.2×10^{-4} , 6.5×10^{-4} and $1.4 \times 10^{-4} \Omega \text{ cm}$, respectively. Sheet resistances of both the ITO and FTO/ITO films were $1.7 \Omega/\text{square}$. After annealing at 450°C for 1 h in the air, the resistivities of the ITO, FTO and FTO/ITO films were 5.0×10^{-4} , 6.1×10^{-4} and $1.4 \times 10^{-4} \Omega \text{ cm}$, respectively. The sheet resistances of the ITO and FTO/ITO films were 6.9 and $1.7 \Omega/\text{square}$, respectively. Though the resistivity of the ITO films increased more than three times by annealing at the temperature range of 400 – 600°C , the resistivity of the FTO/ITO films increased by less than 10%.

Fig. 8 shows I - V characteristics obtained by $100 \times 100 \text{ mm}^2$ -sized (Total photo-electrode area was $90 \times 90 \text{ mm}^2$) cells. For the DSC using the FTO/ITO films $J_{\text{sc}} = 8.47 \text{ mA}/\text{cm}^2$, $V_{\text{oc}} = 736 \text{ mV}$, $\text{FF} = 0.59$ and $\eta = 3.7\%$ were measured. Measurement of the reference cell using the ITO films resulted in values of $J_{\text{sc}} = 8.75 \text{ mA}/\text{cm}^2$,

$V_{\text{oc}} = 689 \text{ mV}$, $\text{FF} = 0.35$ and $\eta = 2.1\%$. These results prove that FTO/ITO films are effective in the electrode of the DSC.

4. Conclusion

New transparent conductive films, FTO/ITO films, were successfully deposited on a glass substrate by the SPD method. The several characteristics of the films were measured. The lowest resistivity of $1.4 \times 10^{-4} \Omega \text{ cm}$ and an optical transmittance of more than 80% in the visible range of the spectrum were obtained. Heat resistance of the films was also measured. The electrical resistance increased by less than 10%, even when exposed to high temperatures of 300 – 600°C for 1 h in the air. Using these heat-resisting films, the DSC were fabricated. Size of the DSC were $100 \times 100 \text{ mm}^2$. As the results of measurements, we demonstrated the good performance of the DSC, which energy conversion efficiency of $\eta = 3.7\%$ was obtained.

References

- [1] B. O'Regan, M. Grätzel, *Nature* 353 (1991) 737.
- [2] H. Matsui, K. Okada, T. Kawashima, N. Tanabe, *Fujikura Gihō* 104 (2003) 37.
- [3] K.L. Chopra, R.C. Kainthla, D.K. Pandya, A.P. Thakoor, *Phys. Thin Films* 12 (1982) 167.
- [4] M.S. Tomar, F.J. Garcia, *Prog. Cryst. Growth Charact.* 4 (1981) 221.
- [5] E. Shanthi, A. Banerjee, V. Dutta, K.L. Chopra, *J. Appl. Phys.* 53 (1982) 1615.
- [6] K.L. Chopra, S. Major, D.K. Pandya, *Thin Solid Films* 102 (1983) 1.
- [7] M. Fantini, I. Torriani, *Thin Solid Films* 138 (1986) 225.
- [8] S. Kaneko, K. Nakajima, T. Kosugi, K. Murakami, *Ceram. Trans.* 100 (1999) 165.
- [9] T. Kawashima, H. Matsui, N. Tanabe, *Thin Solid Films* 445 (2003) 241.
- [10] G. Bradshaw, A.J. Hughes, *Thin Solid Films* 33 (1976) L5.