Heat Resistant Double-Layered TCO

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New TCO films, FTO films coated on ITO films, were developed for DSC. These films were prepared by a SPD method at a substrate temperature of 350°C in ITO and 400°C in FTO. For ITO deposition, an ethanol solution of $InCl_3 \cdot 4H_2O$ and $SnCl_2 \cdot 2H_2O$ [Sn/(In+Sn), 5 at.%] was sprayed on a glass substrate. 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 $SnCl_4 \cdot 5H_2O$ within the saturated water solution of NH_4F. These films achieved the lowest resistivity of $1.4 \times 10^{-4} \Omega$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 to 600°C for 1 hour in the air. The 100×100 mm^2 large size DSC composed of the films were fabricated to confirm the availability of them. Energy conversion efficiency of η=3.7% was obtained. As the result, the FTO/ITO films showed heat-resisting property in sintering TiO_2 for the DSC.

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 dye sensitized solar cells (DSC) [1) 2)], the paste of fine oxide powders such as titanium oxide is coated on the surface of the ITO films. Then, the paste is calcinated at the temperature range of 400 to 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 dye sensitized solar cell 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 films and FTO films to form on a glass substrate [5)-9)]. Characteristics of the films were investigated. Then, the DSC were fabricated using these heat-resisting films. Moreover energy conversion efficiency was measured.

2. Experimental Section

2.1. General Procedures and Chemicals

All preparations and depositions were carried out in the air. $InCl_3 \cdot 4H_2O$ (purity 99.5%), $SnCl_4 \cdot 5H_2O$ (purity 98.0%), NH_4F (purity 99.9%), ethanol (purity 99.5%), butanol (purity 99.0%) and acetonitrile (purity 99.5%) were purchased from Kanto Chemical Co.,Inc. $SnCl_2 \cdot 2H_2O$ (purity 97.0%) was purchased from Junsei Chemical Co.,Ltd. Iodine (purity 99.8%) was purchased from Wako Pure Chemical Industries, Ltd. LiI (purity 99.9%), 4-tert-butylpyridine (purity 99.0%) and methoxyacetonitrile (purity 99.0%) were purchased from Aldrich Chem, Co. 1,2-dimethyl-3-propylimidazolium iodide was purchased from Shikoku Corporation. All chemicals used were reagent grade.

2.2. Film Formation

Preparation of raw material compounds solution for ITO films and FTO films was as follows: $InCl_3 \cdot 4H_2O$ (5.58g) and $SnCl_2 \cdot 2H_2O$ (0.23g) were dissolved in ethanol (100ml). $SnCl_4 \cdot 5H_2O$ (1.40g) was dissolved in

ethanol (20ml), and a saturated aqueous solution of NH_4F (0.24g) was added. The mixture was placed in an ultrasonic washer for approximately 20 minutes to achieve complete dissolution.

Deposition of FTO/ITO films was as follows: The raw material compound solution was atomized by compressed air at 0.06MPa in pressure. The atomized solution was transported onto a heated TEMPAX #8330 glass substrate ($100\times100\times1.1mm^3$). 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 5ml/min, and the nozzle-substrate distance was fixed to be 600mm. The schematic representation of SPD apparatus is shown in Fig. 1.

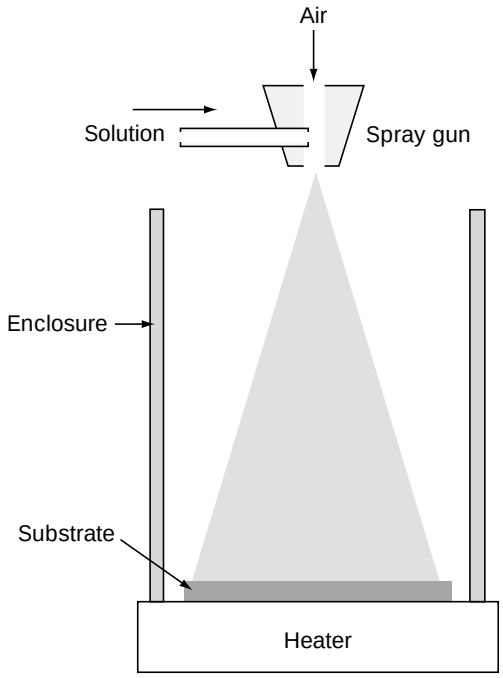

Fig. 1. Schematic Representation of Spray Pyrolysis Deposition Apparatus.

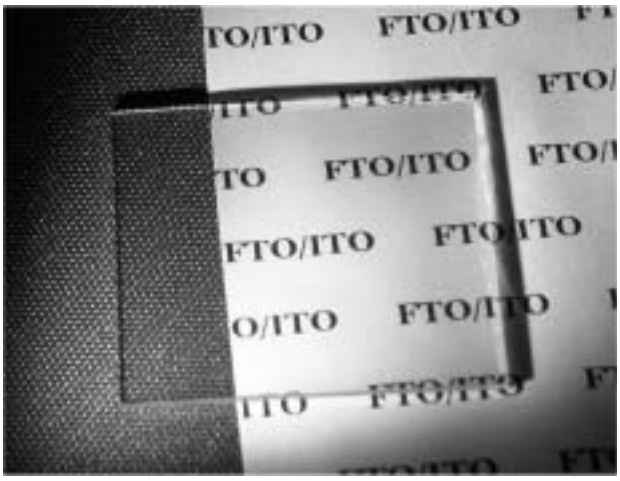

Fig. 2. Photograph of the FTO/ITO Films.

Through the above processes, double-layered films were formed on a glass substrate; ITO films of approximately 720nm in thickness in the first layer and FTO films of approximately 100nm in thickness in the second layer (Fig.2).

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

2.3. 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 also conducted by sequentially applying auger electron spectroscopy (AES) with ion beam sputtering. The AES data was obtained using primary electron beam energy of 5keV which condition was the etching rate of 10nm/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 5kV. The transmittance in the 200-900nm regions was measured with a JASCO V-570 spectrophotometer. The crystal structure of the films was determined by X-ray diffraction (XRD) using Cu-Kα radiation (RIGAKU RAD-1C diffractometer). MITSUBISHI KAGAKU MCP-T600 four-probe type resistance meter measured sheet resistance of the films.

2.4. Solar Cell Fabrication

TiO_2 colloidal printing paste (Ti nanoxide-T, Solaronix SA) was coated on the FTO/ITO films ($100\times100mm^2$) 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 hour. The FTO/ITO films with TiO_2 layer were immersed in 50wt% butanol and 50wt% acetonitrile mixed solution of 0.3mM ruthenium(II) (2, 2'-bipyridyl-4,4'-dicarboxylate)$_2$ $(NCS)_2$ dye (calling as N3 Dye) for 18 hours at room temperature. A counter electrode was prepared with platinum sputtering deposition on a TCO (FTO films; 8Ω/square). Thickness of platinum thin film was approximately 4.0 micron. 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: 0.1M LiI, 0.05M I_2, 0.5M 4-tert-butylpyridine (TBP) and 0.3M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI) in methoxyacetonitrile as solvent.

For purposes of comparison, the same processes were used to make solar cells using the ITO films ($100\times100mm^2$).

2.5. I-V Characterization

I-V characteristics of the solar cells (I_{sc}, V_{oc}, FF and η) were derived with an Schlumberger SI 1286. The solar cells under test were illuminated under a xenon lamp (YAMASHITA DENSO YSS-150A solar simulator, 100mW/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.3). The change of the existence ratio of tin and indium was observed at the thickness of approximately 100nm, therefore the thickness of FTO films in the FTO/ITO films was confirmed as approximately 100nm.

Cross-sectional FE-SEM image of the FTO/ITO films is reproduced in Fig.4. The double-layered films were observed to consist of the ITO in the first layer (thickness of 720nm) and the FTO in the second layer (thickness of 100nm). The surface morphologies of the FTO, ITO and FTO/ITO films are shown in Fig.5. The average grain sizes of FTO and ITO films were approximately 50nm and 150nm, respectively. As for the FTO films on the ITO films, the grain size was observed about the same of FTO films. The grain size of the FTO films was not influenced by the grain size of the ITO films.

Fig. 6 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. 7a shows the XRD spectra of the ITO films. All peaks were assigned to In_2O_3. Fig.7b 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.7c. Although the diffraction peaks of the In_2O_3 in the FTO/ITO films, those of the SnO_2 were hardly observed.

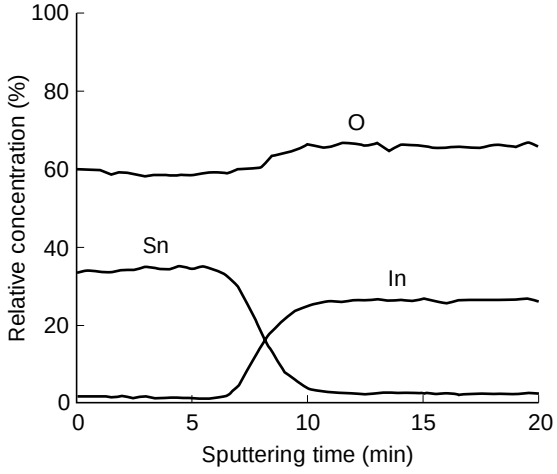

Fig. 3. Depth Profiles of Sn, In, O Concentration in FTO/ITO Films.

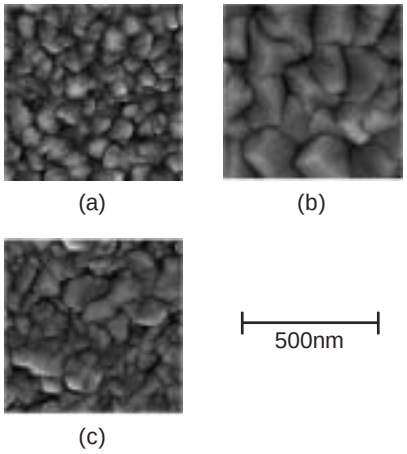

Fig. 5. FE-SEM Images Showing the Surface Morphology of (a) FTO Films, (b) ITO Films and (c) FTO/ITO Films.

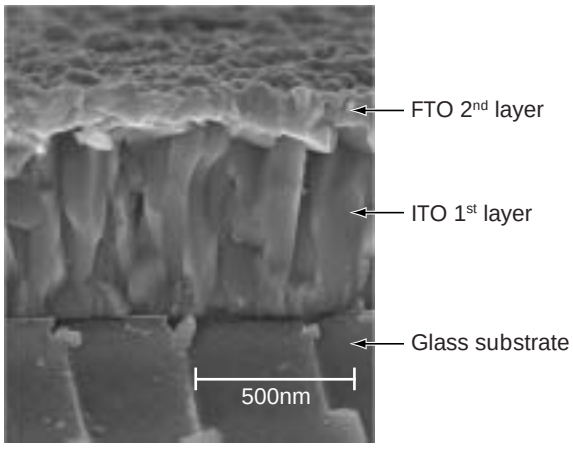

Fig. 4. Cross-sectional FE-SEM Image of the Double-layered Film Composed of ITO 1st Layer and FTO 2nd Layer.

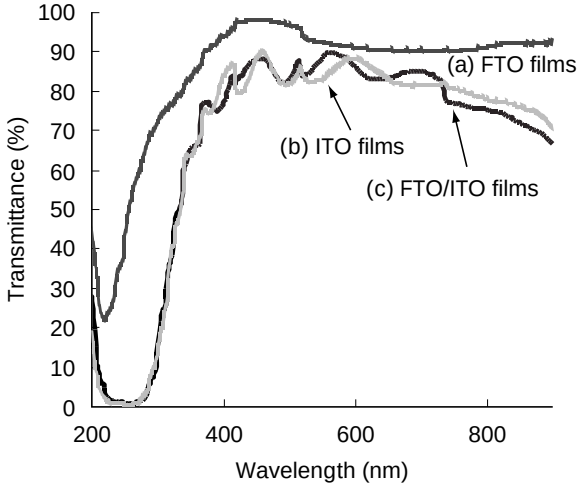

Fig. 6. Optical Transmittance of (a) FTO Films, (b) ITO Films and (c) FTO/ITO Films.

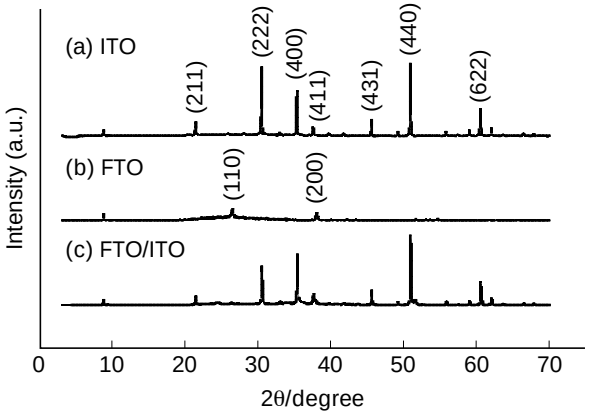

Fig. 7. X-Ray Diffraction Patterns of (a) ITO Films, (b) FTO Films, and (c) FTO/ITO Films.

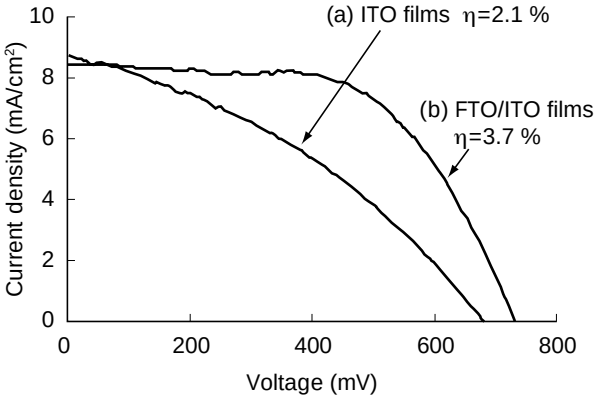

Fig. 9. I-V Characteristics of 100×100 mm² Sized Cells Using (a) ITO Films and (b) FTO/ITO Films.

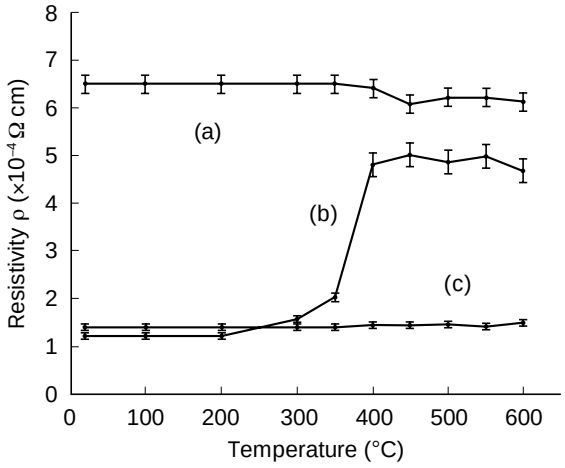

Fig. 8. Dependence of Resistivities on Annealing Temperature for 1 Hour in the Air. (a) FTO Films, (b) ITO Films and (c) FTO/ITO Films.

The resistivities of the ITO, FTO and FTO/ITO films are indicated in Fig.8 as a function of temperature (annealing for 1 hour in the air). Before annealing, the resistivities of the ITO, FTO and FTO/ITO films were $1.2\times10^{-4}\Omega$cm, $6.5\times10^{-4}\Omega$cm and 1.4×10^{-4} Ωcm, respectively. Sheet resistances of both the ITO and FTO/ITO films were 1.7Ω/square. After annealing at 450°C for 1 hour in the air, the resistivities of the ITO, FTO and FTO/ITO films were $5.0\times10^{-4}\Omega$cm, $6.1\times10^{-4}\Omega$cm and $1.4\times10^{-4}\Omega$cm respectively. The sheet resistances of the ITO and FTO/ITO films were 6.9Ω/square and 1.7Ω/square, respectively. Though the resistivity of the ITO films increased more than three times by annealing at the temperature range of 400 to 600°C, the resistivity of the FTO/ITO films increased by less than 10%.

Fig.9 shows I-V characteristics obtained by 100×100mm^2 sized (Total photo-electrode area was 90×90mm^2) cells. For the DSC using the FTO/ITO films J_{sc} = 8.47mA/cm^2, Voc = 736mV, FF = 0.59 and η=3.7% was measured. Measurement of the reference cell using the ITO films resulted in values of J_{sc} = 8.75mA/cm^2, V_{oc} = 689mV, FF = 0.35 and η=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 $1.4\times10^{-4}\Omega$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 to 600°C for 1 hour in the air. Using these heat-resisting films, the DSC were fabricated. Size of the DSC was 100×100mm^2. As the results of meas-urements, we demonstrated the good performance of the DSC, which energy conversion efficiency of η=3.7% was obtained.

References

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