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ABSTRACT

Fluorine doped tin oxide (FTO) transparent conductive oxide (TCO) film for dye-sensitized solar cell (DSSC) was investigated. Haze of the incident light through TCO film was easily tuned by controlling the surface morphology of FTO deposited on tin doped indium oxide (ITO) nano-particle seed layer pre-coated on a glass substrate, and the light harvest within the cell was effectively enhanced with high haze TCO film. The conversion efficiency of DSSC fabricated with TCO film with the haze of 30.1 % reached as high as 7.7 %, attributing to the consequence of the effective light harvest with the scattering within the cell.

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1. Introduction

A dye-sensitized solar cell (DSSC) has been a hot topic as a new energy resource during the decades due to its scientific and technological importance [1-4]. DSSC consists of a working electrode with a dye adsorbed porous TiO_2 layer on a transparent conductive oxide (TCO) film, a platinum counter electrode, and an anhydrous electrolyte. Among many elements for DSSC, since almost half of the production cost of DSSC module was calculated to be occupied by a glass substrate with TCO film, how to reduce the cost is one of the keys to develop DSSCs to a practical use [5]. We have developed spray pyrolysis deposition (SPD) and reported a preparation of TCO film by this simple film formation technique [6-18]. Especially for TCO film for DSSC, the following three features were found to be required; a high electrical conductivity that reduces a charge recombination, a high transmittance that suppresses an optical absorption loss, and an effective light harvest with an antireflective and/or a scattering effect [16, 17]. In a typical silicon solar cell, haze of the incident light through TCO film is reported to be one of the most important factors that enhances the light harvest, and is tuned by controlling the interface morphology between semiconductive junctions [19]. On the other hand, in DSSC with TCO film, several-micrometer-thick fluorine doped tin oxide (FTO) layer is required to promote the grain growth to produce high haze TCO film, which decreases the light harvest within the cell due to an optical absorption with a thick FTO layer [16]. In this study, the problem was solved by inserting tin doped indium oxide (ITO) nano-particle layer between FTO and a glass substrate. FTO grain growth was effectively promoted with ITO nano-particle seed layer, and thick FTO layer declining the transmittance was no longer necessary for high haze TCO film. We found that haze played an important role in enhancing the light harvest within the cell to produce DSSC with high photovoltaic performance.

2. Experimental

FTO film was deposited by SPD technique as follows [8, 11-14, 16-18, 20-23]. 0.1 M of tin(IV) chloride pentahydrate, $SnCl_4 \cdot 5H_2O$ (Wako Pure Chemical Industries), ethanol solution with ammonium fluoride, NH_4F (Wako Pure Chemical Industries), with the molar ratio of $[NH_4F]/[SnCl_4 \cdot 5H_2O]=1.6$ was prepared for a source solution. The solution was sprayed through a nozzle (Fuso Seiki Lumina STA-6R-1mmϕ) by a compressed air onto the glass substrate on a heater. The mist was pyrolized on the substrate at the substrate temperature of 450 ºC to form FTO film in air. Some of the glass substrates underwent the coverage of ITO nano-particle suspension (Aldrich 10 nm in particle size) layer by spin coating technique and dried in air before depositing FTO layer. Transmittance and reflectance of TCO film in the visible light region were measured by a spectrophotometer (JASCO V-570), and the surface morphology of the film was observed by a field emission scanning electron microscope (FE-SEM JEOL JSM-6320F). Hall effect measurement was done to TCO films by Hall system (ECOPiA HMS-3000) using van der Pauw method.

Porous TiO_2 layer was deposited on FTO coated glass substrate by SPD technique from the mixture solution of TiO_2 powder (Degussa P25) and suspension (TAYCA TKC-302) [11-13, 16, 17]. N719 (Solaronix SA Ruthenium 535-bisTBA) dye was adsorbed on the surface of porous TiO_2 layer by refluxing the ethanol solution with the electrode at 80 ºC for 3 h. A few drop of an electrolyte containing I^-/I_3^- (Tomiyama Pure Chemical Industries EL-A1) was sandwiched between the dye-adsorbed TiO_2 electrode and a platinum coated glass substrate to fabricate DSSC. The current-voltage characteristic measurement was done under the quasi-sunlight of AM-1.5 and 100 $mW \cdot cm^{-2}$ (Asahi Specrta HAL-320) directly irradiated to the cells with an apparent area of 0.21 cm^2.

3. Results and discussion

Figures 1(a)-1(c) and 1(d)-1(f) show SEM images of FTO layer deposited on a bare glass substrate and on ITO nano-particle layer, respectively, and Table 1 summarizes the optical and electrical parameters of the films. A pyramidal texture structure consisted of rock-ice FTO grains were detected for all TCO films, which is a typical image of the film deposited from tin(IV) chloride pentahydrate by SPD technique [16]. The grain size increased with the thickness of FTO layer on the bare glass substrate from (a) 100 nm in grain size at 0.91 μm in FTO thickness to (c) 500 nm at 1.74 μm. FTO grain growth was further promoted on ITO nano-particle layer, and the size increased from (d) 300 nm in grain size at 0.91 μm in FTO thickness to (f) 800 nm at 1.74 μm. ITO nano-particles seemed to act as a seed layer for FTO grain growth. According to the mechanism behind the film formation by SPD technique, the mist from the nozzle reaches onto the substrate, spreads widely, and then pyrolizes to form a homogeneous film [24]. On the other hand, on the porous ITO nano-particle layer, the mist is trapped on the particles and pyrolizes rapidly to induce necking between particles, followed by FTO grain growth. Further mist feeding contributes to the thick FTO layer as well as the grain growth. Since the thickness of ITO nano-particle seed layer was less than 100 nm, the apparent transmittance through a glass substrate in the visible light region was kept above 70% for all TCO films, while haze was effectively enhanced with FTO grain size. Haze is defined as a ratio of the diffused light to the whole transmitted light through the film on a glass substrate. The electrical mobility of FTO layer increased with FTO grain growth, while the electrical resistivity was almost comparable for all films due to the decrease in the carrier density owing to the dissipation of fluoride in the film formation. Although the haze is approximately 30 % for both FTO layer (b) and (d), the layer (d) shows higher transmittance than (b), attributing to the fact that thin FTO layer, less than 1 μm in the thickness, suppressed the light absorption to enhance the transmittance of the incident light through the film. In this study, TCO film both with high haze and transmittance was successfully produced and supplied to DSSC.

Figure 2 shows incident photon-to-current efficiency (IPCE) spectra of DSSCs fabricated with various TCO films. IPCE was enhanced in the whole wavelength region between 300 and 800 nm for the cell fabricated with high haze TCO film. The result seems to be different from that of the light confinement effect with the working electrode consisted of large rutile TiO_2 particles / porous anatase TiO_2 double layer, which is reported to be effective only in the higher wavelength region above 600 nm [25-27]. We found that haze is one of the most important parameters to optimize TCO film for DSSCs. Additionally, comparing with the cell (b) and (d), although both cells were fabricated with TCO film with the haze of approximately 30%, IPCE for the cell (d) was larger than that for (b). This is because TCO film with higher transmittance was favorable for the effective light harvest. On the other hand, for the cell with higher haze above 35 %, IPCE was declined with haze due to the low transmittance. TCO film both with high haze and transmittance is an ideal one to fabricate DSSC with high photovoltaic performance.

Figure 3 shows photovoltaic parameters of DSSCs fabricated with TCO films with various haze. The short circuit current density, J_{SC}, was enhanced with high haze TCO film, corresponding to longer optical path length within TiO_2 working electrode in the consequence of a diffusional light, attributing to the light scattering effect within the cell [28]. We found TCO film with ITO nano-particle seed layer was very effective to enhance J_{SC}. Additionally, TCO film consisted of large FTO grains with high electrical mobility reduces the recombination of photoelectrons due to the relatively low carrier density, declining the electron scattering. TCO film with ITO nano-particle layer can achieve both high haze and transmittance, enhancing the light harvest within the cell as shown in Fig. 2. On the other hand, the open circuit voltage, V_{OC}, and fill factor, *FF*, did not depend on haze, indicating that the internal resistance within the cell is almost comparable for all DSSCs, although FTO grain size, or the surface roughness of FTO layer, was strongly dependent on the thickness of FTO layer [29, 30]. TCO film with the haze of 30.4% with the transmittance of 78.0% reached the highest J_{SC}, and the overall conversion efficiency, η, was enhanced as high as 7.7%. However, since TCO film with higher haze above 35 % reduced the transmittance through the thick FTO layer to decrease η as well as J_{SC}, how to produce high haze TCO film without declining the transmittance is our next topic for DSSCs.

4. Conclusions

High haze TCO film was deposited on ITO nano-particle seed layer without declining the transmittance of the incident light through TCO film. Since the increase in haze of TCO film corresponds to the longer optical path length to enhance the light harvest within the cell, the short current density was effectively enhanced to achieve high conversion efficiency. We found that haze is one of the most important parameters in tuning TCO film for DSSC.

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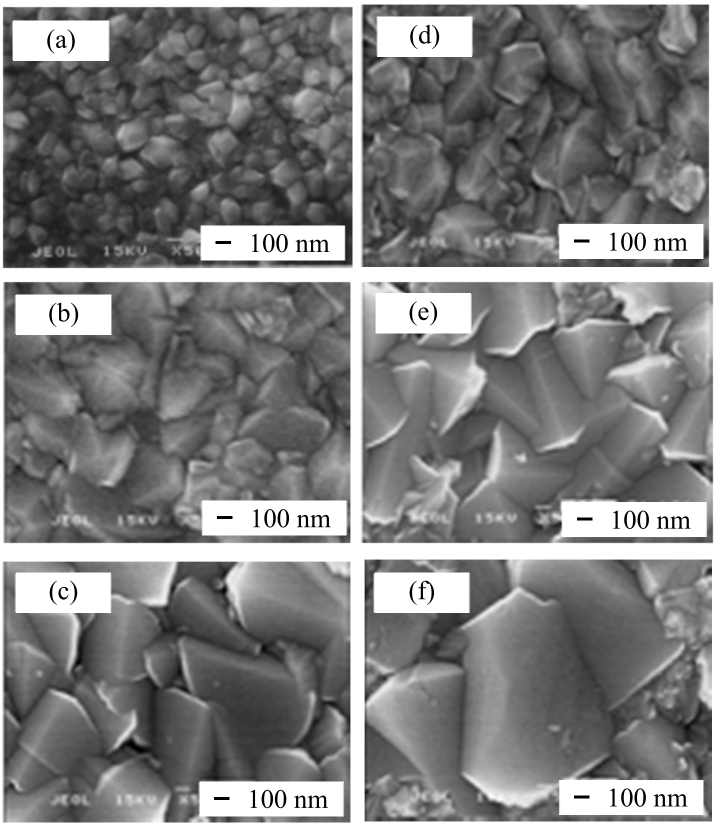

Fig. 1 (Color online) Surface morphology of FTO layer with various film thickness deposited on a bare glass substrate (a)-(c) or on ITO nano-particle pre-coated seed layer (d)-(f). The thickness of FTO layer is 0.91 μm for the film (a) and (d), 1.31 μm for (b) and (e), and 1.74 μm for (c) and (f).

Table 1 Optical and electric properties of FTO layer with various film thickness deposited on a bare glass substrate (a)-(c) or on ITO nano-particle seed layer (d)-(f).

	(a)	(b)	(c)	(d)	(e)	(f)
Seed layer		–			ITO nano-particle	
FTO thickness (μm)	0.91	1.31	1.74	0.91	1.31	1.74
Transmittance [a] (%)	77.5	74.0	71.8	78.0	73.8	71.7
Haze [a] (%)	15.7	36.3	49.1	30.1	41.4	58.3
Carrier density ($\times 10^{20}$ cm^{-3})	10.1	8.5	7.1	9.7	7.7	7.4
Mobility (cm^2·V^{-1}·s^{-1})	12.9	21.5	23.6	18.6	28.0	25.5
Resistivity ($\times 10^{-4}$ Ω·cm)	4.8	3.7	3.4	3.5	3.0	3.2

[a] Average value in the visible light region

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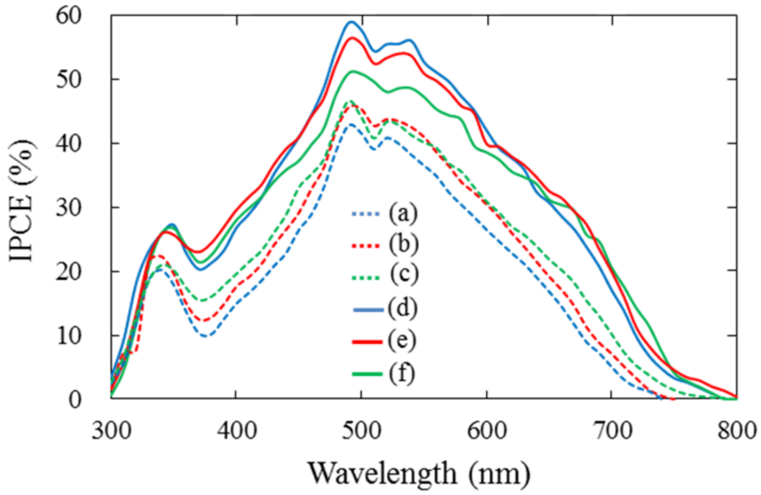

Fig. 2 (Color online) IPCE spectra of DSSCs fabricated with various TCO films. The thickness of FTO layer is 0.91 μm for the film (a) and (d), 1.31 μm for (b) and (e), and 1.74 μm for (c) and (f).

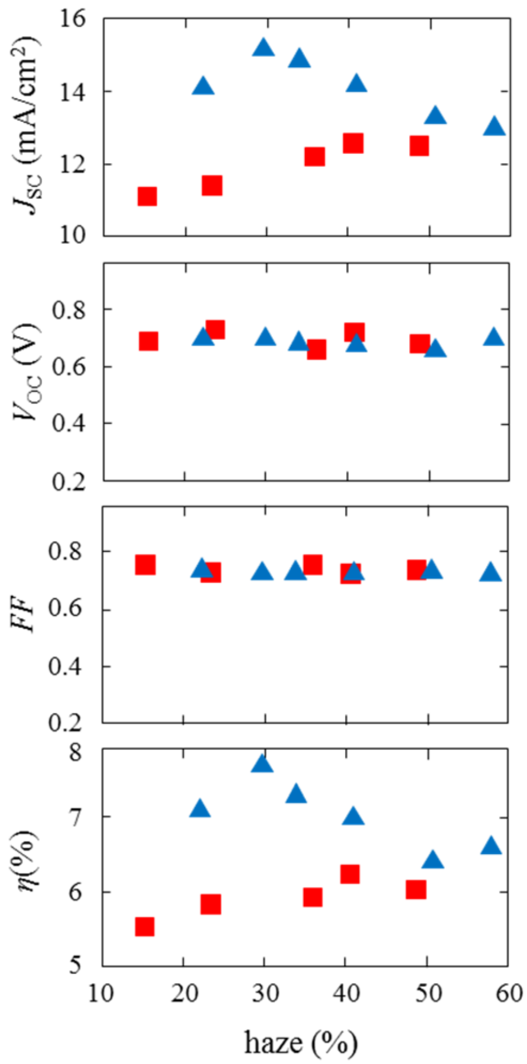

Fig. 3 (Color online) Photovoltaic parameters of DSSCs fabricated TCO films with various haze. The symbol of square and triangle corresponds to TCO film deposited on a bare glass substrate and on ITO nano-particle seed layer, respectively