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Comparison of transparent conductive indium tin oxide, titanium-doped indium oxide, and fluorine-doped tin oxide films for dye-sensitized solar cell application

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Abstract – In this study, we investigate the photovoltaic performance of transparent conductive indium tin oxide (ITO), titanium-doped indium oxide (ITiO), and fluorine-doped tin oxide (FTO) films. ITO and ITiO films are prepared by radio frequency magnetron sputtering on soda-lime glass substrate at 300 °C, and the FTO film used is a commercial product. We measure the X-ray diffraction patterns, AFM micrographs, transmittance, sheet resistances after heat treatment, and transparent conductive characteristics of each film. The value of electrical resistivity and optical transmittance of the ITiO films was 4.15×10^{-4} Ω-cm. The near-infrared ray transmittance of ITiO is the highest for wavelengths over 1,000 nm, which can increase dye sensitization compared to ITO and FTO. The photoconversion efficiency (η) of the dye-sensitized solar cell (DSC) sample using ITiO was 5.64%, whereas it was 2.73% and 6.47% for DSC samples with ITO and FTO, respectively, both at 100 mW/cm^2 light intensity.

Keywords: Titanium-doped indium oxide, Transparent conductive oxide, Dye-sensitized solar cell, RF magnetron sputtering

1. Introduction

The recent advances in photovoltaic technology have triggered considerable interests in the field of solar power as an alternative and renewable source of electricity. Dye-sensitized solar cells (DSCs) devised by Prof. M. Gratzel have attracted much attention over the last decade because of their potentially high-energy conversion efficiency and possible low production cost [1–3]. Typically, DSCs consist of a transparent conducting oxide (TCO) layer and dye-sensitized TiO_2 electrode in contact with electrolyte and is completed by an inert counter electrode. Fig. 1 shows a general image of the DSC structure used in this study. A platinized conductive glass is used as a counter electrode. An electrolyte containing I^-/I_3^- redox couple is filled between the two electrodes. As a part of photoanode in DSCs, TCO should have low electrical resistance, high optical transmittance, and high photoelectrical response (depending on application). TCO films are widely employed as electrodes because they have excellent transmittance (about 90%) in visible wavelength and high electrical conductivity (~10^{-4} Ω-cm). The common TCO materials used for DSCs are fluorine-doped tin oxide (FTO) and indium tin oxide (ITO), which can be prepared by various techniques such as physical vapor deposition (PVD) or chemical vapor deposition (CVD), direct current (DC) and RF magnetron sputtering, electron beam evaporation, spray pyrolysis, and the sol-gel method. Among these, the RF magnetron sputtering method is the most compatible with the circuit processing, which can continuously produce high-quality films at a lower processing temperature. Both FTO and ITO films have limitations for the infrared ray (IR) radiation. Furthermore, ITO films have low thermal stability as a TCO electrode. Thus, it is difficult to further improve the photovoltaic efficiency of the DSCs using either FTO or ITO. Meanwhile, ITiO has not only a low sheet resistance but also high electron mobility and near-IR transmittance, as reported in previous work [4–6].

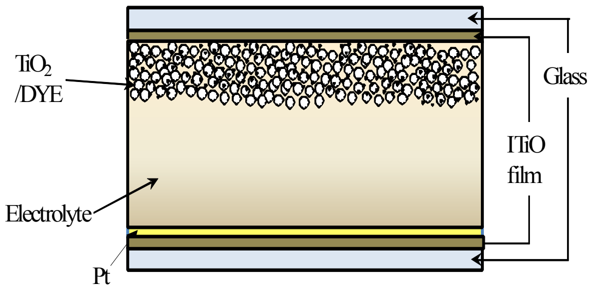

Fig. 1. Image of the fabricated DSC structure

In this study, we investigate the photovoltaic performance of transparent conductive ITO, ITiO, and FTO films.

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ITO and ITiO films are deposited by RF magnetron sputtering on soda-lime glass substrate at 300 °C, and the FTO film used is a commercial FTO glass. The transparent conductive characteristics for the prepared films are investigated, as well as the film structure and morphology, which are then compared with the commercial FTO glass.

2. Experiment

The TCO materials investigated in this study are ITiO, ITO, and FTO. The FTO glass is commercially available from Pilkington Co., whereas the thin films of ITiO and ITO are prepared using RF magnetron sputtering. Table 1 shows the deposition condition of the ITO and ITiO films in this experiment. ITiO thin films were sputter deposited from a target with a composition of 95 wt.% In_2O_3 and 5 wt.% TiO_2 on soda-lime glass substrate at RF power (Prf) of 200 W. The target was 100 mm in diameter, with a sheet resistivity of 8 Ω/sq. The total pressure of Ar (97%) and O_2 (3%) mixed gases was maintained at 4 mTorr during deposition. The growth rate of the film was ~10nm/minute. The substrate was heated at 250 °C during deposition. The ITO films were also sputter deposited at RF power of 200 W and gas pressure of 4 mTorr. The fabrication process of DSCs begins with soaking the TCO/TiO_2 films for 48 hours at room temperature in a dye solution, which is 0.3 mM solution of N3 dye [cis-bis(thiocyanate)bis(2, 2′-bipyridyl-4, 4′-dicarboxylate) ruthenium(II)] in ethanol[7]. The Pt counter electrode was prepared on the ITiO glass by coating a few droplets of 5 mM PtCl4 isopropanol platinum solution followed by heating at 450 °C for 30 minutes. Electrode spacing and sealing were ensured by using 60 μm thick Surlyn film (DuPont) spacers. The electrolyte used in the solar cell contained 0.1 M LiI, 0.1 M I2, 0.5 M 1,2-dimethyl-3-propylimidazolium iodine, and 0.5 M tert-butylpridine (TBP) in methoxypropionitrile. The electrolyte was introduced into the clamped electrode by capillary action. The electrical resistivity of the ITiO films was measured using the four-point probe method. The commercial FTO glass and the as-deposited films of ITiO and ITO were heat treated for 10 minutes at temperatures of up to 500 °C. Their thermal stabilities were examined by measuring the sheet resistance after heat treatment. The various structure processing parameters are measured using X-ray diffraction (XRD; Rigaku Co., D/max 2100H, Japan) and atomic force microscopy (AFM). In addition, the characteristics of the electrochemical impedance analyzer (EIA; IM6, ZAHNER) and the photovoltaic performance of each as-fabricated DSC sample using ITiO, ITO, and FTO were evaluated at 100 mW/cm^2 light intensity.

Table 1. RF magnetron sputtering conditions for ITiO and ITO film deposition

Target	ITiO (Ti: 5 wt%)	ITO	FTO
RF power (W)	200	200	Pilkington glass
Working pressure	4 mTorr	4 mTorr	
Operating gas	Ar/O_2 (3%)	Ar/O_2 (3%)	
Target substrate distance	80 mm	80 mm	
Deposition time	30 minutes	30 minutes	
Annealing temperature (°C)	250	250	

3. Results and discussion

Fig. 2 shows the XRD patterns of the ITiO, ITO, and FTO thin films after annealing at 500 °C. As shown in Fig. 2, the preferred orientation peaks of the ITiO, ITO, and FTO films are (400), (222), and (110), respectively. Furthermore, the intensity of the heated ITO film decreased rapidly, but the diffraction intensities of the ITiO and FTO films heated at 500 °C slightly decreased. It can be generally seen that the ITiO and ITO films are deposited in the crystalline phase, instead of forming amorphous phase at low substrate temperature (~300 °C) and at high deposition rate (~10 nm/minute), allowing sufficient thermal energy.

The variation in the columnar microstructure of the prepared thin films is investigated through AFM observation. Fig. 3 shows the sample AFM images of the ITiO, ITO, and FTO thin films after annealing at 500 °C. The RMS roughness of the ITiO, ITO, and FTO films before annealing was 44, 39, and 236 μm, respectively; the RMS roughness of the heated thin films was 33, 26, and 167 μm, respectively. Thus, through the annealing process at 500 °C, the roughness of films decreased by about 30%. Because FTO films were fabricated by the CVD method, they have the highest roughness value.

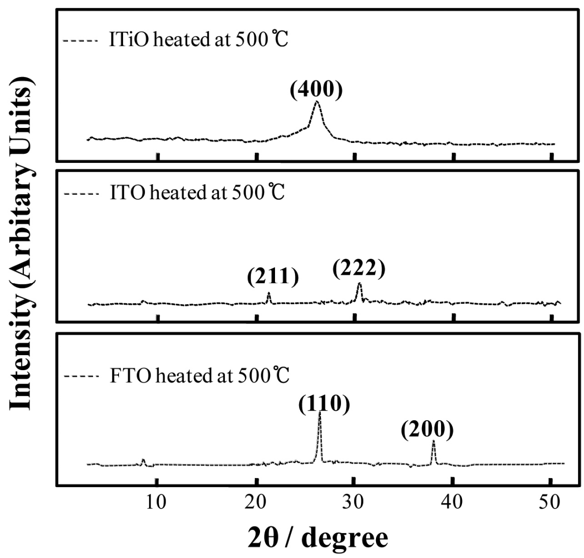

Fig. 2. X-ray diffraction patterns obtained from as-deposited: (a) ItiO; (b) ITO films; (c) FTO glass

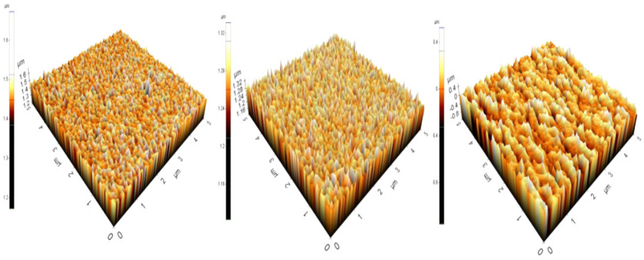

Fig. 3. AFM micrographs showing the surface morphologies of ITiO, ITO films, and FTO glass

Fig. 4 shows the optical transmittance measured over the wavelength range of 350–2,000 nm. The UV absorption edge is located at approximately 350 nm. The transmittance of ITiO is about 85% for wavelengths of UV and visible light, which is a good property for a TCO electrode, although the transmittance of optical spectra shows oscillations in the visible and IR regions. The ITiO film shows high transmittance in the visible region compared to the other ITO and FTO samples. On the other hand, both ITO and ITiO have higher transmittance in the near-infrared (more than 1,200 nm wavelength) region. In addition, the transmittance of ITiO and FTO is similar to that before the heated films after 500 °C annealing, whereas the transmittance of ITO films decreased slightly in the visible and IR regions.

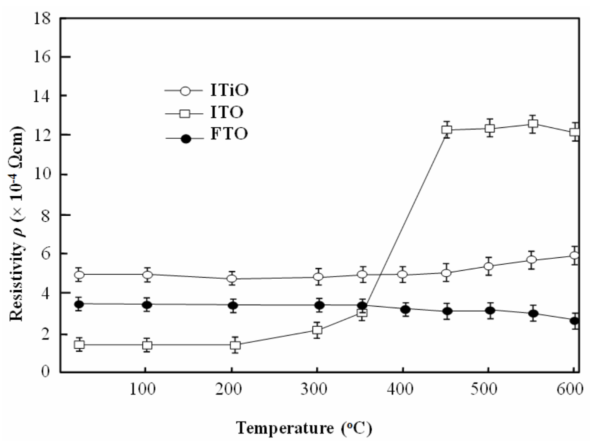

Fig. 4. Optical transmittance of ITiO, ITO flims, and FTO glass

Fig. 5 shows the variation sheet resistance of the FTO glass, ITiO, and ITO films prepared by heat treatment on ambient temperature of up to 800 °C for 10 minutes. The sheet resistance of the ITiO and FTO films became constant at 4.15×10^{-4} Ω-cm and 2.35×10^{-4} Ω-cm, respectively. On the other hand, the sheet resistivity of the ITO films was significantly deteriorated by heating at temperatures over 400 °C, although it is still less than that of the FTO and ITiO films.

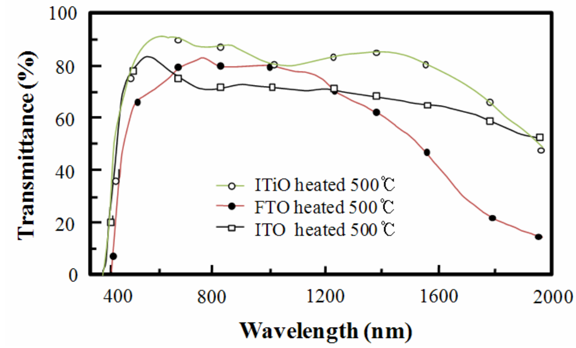

Fig. 5. Variation of sheet resistances after heat treatment at each temperature for 10 minutes

Table 2 shows I-V characteristics of the DSCs using the FTO glass, ITO, or ITiO films. The conversion efficiency η of the samples could be calculated from the following expression:

$$\eta = (J_{sc} \cdot V_{oc} \cdot ff) / P \quad (1)$$

Where J_{sc} is the photocurrent density at the short-circuit condition, V_{oc} is the open-circuit voltage, ff is the fill factor, and P is the intensity of the incident light. The conversion efficiency of 6.47%, 2.73%, and 5.64% was obtained with DSC samples using the FTO glass, ITO, or ITiO films, respectively. Although the DSC sample using ITiO film is less efficient than that using commercial FTO, the differences are not significant since the ITiO film was compared with bulk FTO glass. In general, the bulk condition would be more effective for electron transport than thin film. Considering the as-reported conversion efficiency (η) of ~7.2% for a typical DSC [9], ITiO films can be a promising alternative for FTO.

Table 2. Photovoltaic characteristics of the DSCs using FTO, ITiO, and ITO electrodes

	FTO	ITO	ITiO
V_{oc} (V)	0.78	0.63	0.75
I_{sc} (mA)	3.06	2.59	2.94
J_{sc} (mA/cm^2)	10.96	8.23	10.85
FF	0.53	0.37	0.47
E_{ff} (%)	6.47	2.73	5.64
V_{max} (V)	0.66	0.61	0.64
Area (cm^2)	0.25	0.25	0.25

4. Summary and conclusion

In this study, we investigate the photovoltaic performance of transparent conductive ITiO, FTO, and ITO thin films. ITiO and ITO thin films are deposited on a soda-lime glass substrate by RF magnetron sputter method at relatively low substrate temperature (~300 °C) and at high rate (~10 nm/minutes), whereas the FTO film used is a commercial FTO glass. We investigate the electrical and optical properties of these films such as X-ray diffraction patterns, AFM micrographs, optical transmittance, sheet resistances, and photovoltaic characteristics. The near-IR transmittance of ITiO is the highest for wavelengths over 1,000 nm, which can increase dye sensitization in DSCs compared to ITO and FTO. The photoconversion efficiency (η) of the DSC sample using ITiO was 5.64%, whereas it was 2.73% and 6.47% from DSCs using ITO and FTO, respectively, both at 100 mW/cm^2 light intensity.

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