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ITO/ATO/TiO_2 triple-layered transparent conducting substrates for dye-sensitized solar cells

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ABSTRACT

A novel transparent conductive oxide film based on the triple-layered indium tin oxide (ITO)/antimony-doped tin oxide (ATO)/titanium oxide (TiO_2) has been developed for dye-sensitized solar cells by using radio frequency magnetron sputtering technique. Effects of the absence and presence of TiO_2 layer and the ITO layer thickness were investigated. Deposition of ATO layer was found to stabilize the thermal instability of ITO. Little change in sheet resistance and optical transmittance was observed by introduction of insulating thin TiO_2 layer on top of the ATO layer, whereas photovoltaic performance was significantly influenced. The conversion efficiency was improved from 4.57% without TiO_2 layer to 6.29% with TiO_2 layer. The enhanced photovoltaic performance with addition of TiO_2 layer was attributed mainly to the improved adhesion and partially to the reduced electron loss at the ITO/ATO conductive layer. Increase in the ITO layer thickness resulted in a slight decrease in photocurrent due to the reduced optical transmittance. When compared with the conventional fluorine-doped tin oxide (FTO), the ITO/ATO/TiO_2 conductive material exhibited similar photocurrent density but higher photovoltage and fill factor, resulting in better conversion efficiency.

1. Introduction

Transparent conductive oxides (TCOs) have been widely used for opto-electronic applications and are essential for solar cell application since they provide combined physical properties of visible light transmittance for light harvest and electrical conductivity for collecting current. It is, therefore, obvious that TCO is one of important components for solar cells. Although desirable characteristics of TCO materials are common to all solar cell technologies, each solar cell technology has different requirements for the TCO layers [1].

Unlike the conventional p–n junction solid-state solar cells, dye-sensitized solar cell (DSSC) [2] is a new approach using nanocrystalline TiO_2 (nc-TiO_2) whose surfaces were chemically covered with dye molecules to collect electrons and ionic mediators to collect holes. In DSSC, typically two sheets of fluorine-doped tin oxide (FTO; SnO_2:F) have been used as the back contact for the nanostructured TiO_2 film and the front electrode aided by a thin coating of Pt nanoparticles. FTO is known to be thermally stable up to 650 °C [3] and thereby suitable for thermal process in preparing TiO_2 film at 500 °C. Tin-doped indium oxide (ITO; In_2O_3:Sn) is expected to be better than FTO because of better transparency and conductivity [4]. However, ITO is not suitable for DSSC application because its conductivity decreases remarkably during the thermal process, leading to significant reduction of conversion efficiency in DSSC. Recently, ITO film covered with thin FTO layer was developed to improve heat resistance, where the resistivity of the ITO/FTO film was confirmed to be stable at 600 °C for 1 h in air. Conversion efficiency (3.7%) of the ITO/FTO-based DSSC showed 76% higher than that (2.1%) of the ITO-based one mainly due to thermal stability [5,6]. In addition, ITO/FTO showed much lower resistivity than FTO, which is beneficial to large-area DSSC devices. Similarly, ITO film overcoated with thin SnO_2 film was studied as a TCO layer for DSSC, where the ITO/SnO_2-based cell exhibited higher photovoltaic performance than the ITO-based one [7]. Although the ITO-based bilayered structure demonstrated better photovoltaic performance than ITO as is, there may be an adhesion issue as ITO surface is known to be smooth and flat, yielding poor adhesion with nanoparticle TiO_2 coating. We have thus motivated to develop ITO-based TCO substrates with improved adhesion to nanoparticle TiO_2 coating without any loss in transparency and electrical conductivity.

In this paper, we report on preparation and photovoltaic performance of the triple-layered TCO substrates based on the ITO/ATO (antimony-doped tin oxide)/TiO_2 structure. ITO films with thickness ranging from 150 to 500 nm were first formed on glass substrate, and then ATO layer with thickness of 100 nm was

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deposited on the top of the ITO layer. Finally 30-nm-thick TiO_2 layer was deposited on the ATO-coated ITO film. Effects of the thin TiO_2 layer and the ITO layer thickness on electrical sheet resistance, optical transmittance, photovoltaic properties and adhesion characteristics by electrical contact were studied, and those properties were compared with the conventional FTO substrate.

2. Experimental

2.1. ITO/ATO/TiO2 conducting substrates fabrication

Transparent conducting substrates based on ITO/ATO/TiO_2 triple-layered structure were prepared on glass substrate by radio frequency (rf) magnetron sputtering of In_2O_3–SnO_2 (10 wt%), SnO_2–Sb_2O_3 (6 wt%) and TiO_2 targets. The deposition temperature of ITO was 500 °C, and that of ATO and TiO_2 was 300 °C. For each layer, the optimum oxygen partial pressure predetermined from the study of individual layer was applied. The sputtering deposition of multilayer was carried out successively without breaking vacuum in multi-target sputter chamber. We prepared four different samples of ITO(150 nm)/ATO/TiO_2, ITO(300 nm)/ATO/TiO_2, ITO(500 nm)/ATO/TiO_2 and ITO(300 nm)/ATO, where ATO and TiO_2 layer thicknesses were 100 and 30 nm, respectively, for all the samples. Temperature-dependent resistance was monitored in a specially designed apparatus, which were equipped with multiple probes for the real-time measurement of the resistance change during the heating and cooling cycles. Heat treatments of the as-prepared films were carried out in atmosphere at 500 °C for 1 h. Heating rate was 10 °C/min, and natural cooling without forcing was adopted.

2.2. DSSC fabrication

DSSCs were fabricated as follows. The ITO/ATO/TiO_2 conducting substrates were pre-cleaned ultrasonically in ethanol. For comparison, the conventional FTO conducting glass (TEC8, Pilkington, 8 Ω/□, glass thickness of 2.3 mm) was also used and pre-cleaned with ethanol. Screen-printable nc-TiO_2 pastes were prepared using ethyl cellulose (Aldrich), lauric acid (Fluka) and terpineol (Fluka), as described elsewhere [8]. The prepared nc-TiO_2 paste was coated on the transparent conducting glasses, dried in air at ambient temperature for 5 min and sintered at 500 °C for 30 min. The thicknesses of the annealed films were about 4 μm, as measured with Alpha-step IQ surface profiler (KLA Tencor). For dye adsorption, the annealed nc-TiO_2 electrodes were immersed in absolute ethanol containing 0.5 mM of N-719 dye (Ru[LL′(NCS)$_2$], L = 2,2′-bypyridyl-4,4′-dicarboxylic acid, L′ = 2,2′-bypyridyl-4,4′-ditetrabutylammonium carboxylate) for 2 h at 50 °C. Pt counter electrodes were prepared by thermal reduction of thin film formed from 7 mM of H_2PtCl_6 2-propanol solution at 400 °C for 20 min. The dye-adsorbed nc-TiO_2 electrode and Pt counter electrode were assembled using 25-μm-thick surlyn (Dupont 1702). An electrolyte solution was introduced through a drilled hole on the counter electrode, where the electrolyte solution was composed of 0.7 M 1-propyl-3-methyl immidazoliuim iodide (PMII), 0.03 M I_2, 0.05 M guanidinium thiocyanate (GuSCN) and 0.5 M 4-*tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (v/v, 85:15). The active areas of dye-coated TiO_2 films were measured by an image analysis program equipped with a digital microscope camera (Moticam 1000).

2.3. Measurements

Photocurrent–voltage measurements were performed using a Keithly model 2400 source measure unit. A class-A solar simulator (Yamashita Denso, model YSS-200A) equipped with a 1600 W xenon lamp was used as a light source, where light intensity was adjusted using a Fraunhofer ISE-calibrated mono Si solar cell with KG-3 filter for approximating AM 1.5G one sun light intensity. During photocurrent–voltage measurement, DSSC was covered with a black mask with an aperture to avoid additional light coming through lateral space [9,10]. Incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 300 to 800 nm using a specially designed IPCE system for DSSC (PV Measurements, Inc.). A 75 W xenon lamp was used as a light source for generating monochromatic beam. Calibration was performed using a silicon photodiode, which was calibrated using the NIST-calibrated photodiode G425 as a standard, and IPCE values were collected under bias light at a low chopping speed of 10 Hz. Transmittance spectra for the ITO/ATO/TiO_2 conducting glasses were recorded using a Perkin-Elmer Lambda 35 UV–vis spectrometer. The electrochemical impedance spectra were measured with a potentiostat (Solartron 1287) equipped with a frequency response analyzer (Solartron 1260), with the frequency ranging from 10^{-1} to 10^6 Hz. The magnitude of the alternative signal was 10 mV. Impedance parameters were determined by fitting of impedance spectrum using Z-view software. The impedance measurements were carried out at open-circuit potential under AM 1.5 one sun light illumination.

3. Results and discussion

In the ITO/ATO/TiO_2 structure, thickness of the ITO layer is varied from 150 to 500 nm, while the ATO and TiO_2 layers are fixed to be at 100 and 30 nm, respectively. The sheet resistance decreases from 9.4 to 2.4 Ω/□ with increasing ITO layer thickness from 150 to 500 nm (Table 1). The deposition of TiO_2 layer on the top of the ATO layer is aimed at improving adhesion with nanoparticle TiO_2 film. It cannot be ruled out that the introduction of TiO_2 layer may affect the electrical conductivity; however, almost no change in the sheet resistance is observed after deposition of 30-nm-thick TiO_2 layer, as shown in Table 1, which indicates that the deposition of insulating TiO_2 layer does not alter the electrical conductivity.

Fig. 1 shows the UV–vis spectra of the ITO/ATO/TiO_2 conducting glasses as a function of wavelength, along with the conventional FTO glass. The transmittance decreases slightly with increasing the ITO layer thickness. The relative transmittances integrated in the measured wavelength range from 250 to 1100 nm are estimated to be about 100%, 93% and 91% for the ITO thickness of 150 nm (ITO(150)), 300 nm (ITO(300)) and 500 nm (ITO(500)), respectively. It is noticed that the ITO/ATO/TiO_2 conducting glasses show better transmittance than the conventional FTO glass in the range 250–1100 nm, especially much higher transmittance in the wavelength ranges from 300 to 600 nm. The maximum transmittance of 89% at 495 nm is observed for the ITO(150)/ATO/TiO_2 sample, whereas FTO shows transmittance of about 80% at around 600 nm. For the case of ITO layer thickness of 300 nm, the overall transmittance is hardly

Table 1
Dependence of sheet resistance on ITO layer thickness for the ITO/ATO/TiO_2 transparent conducting glasses

Transparent conducting layers	ITO thickness (nm)	Resistance (Ω/□)
ITO(150)/ATO/TiO_2	150	9.4
ITO(300)/ATO/TiO_2	300	4.8
ITO(500)/ATO/TiO_2	500	2.4
ITO(300)/ATO	300	4.8

The ATO and TiO_2 layers were fixed to be 100 and 30 nm, respectively.