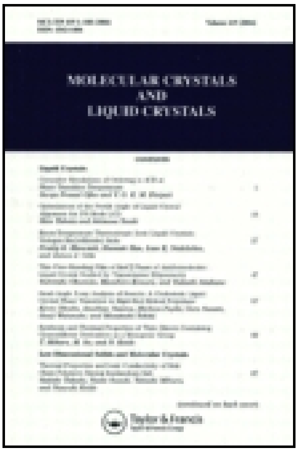

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Transparent Zn-Doped In_2O_3 Electrode Prepared by Radio Frequency Facing Target Sputtering for Flexible Dye-Sensitized Solar Cells

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Transparent Zn-Doped In_2O_3 Electrode Prepared by Radio Frequency Facing Target Sputtering for Flexible Dye-Sensitized Solar Cells

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For the application to transparent electrode in flexible dye-sensitized solar cells (DSSCs), Zn-doped In_2O_3 (In_2O_3:Zn) thin films have been fabricated on polyethylene naphthalate (PEN) substrate by the radio frequency facing target sputtering method, and their characteristics have been investigated as a function of deposition pressure. X-ray diffraction study reveal that the structure of In_2O_3:Zn thin films is amorphous nature. The film morphology is slightly sensitive to the deposition pressure. At the sputtering pressure of 0.40 Pa, In_2O_3:Zn thin film on PEN exhibits a sheet resistance of about 12.4 $\Omega/\square$ and average transmittance of about 85% at 550 nm wavelength, resulting in the highest value for figure of merit. The flexible DSSC device with the In_2O_3:Zn electrode shows the efficient solar-to-electrical power conversion efficiency (η), which is the maximum η value of 4.6% under simulated air mass 1.5 irradiation (100 mW/cm^2).

Keywords Flexible dye-sensitized solar cell; In_2O_3:Zn thin film; radio frequency facing target sputtering; transparent electrode

Introduction

Recently, transparent conducting oxide (TCO) thin films grown on polymer substrates have attracted much attention for the application of flexible displays and flexible solar cells [1–3]. In particular, TCO thin films as the transparent electrode in flexible dye-sensitized solar cells (DSSC) are known to be an important issue with a viewpoint of the DSSC performance [4].

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Sn-doped In_2O_3 (ITO) films are commonly used as ones of TCO films and mainly deposited by magnetron sputtering [5]. However, in order for the ITO films to have the low resistivity of $1{\sim}4 \times 10^{-4}\,\Omega$cm, the substrate needs to be heated to more than 200°C. Among TCOs, a promising material is Zn-doped In_2O_3 (In_2O_3:Zn) because of their possibility for use as TCO films with high electrical conductivity and optical transparency in the low temperature deposition [6–8].

In order to realize the deposition of In_2O_3:Zn films on plastic substrate, researches on the fabrication process at low temperature are necessary to obtain the film with low sheet resistance and high optical transmittance. It has been reported that facing target sputtering (FTS) method is useful to deposit TCO films with low resistivity at a low temperature [9,10]. Also, compared to other sputtering system, the FTS system has the advantages such as high sputtering efficiency, damage-free from plasma, and high atomic mobility at the surface of the substrate [11–13]. Therefore, FTS technology can be the subject of considerable attention as one of low temperature deposition process for transparent In_2O_3:Zn electrode in flexible DSSCs.

In the sputtering system, discharge mode is divided direct current (DC) into radio frequency (RF) with respect to applied power for the plasma generation. In general, even when using the same discharge chamber and similar pressures, RF discharge modes indicate different current – voltage relationships of the plasma against DC discharge, offering different sources for energetic particles into the growing film [14]. Hence, depending on the plasma mode, an essential difference of optimum sputtering conditions such as discharge power density and sputtering pressure can be observed, as well as a difference in the microstructure and morphology of the films [15]. To our best knowledge, although some reports [16,17] have documented the characteristics of In_2O_3:Zn electrode grown by DC-FTS, there have been no reports on the properties of the In_2O_3:Zn films deposited by RF-FTS and the use of an electrode in flexible DSSCs.

In this work, we have prepared the In_2O_3:Zn thin films on polyethylene naphthalate (PEN) substrate at room temperature by RF-FTS method with varying the working pressure during deposition, and their properties and the application to flexible DSSC device were investigated.

Experimentals

In_2O_3:Zn thin films were deposited on the PEN (Teijin Dupont Films) substrate, using a RF-FTS method, at room temperature with varying working pressure. Prior to deposition, PEN substrates were cleaned with acetone, methanol and de-ionized water for 10 min in an ultrasonic bath. The base pressure in the chamber was adjusted to 1.33×10^{-4} Pa. Then, high purity argon gas was introduced into the chamber through mass flow controller. The substrate temperature was maintained at room temperature. The sputtering RF power was controlled at 80 W. The composition ratio of 3 inch sputtering dual target used in the experiment was In_2O_3: ZnO = 90:10 in weight percentage with purity of 99.99%.

Thickness of the thin films was determined by a surface profiler (KLA Tencor, Alpha-Step IQ). X-ray diffraction (XRD, Rigaku, D/MAX-2500) was used to examine the crystallinity of the films. Electrical properties of In_2O_3:Zn thin films were measured by the 4-ponit probe and Hall Effect measurement (Ecopia, HMS-3000) examinations. Optical transmittance characteristics of the films were measured by means of an ultraviolet-visible spectrophotometer (Otsuka, MCPD-7000) in the visible region.

Using the prepared In_2O_3:Zn electrodes on PEN, we fabricated flexible DSSCs in order to investigate the possibility as efficient transparent electrode for the DSSC. The commercial TiO_2 paste (Solaronix Co. Ltd.) was coated on the Ti-foil substrate by doctor blade method. The coated Ti-foil substrates were fired at 500°C for 30 min. For dye adsorption, the prepared photoelectrodes were immersed into the anhydrous ethanol containing 3×10^{-4} M N3 dye (Solaronix Co. Ltd.) at room temperature for 24 hr. Pt counter electrodes were prepared at room temperature on the In_2O_3:Zn/PEN substrates by DC magnetron sputtering. The two substrates embedded with respective dye-adsorbed photoelectrode and Pt counter electrode were assembled using 60 μm-thick Surlyn (Dupont 1702) as a bonding agent. A liquid electrolyte was introduced to the DSSC cell through a pre-punctured hole on the counter electrode. The electrolyte was composed of 0.1 M of LiI, 0.6 M of 1,2-dimethyl-3-propylimidazoleium iodide (DMPImI), and 0.05 M of 4-tert-butylpyridine in acetonitrile. Finally, the hole was sealed using additional cover polymer films. For the characterizations of flexible DSSCs, current density–voltage (J-V) measurements were carried out by using a Solar Simulator (Sun 2000 solar Simulator, ABET Technologies) under an irradiation intensity of air mass (AM) 1.5 G (100 mW/cm^2). The intensity of incident solar illumination was adjusted to 1 sun condition using NREL certified Si reference cell equipped with a KG-5 filter. The active areas of the flexible DSSCs were estimated by a digital microscope camera (Moticam 1000), which is about 5×20 mm^2.

Results and Discussion

The XRD patterns of In_2O_3:Zn thin films grown on PEN substrate by RF-FTS with varying deposition pressure are shown in Figure 1. For reference, the XRD pattern of PEN is also indicated. All XRD patterns are found to be practically similar

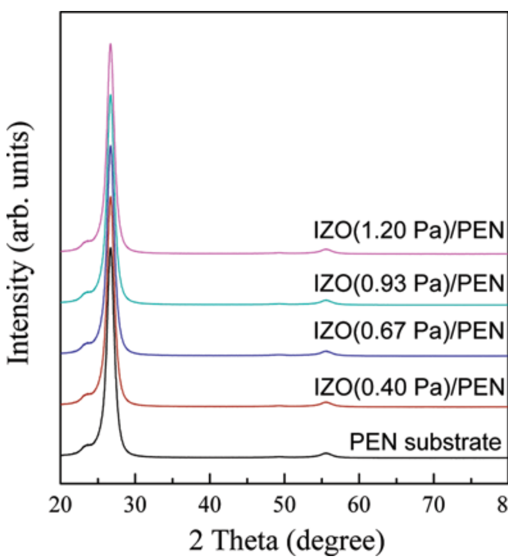

Figure 1. X-ray diffraction patterns of In_2O_3:Zn thin films deposited on PEN substrate.

regardless of the working pressure, and indicated only a sharp diffraction peak at about $2\theta = 26.7°$. It can be considered that because the peak at 26.7° is attributed to the PEN substrate, the XRD patterns of In_2O_3:Zn thin films do not contain any peaks attributable to crystal. Hence, it is believed that the structure of the In_2O_3:Zn thin films is completely amorphous due to low substrate temperature during FTS process.

Figure 2 shows the effect of sputtering pressure on the thickness of In_2O_3:Zn thin film. It is observed when sputtering pressure increases from 0.40 to 1.20 Pa, the film thickness is decreased from 140 to 85 nm. In the FTS process, sputtered particles from target are known to be arrived on the substrate through collisions. At high pressure, owing to the mean free path of the sputtered particles is relatively small, the amount of the particles arriving at the substrate is reduced, resulting in the decrease the growth rate of the films.

Figure 3 shows the AFM images of the In_2O_3:Zn films deposited at working pressure in the range of 0.40~1.20 Pa. The surface roughness of the In_2O_3:Zn films was quantified by the average roughness (R_a). The AFM images of In_2O_3:Zn films indicate the change of roughness ranging from 1.4 to 2.1 nm. The lowest Ra values of 1.4 nm for In_2O_3:Zn films can be obtained at 0.40 Pa working pressure. It is well known that the morphological properties of the sputtered films depend on the kinetics of the arriving species and the surface migration of the atoms at the substrate. At lower pressure, there is a less chance of inter-particle collisions. Therefore, the sputtered species arrive at the substrate surface with higher kinetic energy, which promotes the adatom mobility, resulting in the improvement of film density and subsequently smoother surface.

Figure 4 shows the electrical properties of In_2O_3:Zn films on PEN deposited at different working pressure. It is observed that when working pressure increases, the resistivity and sheet resistance of the In_2O_3:Zn films increases. The resistivity of TCO films is reported to be dependent on the microstructure of the thin film [18]. Also, it

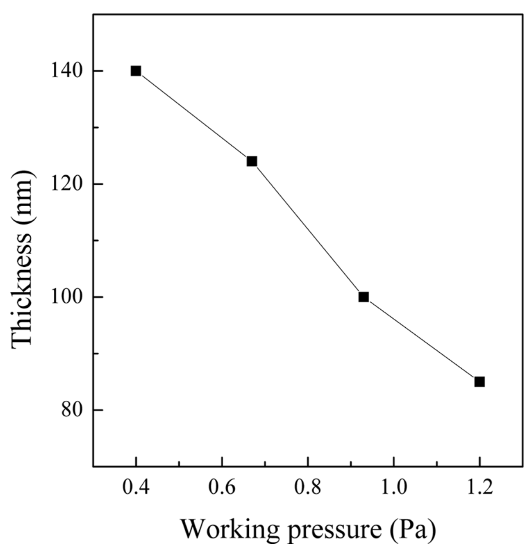

Figure 2. Thickness variation of In_2O_3:Zn thin films under different working pressure.

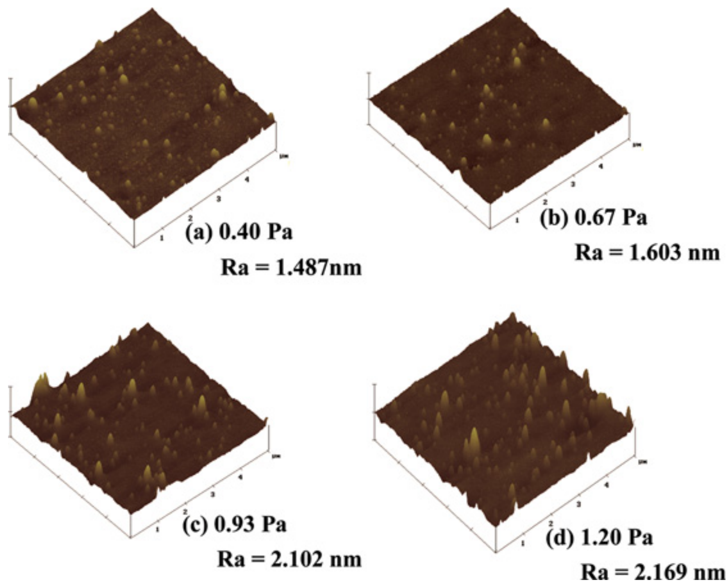

Figure 3. AFM images of In_2O_3:Zn thin films.

has been well known that the density of In_2O_3:Zn films are critically dependent on the mean free path of the sputtered particles. As the deposition pressure increases, due to the decrease of the mean free path, the energy of the ions become smaller and the binding energy becomes weaker, which causes the degraded density of the films. To the contrary, at lower pressure, the particles from the sputtering target have

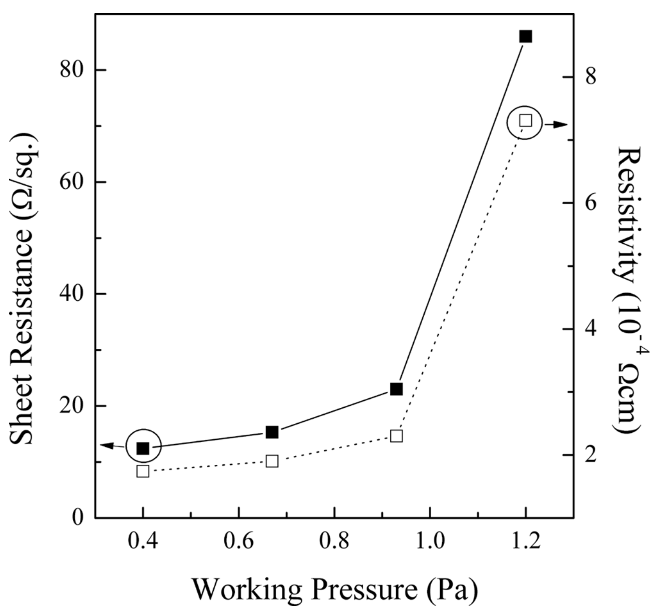

Figure 4. Sheet resistance and resistivity of In_2O_3:Zn thin films.

very large energies to collide with the substrate, which have enough energy to diffuse and results in the formation of the more compact film. Accordingly, the film resistivity increases with increasing working pressure. In addition, from the above analysis, the variations of resistivity and sheet resistance of In_2O_3:Zn films are related to the surface morphology. From the figure, it is also observed that the minimum sheet resistance of 12.4 Ω/□ and resistivity of 1.74×10^{-4} Ωcm are obtained at the working pressure of 0.40 Pa. Recently, Kwak, *et al.* [19] have reported the Al-doped ZnO electrode on polyethylene terephthalate prepared by RF magnetron sputtering with the resistivity of 2.1×10^{-3} Ωcm for use in the flexible DSSCs. It can be easily found that the resistivity of our In_2O_3:Zn electrode is much lower than that of the Al-doped ZnO electrode, indicating superior electrode performance.

Figure 5 shows the optical transmittances of In_2O_3:Zn films on PEN under different working pressure. All the In_2O_3:Zn films on PEN except for 1.20 Pa pressure are highly transparent in the visible region, showing average transmittance of about 85%. Haacke suggested that the figure of merit (FOM) value could provide a useful tool for comparing the performance of transparent electrode with similar transmittance and resistivity [20]. From sheet resistance and optical transmittance of In_2O_3:Zn films at 550 nm wavelength, we can calculate the FOM value using following equation [21].

$$\mathrm{FOM} = \mathrm{T}^{10}/\mathrm{Rs},$$

where T is transmittance at 550 nm wavelength and Rs is sheet resistance of the In_2O_3:Zn films. The values of FOM for 0.40 and 0.67 Pa are 15.6×10^{-3} and 8.4×10^{-3} Ω^{-1}, respectively. From the calculated FOM value of the In_2O_3:Zn films,

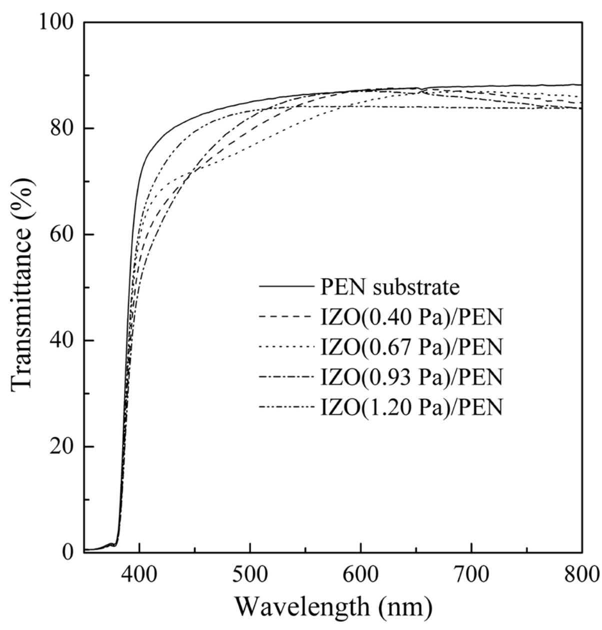

Figure 5. Optical transmission spectra of In_2O_3:Zn electrode on PEN in the visible region.

we decide that the pressure of 0.40 Pa is the condition for the best performance of transparent electrode.

Photocurrent density-voltage curves of the flexible DSSCs with In_2O_3:Zn electrodes at sputtering pressure of 0.67 and 0.40 Pa are indicated in Figure 6. A flexible DSSC devise with In_2O_3:Zn film deposited at 0.67 Pa exhibits an open-circuit voltage (V_{oc}) of 718 mV, a short-circuit current (J_{sc}) of 7.9 mA/cm^2, a fill factor (FF) of 0.723, and a power conversion efficiency (PCE) of $\eta = 4.1\%$, whereas the devise with In_2O_3:Zn electrode grown at 0.40 Pa shows the Voc of 711 mV, the J_{sc} of 8.9 mA/cm^2, the FF of 0.728, and the PCE of $\eta = 4.6\%$. These data represent that both devises show similar Voc and FF values. However, flexible DSSC devise with In_2O_3:Zn film deposited at 00.4 Pa shows only higher Jsc than that with In_2O_3:Zn electrode grown at 0.67 Pa. It has been well known that sheet resistance of the electrode to current flow significantly affects current density of the solar cells. In addition, the PCE of the DSSC fabricated using a transparent electrode is strongly dependent on its optical transmittance. Therefore, higher PCE of flexible DSSC devise with In_2O_3:Zn electrode deposited at 0.40 Pa can be explained by the FOM value for transparent electrode. Consequently, our results in this work suggest that the photovoltaic performances of flexible DSSC are good agreement with variation of the FOM value for transparent electrode. Chen, *et al.* [22] have reported the performance of flexible DSSC fabricated on Ti substrate using a commercial ITO/PEN electrode (Peccell Technologies, Inc.) with the sheet resistance of 15 Ω/□ and the light transmittance of 80% at 550 nm wavelength, representing the PCE of $\eta = 5.41\%$. Characteristics of In_2O_3:Zn electrode prepared by RF-FTS is found to show excellent electrical properties and higher optical transparency as compared with commercial ITO/PEN electrode. Although the PCE of the flexible DSSC with the In_2O_3:Zn electrode is lower than that of the DSSC with the ITO electrode, which may be originated in the differences of active area and fabrication method for the

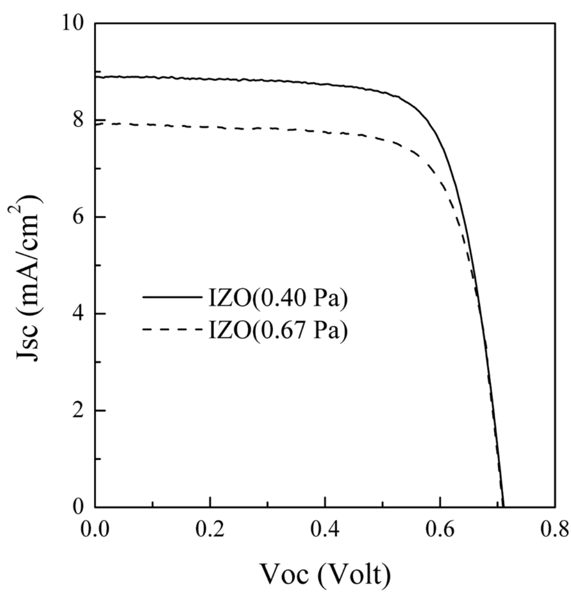

Figure 6. Photocurrent density – voltage curves of flexible DSSCs with In_2O_3:Zn electrode.

device, further studies on In_2O_3:Zn film with a high quality can give rise to the improving performance of the flexible DSSC embedded with In_2O_3:Zn electrode. Hence, investigations on the RF-FTS process for In_2O_3:Zn electrode and photovoltaic properties of flexible DSSC with In_2O_3:Zn electrode are needed.

Conclusions

Transparent conductive oxide films, In_2O_3:Zn electrodes, were successfully deposited on a PEN polymer substrate by RF-FTS method. The lowest resistivity of $1.74 \times 10^{-4}\,\Omega$cm and an optical transmittance of about 85% in the visible range of the spectrum were obtained for the In_2O_3:Zn/PEN film grown at 0.40 Pa pressure. Also, we get the good performance of the flexible DSSC with the In_2O_3:Zn electrode, which PCE of $\eta = 4.6\%$ was obtained under $100\,mW/cm^2$ illumination with AM 1.5 G condition. From these results, we suggest that In_2O_3:Zn electrode grown by RF-FTS are a promising TCO electrode for flexible DSSCs. Further investigations into photovoltaic properties of flexible DSSCs within In_2O_3:Zn electrode are currently in progress and the results will be reported when they are verified.

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