Solar Energy Materials & Solar Cells 134 (2015) 5–14

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Fluorine doped zinc tin oxide multilayer transparent conducting Oxides for organic photovoltaic's Cells

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ARTICLE INFO

Article history:
Received 2 August 2014
Received in revised form
27 September 2014
Accepted 8 November 2014
Available online 27 November 2014

Keywords:
F doped ZTO (FZTO)
Multilayer transparent conducting electrode
Electrical and optical properties
Bulk hetero-junction Organic Photovoltaic's Cells (BHJ-OPVs)
Power conversion efficiency

ABSTRACT

Few nm of Ag layer embedded in fluorine doped zinc tin oxide FZTO/Ag/FZTO was fabricated on glass by radio frequency magnetron sputtering at room temperature for the applications of organic photovoltaic's cells. The structural, electrical and optical properties of FZTO thin films were investigated. The multilayer of the FZTO (40 nm)/Ag (9 nm)/FZTO (40 nm) electrode shows the maximum optical transmittance (λ=380–770 nm) of 88.15%, quite low electrical resistivity of $\sim 8\times10^{-5}\ \Omega$ cm and the corresponding figure of merit (T^{10}/R_{sq}) is equivalent to $3.46\times10^{-2}\ \Omega^{-1}$. A normal organic photovoltaic's (OPV) structure of poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b]dithiophene-2,6-diyl][3-fluoro-2-[(2 ethylhexyl)carbonyl]thieno[3,4-b]-thiophenediyl] (PTB7): phenyl-C70-butyric acid methyl ester (PC70BM) was fabricated on glass/FZTO/Ag/FZTO to examine the compatibility of OPV as a transparent conducting electrode. The bulk hetero-junction organic photovoltaic's device fabricated on the multilayer FAF electrode exhibited open circuit voltage (V_{oc}) of 0.72 V, a short circuit current (J_{sc}) of 12.28 mA/cm^2, a fill factor (FF) of 0.54. These properties are analogous to V_{oc}=0.75 V, J_{sc}=14.87 mA/cm^2, FF=0.53 on commercial indium tin oxide (ITO). A resultant power conversion efficiency of 4.84% is comparable with the 5.90% of the same OPV structure on the commercial ITO as a reference. This reveals that FZTO/Ag/FZTO multilayer electrode is a promising electrode scheme for bulk hetero-junction organic photovoltaic's cells (BHJ-OPVs).

1. Introduction

Transparent conducting oxide (TCO) thin films have been extensively studied as key optoelectric material. Due to their unique combined electrical and optical properties they are applied for transparent and flexible device applications such as flat panel displays, plasma display panels, touch panels, organic light emitting diode, solar cells, and gas sensors [1]. The most common TCO consists of large band gap semiconducting metal oxides such as indium, tin, cadmium and zinc oxide doped with group III (Al [2–5], B [6,7], Ga [8–10] or group VII (F [11], Cl [12] elements by reducing their resistivity and retaining high transparency in the visible range (λ=380–770 nm). Due to high conductivity, transparency, and the possibility to generate very flat films with good reproducibility, indium tin oxide (ITO) is one of the most employed TCO [13]. Because of the cost and scarcity of indium in TCO, there is urgent need of an alternative material with low cost and similar properties [1]. In these days, researchers are dedicated to find new transparent conductive electrodes such as carbon nanotubes, graphene, metal nanowires, dielectric-metal-dielectric (DMD) and so on. DMD materials have been suggested as a candidate to overcome the limits of both the electrical and optical properties of single layer TCOs ever reported. It allows both the overall carrier concentration and the mobility to be increased, prevailing to some extent the limitation imposed by ionized impurity scattering in metal oxide single layers [14]. DMD sandwiched film structures with different metal mid layers have been explored to improve the conductivity and near infrared reflectance of TCOs without significantly degrading visible transmission. In DMD structure, an insertion of metal layer as Au [15], Cu [16], Ni [17], Pt [18], and Ag [19] shows good conductivity. But, Ag has been shown to exhibit the lowest absorptivity in the visible region as a thin metal layer. Previously, AZO/Ag/AZO [14], GZO/Ag/GZO [20], ZnO/Ag/ZnO [21], SnO_x/Ag/SnO_x [22], ZTO/Ag/ZTO [23,31], TiO_x/Ag/TiO_x [24,25], IZO/Ag/IZO [26], TiO_2/Ag/SiO_2 [27] etc multilayer

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http://dx.doi.org/10.1016/j.solmat.2014.11.021
0927-0248/

electrodes have been investigated for indium free transparent conducting oxides for organic photovoltaic's cells (OPVs). Ellmer et al. [28] recently published; either Ag nanostructures or DMD multilayer structure electrode has been suggested to attain lower resistivity than $1\times10^{-4}\,\Omega$ cm of ITO. Low resistivity, high transparency and low cost of ZnO and SnO_2, zinc tin oxide (ZTO) thin film is one of the most promising materials. They have both the advantages of good thermal stability and mechanical strength of SnO_2 and good stability of ZnO under the reducing atmosphere. Amorphous ZTO (a-ZTO) film has a smoother surface morphology and cleaner etched profile than those of the crystalline ITO films [29]. Fluorine can be a promising anion doping candidate with its ionic radius similar to that of oxygen ($F^-=1.31$ Å, $O_2^-=1.38$ Å). When fluorine substitutes zinc, a strong local perturbation to the conduction band leads to strong scattering of electrons and reduce their mobility. On the other hand, when fluorine substitutes for oxygen, the electronic perturbation is largely confined to the filled valence band and the scattering of conduction electrons is reduced leading to high electron mobility as well as low absorption [30]. The FZTO single layer as anode electrode is difficult to apply for organic photovoltaic's (OPVs) due to the limited optical and electrical properties. Very recently it was reported that F-doped ZTO (FZTO) thin films was deposited on glass and their optical and electrical properties were investigated with the variations of relative partial pressure of oxygen to CF_4 and post annealing temperature. From the result, F was still incorporated in FZTO thin films below 400 °C annealing in environmental atmosphere identified by x-ray photoelectron spectroscopy and showed improved transparency than ZTO [30]. To the best of our knowledge, there is no report about the multilayer fluorine doped zinc tin oxide (FZTO) thin films for the applications of organic photovoltaic's cells using radio frequency magnetron sputtering which have been used for the fabrication of TCO films. The structural, electrical and optical properties of single and multilayer FZTO/Ag/FZTO (FAF) thin films are characterized. The thickness effect of Ag, FZTO (top and bottom layers) for the FAF stacked layers was also analyzed to tailor the transparency and electrical properties of the fabricated films. The thermal stability of the FAF stacked layer after annealing was also explored. Bulk hetero-junction (BHJ-OPVs) devices with a normal structure were fabricated on FZTO/Ag/FZTO (FAF) multilayer electrodes at room temperature in which the PEDOT: PSS layer was used as a hole transparent layer (HTL). A thin layer of poly (ethylene dioxythiophene) doped with polysulfonic acid (PEDOT: PSS) is the most widely used material to help charge transportation at the interface of electrode/organic (ITO/organic or FAF/organic). PEDOT: PSS is a p-type semiconductor, a good hole transport material and assures better hole collection from the polymer into the electrode (commercial ITO or multilayer). These devices were then characterized in terms of the open circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) which were compared to OPV devices with an ITO electrode as a reference.

2. Experimental

Highly transparent and conducting FAF multilayer thin films were prepared on glass substrates (Corning Eagle XG 0.7 mm, Alkaline Earth Boro-Aluminosilicate) for the fabrication of the OPVs device by radio frequency sputtering (rf, 13.56 MHz) in 2-in ZTO ceramic target composited with 30 wt% ZnO and 70 wt% SnO_2. The F-doping was carried out by introducing a mixed gas of pure Ar, CF_4, and O_2 forming gas into the sputtering chamber while sputtering ZTO target. The substrate was ultrasonically precleaned in acetone, methanol and deionized water respectively for 10 min each in order to remove impurities on the substrate surface. The bottom FZTO layer was sputtered at an RF power of 100 W and working pressure of 0.27 Pa. Silver (Ag) (RND, Korea, Ag 99.99%) intermediate metal layer was successively deposited by RF magnetron sputtering at 50 W under an Ar plasma gas pressure of 0.27 Pa. Finally, the top FZTO layer was sputtered through the same method used to sputter the FZTO bottom layer composited with 30 wt% ZnO and 70 wt% SnO_2 and by introducing a mixed gas of pure Ar, CF_4, and O_2 forming gas into the sputtering chamber while sputtering ZTO target. For the uniformity of the FAF films, the substrate was constantly rotated at a constant rate of 7 rpm during sputtering process. The target to substrate was fixed at 70 mm during the sputtering process. The optimized FAF multilayer and commercial ITO electrodes were specially designed laser patterned for the fabrication of the conventional bulk hetero-junction OPVs. FAF multilayer and commercial ITO electrodes were exposed to UV-ozone plasma treatment for 15 min to increase the hydrophilic nature of the surface. The PEDOT: PSS layer was spin-coated onto the FAF electrode and therefore prevented any possible short circuiting. It is admitted that this buffer layer enhances the adhesion of the organic layer. PEDOT: PSS layer was spin coated at 4000 rpm for 35 s onto the electrode substrates, annealed at 110 °C for 10 min on a hot plate. A bulk hetero junction layer was also spin coated at 1000 rpm for 30 s from a solution of poly[4,8-bis[(2-ethylhexyl)oxy] benzo[1,2-b:4,5-b]dithiophene-2,6-diyl][3-fluoro-2-[(2 ethylhexyl) carbonyl]thieno[3,4-b]-thiophenediyl] (PTB7): [6,6]-phenyl C70-butyric acid methyl ester (PC70BM) (1:1.5 by volume) in dichlorobenzene. The annealing process was performed at 150 °C for 15 min inside glove box. After the evaporation of the solvent, the sample was loaded into a vacuum chamber and TiO_2/Al thin film (0.6/100 nm) was deposited as a cathode electrode. Schematic diagrams depicting the overall device structure of the OPVs are illustrated in Fig. 10(a). X-ray diffraction (XRD) analysis (Rigaku Dmax 2500/server) with CuKα radiation (wavelength (λ)= 1.5418 Å) was performed to investigate the crystallographic structure of FZTO thin films. The electrical resistivity, carrier concentration, and hall mobility of the films were characterized using Hall-effect measurement (Ecopia HMS 3000). The optical transmittance of the films was measured using a UV-Visible spectrometer (Perkin Elmer UV/Vis spectrometer Lambda 18) in the wavelength range from 200∼900 nm. Work functions of FZTO thin films were determined by the positions of the Fermi level measured from the tangent line extrapolation of the onset from the secondary electron cutoff peak in the ultraviolet photoelectron spectroscopy (UPS) (UPS, Kratos AXIS-NOVA) spectra. Photon energy of the UPS light source (He (I) resonance line) was $h\nu=21.2$ eV and the energy of the band pass filter in the analyzer were fixed at 20 eV. The surface microstructure of the Ag thin films deposited on the FZTO/glass substrate with the variation of Ag thickness and annealed FAF films was observed by using scanning electron microscopy (NOVA Nano SEM 200). Cross sectional microstructure of optimized FAF multilayer electrode was obtained from transmission electron microscopy (TEM) (Tecnai G2F30ST).The active area of the fabricated device was 0.09 cm^2. The electrical properties of the OPV devices were recorded using a Keithely 2400 source-measure unit under ambient conditions. The photocurrent was obtained under illumination from a Thermal Oriel solar simulator (Am 1.5 G, 100 mA/cm^2). The light intensity was calibrated using Si photovoltaic's (PV) solar cells.

3. Results and discussion

3.1. Characterization of FZTO and Ag films

The transmittance and sheet resistance of the tin oxide (SnO_2) based transparent conducting films doped with Zinc (Zn), Gallium (Ga), Antimony (Sb), Manganese (Mn), and Fluorine (F) at room