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Influences of dopant concentration in sol–gel derived AZO layer on the performance of P3HT:PCBM based inverted solar cell

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ABSTRACT

Organic solar cells based on P3HT:PCBM bulk heterojunction with an inverted structure have been fabricated using aluminum doped ZnO (AZO) as their electron transport layer, which was prepared by sol-gel route with 2-methoxyethanol as the solvent. The influences of Al concentration on the surface morphology and electrical properties of AZO layer were investigated by atomic force microscopy, X-ray diffraction and Hall effect measurements. The experimental results indicate that Al concentration has major influence on the grain size and only minor influence on crystallite size, leading to different surface morphology for different doping concentrations. Doping at high concentration produces higher charge carrier density, but not for charge carrier mobility and its electrical conductivity, which may be also influenced by the surface morphology. The effects of Al concentration in AZO layer were also observed in the J–V (current density–voltage) and small AC impedance characteristics of the fabricated solar cells. The resistance increases with Al concentration, but the capacitance decreases. The solar cell using AZO layer with doping concentration of 0.5 wt% shows the smallest impedance and the best J–V characteristics with the highest conversion efficiency. These characteristics seem to be correlated with the properties of AZO layer and its interface with the active layer.

1. Introduction

In some recent years, there is a deep interest to apply metal oxides such as ZnO and TiO_2 as electron transport layer (ETL) or electron extraction layer (EEL) in hybrid solar cells with inverted structure [1–7]. The use of metal oxide layer may give an advantage in preventing the active layer from the unwanted oxidation due to UV light radiations of the sunlight and humidity exposure [5,6]. The use of ZnO layer in solar cell with inverted structure, such as in ITO/ZnO/C_{60}/P3HT/Au structure configuration, improves charge carrier extraction as a result of the lowering of Fermi energy level at the cathode [8]. Moreover, Beek et al. has also reported the observation of charge transfer between poly(3-hexylthiophene) (P3HT) and ZnO, indicating the role of ZnO as an electron acceptor layer [9]. After this report, many studies concern on the role of ZnO and its nano-structured layer on exciton dissociation and charge carrier extraction [10,11]. While some reports shows clearly the improvement of the solar cell performance by addition of ZnO layer, but other reports cannot show such improvement. It seems that the role of ZnO as electron acceptors is affected by some factors which are still not well understood at the moment.

It should be also noted that, in the past two decades, ZnO has been intensively studied as transparent conducting oxide (TCO) thin film [12,13]. ZnO is one type of non-stoichiometric metal oxides with native defect such as zinc interstitial and oxygen vacancies, which intrinsically forms the *n*-type amorphous semiconductor [14]. The conductivity of ZnO thin film can be improved by addition of a small amount of metal ions, such as Al, Ge, etc. [15]. Aluminum doped ZnO (AZO) is one of the most studied ZnO film for TCO applications, which is considerable prospective material as a substitute of Sn-doped In_2O_3 (ITO), the

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most widely used TCO nowadays. Similar as the undoped ZnO, AZO can be prepared by various methods such as direct current (DC) magnetron sputtering, solvothermal, self assembly monolayer and sol–gel process [14]. The preparation method by sol–gel process is attractive because it is possible for fabrication of large area TCO with more simple and inexpensive equipments in comparison to other methods. For the preparation of AZO by sol–gel process, aluminum chloride ($AlCl_3$) and aluminum nitrate $Al(NO_3)$ are commonly used as the precursor of Al dopant ion [16]. The preparation of AZO from aluminum acetate $Al(OAc)_2$ through aqueous solution processing at relatively low temperature of around 140 °C has been also reported [18,19]. At that temperature regime, AZO layer then can be prepared on the top of plastic substrate (PET) by roll-to-roll (R2R) technique, which is an emerging technique for flexible electronics manufacturing technology. The fabrication of large area plastic solar cell with AZO layer as its transport layer by R2R has been demonstrated recently [5].

The presence of Al dopant may increase the density of states (DOS) near Fermi energy level and thus increases charge carrier density, leading to the increase in electrical conductivity [15,16]. By using AZO thin film instead of the undoped ZnO layer, one may thus expect the reduction of the solar cell impedance and thus the improvement in solar cell performance. Moreover, because AZO has relatively larger charger carrier concentration and charger carrier mobility in comparison to the organic transport layer, the solar cell performance is also almost unaffected by the layer thickness variation [17]. However, the effect of using doped ZnO layer on the performance of organic solar cell has not been investigated in detail. Therefore, in this paper, we present the effect of doping concentration of AZO layer on the characteristics of organic solar cells with bulk hetero-junction of P3HT:PCBM as their active layer. The characteristics of those solar cells were investigated by the current density–voltage (J–V) and small AC-impedance measurements. The present experimental result shows the relationship between the Al dopant concentration on the J–V characteristics and small AC impedance, which will be discussed in the following sections.

2. Experimental details

Aluminum doped ZnO precursor solution was prepared by dissolving 0.5 M zinc acetate dihydrate ($(Zn(CH_3CO_2)_2 \cdot 2H_2O)$) in anhydrous 2-methoxyethanol (99.8%, Sigma–Aldrich) with diethanolamine as complexing agent (stabilizer). $AlCl_3$ was added into the solution and the mixture solution was then stirred on a magnetic stirrer for about 1 h until the solution changed to a clear transparent solution. The precursor solution was spin coated onto glass or patterned ITO substrate. The thin films of this precursor were then subjected to heat treatment up to 500 °C using a hot plate in order to convert the precursor into ZnO, following the procedure already reported in the literatures with a slight modification in the heating process [16,20]. Using this precursor solution with 0.5 M zinc acetate hydrate and the spin coating rotation speed of 1000 rpm for 30 s, the thickness of AZO layer was around 50–70 nm as estimated from the scanning electron microscopy (SEM) image of cross-sectional cut of the AZO layer [17,21].

Solution of P3HT:PCBM blend was prepared by dissolving P3HT and PCBM with 1:1 wt% ratio in 1 ml chlorobenzene followed by stirring overnight at 35 °C. This polymer blend solution was then spin coated on the top of AZO layer on ITO substrate glass. The films were then annealed at 130 °C for 15 min in order to improve the contact between the polymer and AZO layer. Furthermore, this heat treatment has also benefit to the crystallization process of P3HT:PCBM, leading to better polymer morphology and better balance of domain size between P3HT and PCBM [17]. PEDOT: PSS was subsequently spin coated as the hole transport layer. Finally, silver (Ag) layer as the top electrode was thermally evaporated through a shadow mask to define an active area 4 mm^2 per cell.

For AZO layer characterizations, X-ray diffraction (XRD) measurements were done by Philips Analytical PW 1710 diffractometer, which use Cu Kα monochromatic X-ray source ($\lambda = 0.154$ nm). The Hall effect measurement was carried out under external magnetic field varying from 3.2 mT to 335 mT. The characterization by atomic force microscope (AFM) was also carried out in order to evaluate the surface roughness of the AZO layer. The J–V characteristic of the fabricated solar cells was measured by using a solar simulator (Oriel, 100 mW/cm^2), which was calibrated with a standard silicon solar cell prior to the measurement, and a digital source meter (Keithley 2400). AC impedance measurements were carried out by using a LCR meter (Agilent E4980A) with the frequency range from 20 Hz to 2 MHz and the amplitude of alternating signal of 5 mV. The obtained data were fitted by using software called EIS spectrum analyzer [22].

3. Results and discussions

Figs. 1 and 2 show the schematic structure of the device that investigated here and the AFM images taken from ITO substrate and AZO layers with various concentrations of Al doping, namely 0.5, 0.8, and 1 wt%. It seems that the surface morphology is affected by the Al concentration. Increasing the doping concentration seems to reduce the grain size but increase the appearance number of bulges on the surface. This characteristic may be related with the increase in ZnO grain packing density with increasing dopant concentration, resulting in the reduction of ZnO grain size, as also already reported by Lee et al. [12]. The surface morphology of the 0.5 wt% seems to have more flat surface with less bulge structures.

Fig. 3 shows the XRD patterns of AZO layers at various Al concentrations, which indicate that all layers have polycrystalline structure of hexagonal form with preferential (100), (002) and (101) axis orientations. Although the peak intensity is almost similar, the peak width seems to vary depending on the Al concentration. Here, we assume that this AZO film does not form a homogeneous thin film, but it is composed of a packing of ZnO grains. Each grain may be constructed of several nano-crystallites with either the same or different crystallinity. Grains are formed as the result of simultaneous crystallite aggregation and crystal growth during gelation process [23]. The X-ray diffraction only measures the crystallite sizes, which certainly have finite small size, and thus we may estimate the crystallite sizes according to

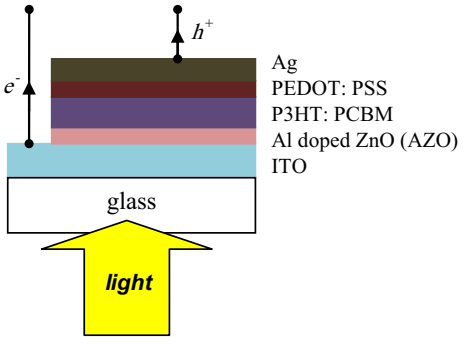

Fig. 1. Schematic structure of inverted type of organic solar cells based on P3HT:PCBM with AZO as its electron transport layer.