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Electric field assisted spray deposited MoO_3 thin films as a hole transport layer for organic solar cells

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ABSTRACT

Spray deposition of molybdenum trioxide (MoO_3) hole transport layer under a DC voltage (500 V and 1000 V) applied to the nozzle yielded orthorhombic phase of MoO_3 (α-MoO_3) with no other phases present. The films had uniform, compact surface morphology with reduced roughness, increased transmittance and band gap as compared to those for spray deposited MoO_3 layer deposited without applying the DC voltage. In addition an increase in the work function was also observed possibly due to the change in the nanostructures formed on the surface. XPS result showed that the application of DC voltage during spray deposition reduced the oxygen vacancies. The reduced potential barrier height between MoO_3 and P3HT layer can be useful in organic bulk-heterojunction solar cell (ITO/MoO_3/P3HT:PCBM/Al). This was indeed proven by organic bulk-heterojunction solar cell fabricated using the electric field assisted spray deposited MoO_3 layer yielding 2.71% power conversion efficiency with short circuit current density (J_{SC}) of 10.0 mA cm^{-2}, open circuit voltage (V_{OC}) of 0.57 V and fill factor (FF) of 47.4%. The organic solar cell fabricated using electric field assisted spray deposited MoO_3 layer showed an improved performance as compared to the standard spin coated solar cell.

1. Introduction

Polymer solar cells have attracted considerable attention for their potential of the large area fabrication, flexible, roll to roll deposition and simple lightweight structure (Park et al., 2009; Dou et al., 2012; Gong et al., 2009; Small et al., 2012; Tan et al., 2016; Li et al., 2016). Significant improvements in the power conversion efficiency (PCE) of polymer solar cell have been reported with a value of ~10% (He et al., 2012; You et al., 2013; Liu et al., 2014). However, the limited lifetime of conventional organic solar cell is still a big challenge for the commercialization. The choice of an interfacial layer providing proper energy alignment is an effective way to improve the performance of organic solar cell. For the interface modification between active layer and anode, different hole collecting buffer layers are used such as poly (3,4-ethylene dioxythiophene):poly (styrenesulfonate) (PEDOT:PSS), MoO_3, NiO, WO_3 and V_2O_5 (Xie et al., 2013; Lin et al., 2009; Stubhan et al., 2012; Steirer et al., 2010; Tan et al., 2014; Wong et al., 2012). PEDOT:PSS is known as a "work horse" material used as a hole transport layer in the organic solar cells (Stubhan et al., 2011; Wang et al., 2016). Unfortunately, PEDOT:PSS is also recognized as a major source of organic solar cell degradation in ambient conditions due to its hygroscopic as well as acidic (pH ~ 1) properties (Liu et al., 2010). Transition metal oxides reported above have been demonstrated as an alternative for PEDOT:PSS due to their good stability in ambient atmosphere (Hu et al., 2014). The interface properties between the active layer and the anode have great importance for the improvement of solar cell performance. Among the transition metal oxides molybdenum trioxide (MoO_3) is the most interesting material due to its higher transmittance and high work function. MoO_3 as a HTL reduces the charge recombination and resistance at the interface of photoactive layer and anode (Subbiah et al., 2010). MoO_3 also acts as an optical spacer for enhancing light absorption in the active layer as well as photocurrent (Zhao et al., 2010, 2009). Comparable performance and increased lifetime of organic solar cell are reported with thermally evaporated MoO_3 as a replacement of acidic PEDOT:PSS (Voroshazi et al., 2011). The MoO_3 layer can effectively prevent the humidity diffusion as compared to highly hygroscopic PEDOT:PSS film. Recent studies have shown the use of solution processed MoO_3 layer and MoO_3 nanoparticle based interfacial layer as a hole transport layer in organic solar cells (Girotto et al., 2011; Stubhan et al., 2011; Hu et al., 2014; Meyer et al., 2011). From

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the perspective of large area and low cost deposition, spray deposition can be a better suited technique (Boukhachem et al., 2012; Boughalmi et al., 2013; Chaturvedi et al., 2014; Chaturvedi et al., 2013; Swami et al., 2014, 2015, 2016; Bouzidi et al., 2003; Kannan et al., 2014; Chaturvedi et al., 2016).

Spray deposition of MoO_3 layer is already reported in the literature (Bouzidi et al., 2003; Kannan et al., 2014). In this paper for the first time the effect of applied DC voltage during spray deposition on the optical, morphological and structural properties is reported. The MoO_3 layer is then used as a hole transport layer (HTL) in organic bulk-heterojunction solar cell (OBHJ) (ITO/MoO_3/P3HT:PCBM/Al).

2. Experimental

For the spray solution 0.001 M ammonium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) is dissolved in de-ionized water. The reaction taking place for the formation of the molybdenum trioxide from the precursor solution is as follows (Kannan et al., 2014):

$$(NH_4)_6Mo_7O_{24} \cdot 4H_2O = 7MoO_3(s) + 6NH_3(g) + 7H_2O(g) \quad (1)$$

The optimized deposition parameters used for MoO_3 spray deposition are substrate temperature 400 °C, distance between nozzle and substrate 20 cm and solution flow rate 1 mL min^{-1}. Nitrogen gas is used as the carrier gas for deposition.

An electric field was created by applying DC voltages (500 V and 1000 V) between the nozzle and a circular electrode placed 4 mm below to the nozzle. The MoO_3 layer spray deposited without applying the DC voltage (0 V) is termed as Mo-0 and that with the applied DC voltage of 500 V as Mo-500 and 1000 V as Mo-1000.

The spray deposited MoO_3 layer was characterized by ZEISS EVO-50 model Scanning electron microscope (SEM) for morphological studies and Bruker Dimension Icon atomic force microscope (AFM) in tapping mode for roughness analysis, UV–vis transmittance using Perkin Elmer Lambda 1050 UV–vis–NIR spectrophotometer. X-ray diffraction (XRD) studies were done using X-ray diffractometer (Phillips X'PERT PRO), having Cu Kα incident beam ($\lambda \sim 1.54$ Å). Raman spectra had been obtained using Renishaw micro-Raman spectroscopy operating at 514.5 nm excitation. Kelvin probe force microscopy (KPFM) available with the AFM was used for work function measurement. XPS analysis was carried out for surface analysis using SPECS system with Mg Kα (1253.6 eV) as an excitation source. Thickness of the deposited film was measured by Dektak XT surface profiler.

For the fabrication of OBHJ solar cell, patterned ITO glass substrates were cleaned sequentially with ultra-sonication in soap solution, DI water and acetone, respectively, followed by boiling in acetone and 2-propanol. MoO_3 hole transport layer (HTL) was spray deposited on cleaned ITO substrate (anode) at the temperature of 400 °C with a thickness of ~25 nm. For reference cell MoO_3 layer was spin coated according to previously published method in which the pH was modified to 1–1.5 using HCl (Liu et al., 2010). A mixture of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) (both from Sigma Aldrich) with a weight ratio of 1:0.8, dissolved in chlorobenzene, was used as the active layer. The active layer was spin coated on the MoO_3 layer with thickness of 200 nm. The deposited layer was annealed at 120 °C for 20 min. Finally, Al (cathode) with a thickness of 100 nm was deposited on the active layer through a shadow mask using thermal evaporation to obtain an active cell area of 0.09 cm^2. Each substrate of ITO consists of six pixels of solar cells. J-V characteristics of OSCs were measured under AM 1.5G illumination using an Oriel Sol 3A, a class AAA solar simulator with a Keithley 2440 source meter calibrated by NREL certified Si solar cell.

3. Results and discussion

3.1. Morphological properties

MoO_3 films are spray deposited at different substrate temperatures of 200 °C, 300 °C and 400 °C, respectively. Poor surface morphology with non-uniform coverage and cracks can be seen for the deposition at 200 °C and 300 °C (Fig. 1a and b). This is because at lower temperatures, the solvent cannot evaporate quickly to give uniform coverage. Better deposition of MoO_3 film can be seen for spray deposition at the temperature of 400 °C (Fig. 1c). In Fig. 1c one can see the formation of nanostructures for spray deposited Mo-0 layer, but the deposited film is not compact and agglomeration of particles is seen.

The atomization in this case results in bigger droplets which evaporate slowly leading to agglomeration and poor surface quality. On the other hand application of the DC voltage to the nozzle results in electrostatically charged droplets which undergo columbic fission. The droplets arriving on the substrate are finer which then get evaporated quickly making the MoO_3 film compact (Fig. 2c). Therefore, the SEM images (Fig. 2b and c) show the formation of different nanostructures for Mo-500 and Mo-1000 layers.

Further investigation of surface morphology and surface roughness is carried out by AFM topography image at the scale of 10 μm × 10 μm (Fig. 3). The root mean square (RMS) surface roughness of Mo-0 layer is 82.4 nm which reduces to 63 nm for Mo- 500 and further to 37 nm for Mo-1000. The AFM results confirm that because of large droplet size Mo-0 has a coarser surface morphology. For Mo-500 and Mo-1000 the electric field results in the droplets spreading in corona cone and giving rise to a smoother and more uniform surface morphology over a larger deposition area. This reduced roughness is expected to contribute

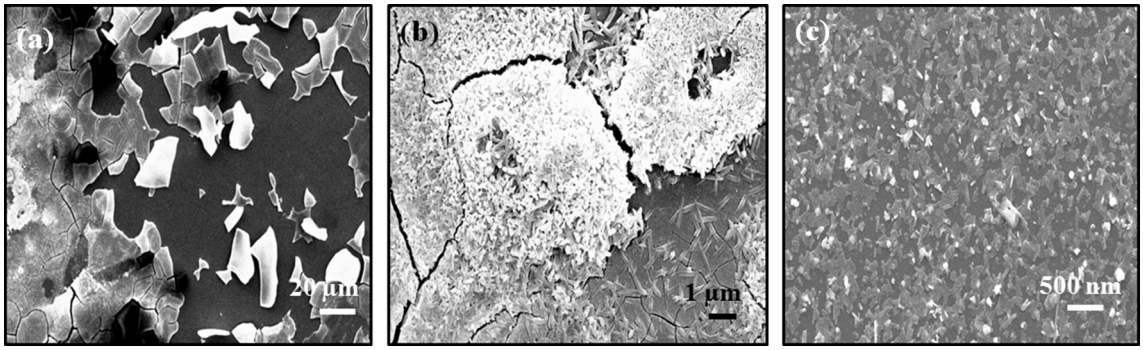

Fig. 1. SEM images of MoO_3 layer at (a) 200 °C, (b) 300 °C and (c) 400 °C.