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MoO_x Doped Single-Walled Carbon Nanotube Films as Hole Transport Layer for Organic Solar Cells

F. Çolak[a], Z. Dalkiliç[b], A. Tabatabaei[c], R. Atlibatur[b], Ü. Çolak[a], E. Arici[a] and N. Karatepe[a,*]

[a]Istanbul Technical University, Energy Institute, 34469 Istanbul, Turkey

[b]Istanbul Technical University, Department of Chemistry, 34469 Istanbul, Turkey

[c]Istanbul Technical University, Division of Nanosicence and Nanoengineering, 34469 Istanbul, Turkey

Metal-oxide thin films have recently become good candidates for the hole transport layer material, for solving the stability problem in organic photovoltaic devices. Metal oxide semiconductors (MoO_x, WO_3, V_2O_5) are very promising because of their suitable optoelectronic properties, ambient stability, high work function, and solution processability. Intrinsic n-type behavior of molybdenum oxide (MoO_x) is found to enhance p-type doping effect on single-walled carbon nanotubes. In this study, the effect of using MoO_x doped single-walled carbon nanotube films as hole transport layer in organic solar cells was investigated. Thin films and organic solar cells were characterized using scanning electron microscopy, atomic force microscopy, UV-NIR absorption spectroscopy and device current-voltage measurements.

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1. Introduction

Organic solar cells (OSCs) are considered potentially cost-effective for photovoltaic applications due to their solution-processability [1]. One of the most important components of OSCs is the hole transport layer (HTL). Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is the most widely used HTL material due to its solution processability. Although PEDOT:PSS is a highly conductive material, its acidic character causes the diffusion of In ions into both PEDOT:PSS layer and in photoactive layer, resulting in degradation of cell efficiency [2]. Therefore, alternative materials have been studied to improve the stability of OSCs. Metal oxide semiconductors (MoO_x, WO_3, V_2O_5) are very promising because of their suitable optoelectronic properties, ambient stability, high work function and solution processability [3, 4]. Intrinsic n-type behavior of molybdenum oxide enhances p-type doping effect on single-walled carbon nanotubes (SWCNTs) which makes significant improvement in solar cell efficiency and stability, providing more economical long-term energy production.

Since the discovery of carbon nanotubes, various doping materials (HNO_3, $SOCl_2$, H_2SO_4, $FeCl_3$, $AuCl_3$, etc.) have been intensively researched. However only few studies can be found on the molybdenum oxide doping method [5, 6]. Therefore, p-type doping effect of molybdenum oxide on the electronic structure of carbon nanotubes is not clear and needs to be investigated.

The objective of this study was to investigate the effect of using MoO_x doped SWCNT films with different configurations as HTL in OSCs. For this purpose, substoichiometric molybdenum oxide (MoO_x, $x < 3$) thin films were deposited, using two different techniques (solutions based, thermal evaporation), on SWCNT/ITO (indium tin oxide)/glass substrates. The structural, electronic and surface properties of MoO_x/SWCNT bilayers were investigated and cell efficiencies were compared.

2. Materials and equipment

2.1. Preparation of MoO_x solution

0.1 g of metallic molybdenum powder were dissolved in 10 ml of 2-ethoxyethanol and added to 0.3 ml of H_2O_2. The prepared solution was left to stir overnight. The color of the metal oxide solution had turned from grey to blue after the reaction.

2.2. Preparation of SWCNTs solution

Sodium dodecyl sulfate (SDS)-assisted SWCNT dispersion was prepared with concentration of 0.05 wt.% of SWCNTs in DI water (deionized water). The solution was sonicated for 15 minutes using a 20 kHz tip-sonicator (Bandelin, HD 2200), operating at 20% of sonication power of 70 Watts. Then the solution was centrifuged at 14 000 rpm for 30 minutes, and the upper 80% of the supernatant were decanted for further procedures.

2.3. Preparation of MoO_x/SWCNT bilayers

ITO substrates were sonicated in DI water and in isopropyl alcohol for 15 min in each and then treated under UV-ozone for 10 min. The SWCNT solution was then repeatedly sprayed onto ITO/glass substrates, placed onto a hot plate, maintained at 100 °C, until the desired transmittance was obtained. MoO_x thin films were prepared by two different routes (thermal evaporation, solution

*corresponding author; e-mail: kmnilgun@itu.edu.tr

based). For solution based procedure, MoO_x solution (s-MoO_x) was spin-coated on SWCNT/ITO/glass substrates at 6000 rpm. 10 nm of MoO_3 (e-MoO_x) were also deposited under vacuum via thermal evaporation with the average rate of 0.2 Å/s. Then samples were subjected to heat treatment at the optimum temperature of 300 °C in nitrogen atmosphere for two hours for the doping procedure.

2.4. Device fabrication

PEDOT:PSS layer was spin coated on SWCNT/MoO_x bilayers at 2000 rpm and subsequently annealed at 120 °C in N_2. For deposition of the active layer, a mixture of P3HT:PC_{61}BM (1:0.5) in dichlorobenzene was spin-coated on MoO_x/SWCNT bilayers. Then 0.5 nm of LiF was evaporated as the electron transport layer, followed by evaporation of 100 nm of Al, as the electrode. Finally, the devices were annealed at 150 °C for 10 min.

Absorption spectra of the films were measured using a UV-vis-NIR spectrophotometer (Shimadzu UV-3600). Molybdenum oxide oxidation states were analyzed using XPS system (Thermo K-Alpha). The surface morphology of the MoO_x layer was observed by atomic force microscopy (Nanomagnetics). Current density-voltage ($J-V$) curves were measured with a digital source meter (Keithley, Series 2400) in dark or with AM 1.5 light irradiation (100 mW cm^2). A solar simulator (Oriel LCS100) was used as a light source. The measurements were carried out under ambient atmosphere without any encapsulation of the cells. The irradiation area of the light was defined as 6.25 mm^2 using a photomask.

3. Results and discussion

SEM and tapping mode AFM were employed to investigate the surface morphology of MoO_x film and SWCNT/MoO_x bilayer, Fig. 1. The SEM images of s-MoO_x thin film and of the SWCNT/MoO_x bilayer have revealed that the films were uniformly deposited on the ITO substrate (Fig. 1a and b). On the other hand, it

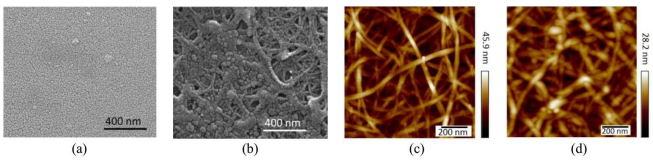

Fig. 1. SEM images of (a) s-MoO_x thin film, (b) SWCNT/MoO_x bilayer. AFM images of (c) SWCNT thin film and (d) SWCNT/MoO_x bilayer.

was also observed that the annealing procedure at 300 °C introduces pinholes in MoO_x film (Fig. 1b). In order to obtain desired doping characteristics, the temperature should be kept as high as possible, to promote better charge transfer from the SWCNTs and to assure film robustness. Normally, the temperature limit is determined by the degradation of ITO. However in our case the temperature was chosen as 300 °C in order to avoid further pinhole formation. The AFM surface topographies of the SWCNT film and SWCNT/MoO_x bilayer are also shown in Fig. 1c and d. The RMS roughness of SWCNT film has decreased from 7.3 nm to 4.1 nm after the deposition of MoO_x layer and has exhibited a suitable surface morphology for the interfacial layer in OPVs.

To study the purity and composition of the solution-processed MoO_x film, XPS was employed to investigate the film. The results are shown in Fig. 2. Figure 2a shows a full survey scan spectrum of the MoO_x film. The whole spectrum of MoO_x film shows five individual sharp peaks corresponding to O, Mo and C elements. The peak located at 399.1 eV corresponds to Mo 3p, showing a nearly stoichiometric MoO_x film composition. This was also confirmed by the more intense Mo 3d core level, shown in Fig. 2b. Annealing the MoO_x sample in the oxygen deficient N_2 environment therefore presents Mo^{5+} and Mo^{4+} states that can be attributed to the generation of O-vacancies.

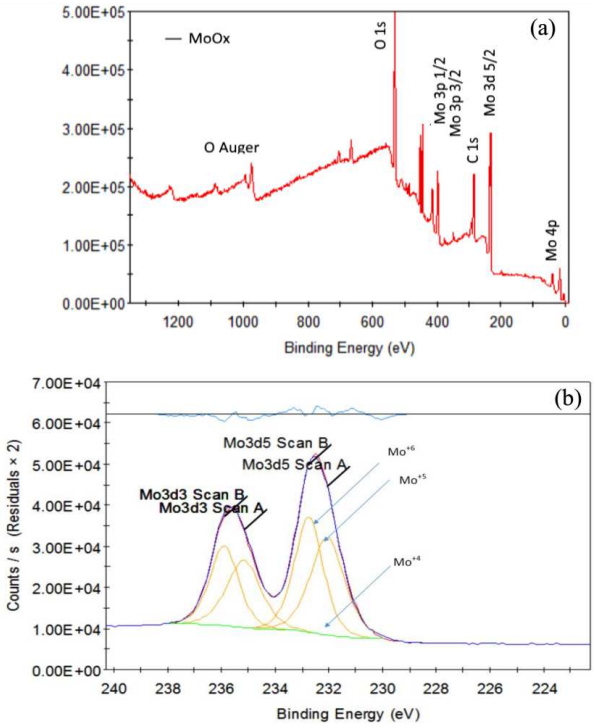

Fig. 2. XPS spectra of the s-MoO_3 film, (a) full scan and (b) Mo 3d core level.

In addition to solution-based processing of MoO_x film, thermal evaporation process was also applied. Thermal evaporation is commonly used for similar film coating applications. Once the samples coated using this process were characterized by XPS analysis, only stoichiometric compound was observed. However, we would expect the presence of nonstoichiometric MoO_x for better charge transfer. Therefore, coating with thermal evaporation did not yield the desired result.

Absorption spectroscopy has provided some insight into the doping mechanism and interaction between the MoO_x and SWCNTs. Doping effect after annealing at 300 °C was confirmed by absorption spectra of SWCNT and SWCNT/MoO_x films (Fig. 3). Clear peaks for transitions of E_{11}, E_{22}, and M_{11} in SWCNT indicate the high quality of SWCNTs. Those peaks were slightly suppressed after deposition of MoO_x, followed by 2 h of thermal treatment, as an indication of successful doping.

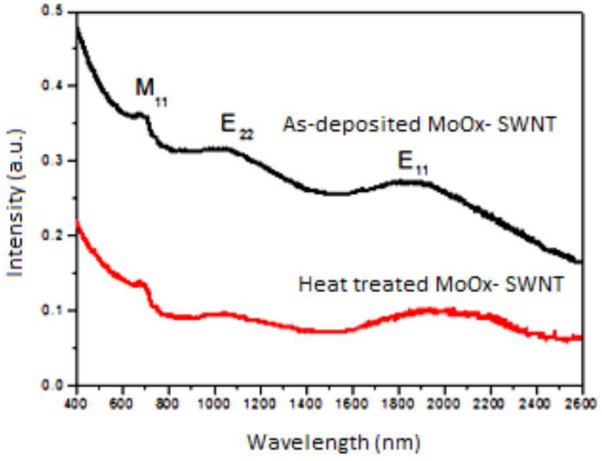

Fig. 3. Absorption spectra of as-deposited and heat-treated s-MoO_x/SWCNT bilayer.

In order to improve surface morphology and fill the pin holes caused by heat treatment, PEDOT:PSS thin films were deposited on SWCNT/MoO_x bilayers. Hydrophilic nature of hydroxyl groups on MoO_x and the solution coating method, allow PEDOT:PSS to fill up the pinholes effectively. Furthermore, the acidic PEDOT:PSS can also function as a weak additional dopant [6].

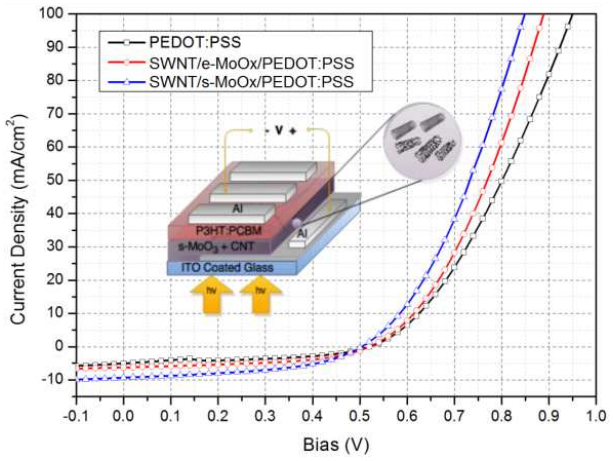

Fig. 4. $I-V$ characteristics of photovoltaic devices using SWCNT/MoO_x bilayers.

$I-V$ characteristics of photovoltaic devices using SWCNT/MoO_x bilayer as HTLs are depicted in Fig. 4 and detailed parameters are summarized in Table. The device fabricated as SWCNT/s-MoO_x bilayer shows power conversion efficiency (PCE) of 2.2%, with open-circuit voltage (V_{oc}) of 0.520 V, short-circuit current (J_{sc}) of 9.3 mA/cm^2, and fill factor (FF) of 46%, which is comparable to those of PEDOT:PSS (PCE=2.36%) and better than those of thermally evaporated MoO_x (PCE=1.57%).

TABLE

Photovoltaic performance for the SWCNT/MoO_x bilayers used as HTLs.

HTL layer	J_{sc} [mA/cm^2]	V_{oc} [mV]	FF [%]	Efficiency [%]
PEDOT:PSS	7.7	520	59	2.36
SWCNT/e-MoO_x/PEDOT:PSS	6.23	540	47	1.57
SWCNT/s-MoO_x/PEDOT:PSS	9.3	520	46	2.2

4. Conclusions

In summary, this study indicates that SWCNT/MoO_x bilayers can be incorporated into OSCs as HTLs, and their performance could be further improved by using PEDOT:PSS as the pinhole filler and the weak dopant. Moreover, it can be also concluded that s-MoO_x exhibits a better optoelectronic performance than e-MoO_x, yielding higher solar cell efficiency.

Acknowledgments

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