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Performance characteristics of p-i-n hetero-junction organic photovoltaic cell with CuPc:F_4-TCNQ hole transport layer

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ABSTRACT

We have investigated the effect of strong p-type organic semiconductor F_4-TCNQ-doped CuPc hole transport layer on the performance of p-i-n hetero-junction photovoltaic device from ITO/PEDOT:PSS/CuPc:F_4-TCNQ (5 wt%)/CuPc:C60 (blending ratio 1:1)/C60/BCP/LiF/Al, fabricated via vacuum deposition process and have evaluated the *J–V* characteristics such as short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and energy conversion efficiency (η_e) of the device. By doping of F_4-TCNQ into CuPc hole transport layer, absorption intensities in absorption spectra were increased, which supports that uniform dispersion of organic molecules in the hole transport layer with lowered value of surface roughness can be obtained. Eventually, current injection was enhanced through the layer, which comparatively improves the performance of the photovoltaic cell with energy conversion efficiency of 0.50% in this study.

1. Introduction

Organic photovoltaic devices have been one of the most exciting frontiers of current renewable energy research because of their advantages such as low cost of fabrication, light weight and easy processing [1–4]. Tang [5] reported the first promising hetero-junction photovoltaic cell based on molecular materials grown by organic molecular beam deposition. In last ten years, the performance of organic photovoltaic cells has been steadily improved. However, the power conversion efficiency (PCE) of organic photovoltaic cells is still low compared to their inorganic counterparts. Various researchers have been involved to enhance the efficiency of organic photovoltaic cells such as improving the work function of the electrode with different surface treatments [6,7], and also by inserting a buffer layer between the electrode and hole or electron transporting layer [8,9]. Moreover, the small molecules of organic photovoltaic cells have been actively studied and the best results have been obtained by vacuum co-sublimation of the Copper phthalocyanine (CuPc)–Fullerene (C60) donor–acceptor couple [10,11]. This type of photovoltaic cells is paid much attention due to its potential application in the future.

CuPc have been widely used as p-type materials in organic photovoltaic cells [10–15]. Tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) is very familiar organic acceptor material and the peripheral electronegative fluorine substituents of the dopant F_4-TCNQ increase its acceptor effect as already known from other classes of molecules [16–20]. Furthermore, the electron affinity of F_4-TCNQ (5.24 eV) and the ionization energy of CuPc (5.17 eV) are found to be energetically compatible with an electron transfer between the highest occupied molecular orbital (HOMO) of the CuPc to the lowest unoccupied molecular orbital (LUMO) of the F_4-TCNQ molecule [18]. In additional in some works, in situ on post thermal annealing of organic/polymeric layers in organic electronic devices including photovoltaic cells has been employed to obtain better film morphology and to improve the power conversion efficiency of devices [21,22].

In this study, we investigated the substantial changes in the surface morphology of the PEDOT:PSS layer after the oxygen plasma treatment by scanning electron microscopy (SEM) and we found that the appropriate plasma treatment can form uniformly distributed nano-scaled hillocks on the surface of PEDOT:PSS layer. We anticipated that the nano-structured surface morphology might improve the contact between the anode and hole transport layer. Moreover, considering the imbalance of carrier mobility between CuPc and C60, we doped F_4-TCNQ into CuPc to improve the carrier mobility of CuPc and thus the performance of organic photovoltaic cells [20]. Doping F_4-TCNQ in the organic photovoltaic cell is expected to balance the carrier mobility of the acceptor and donor and thus improve the carrier collection efficiency. Vacuum deposited films were thermally annealed to obtain denser film morphology as well as to improve performance efficiency of photovoltaic cells throughout this study.

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2. Experimental

2.1. Materials

PEDOT:PSS(poly(3,4-ethylenedioxythiophene)-poly(styrene-sulfonate) (Baytron, Bayer AG) as a hole injection layer was on to the transparent pre-patterned ITO glass substrate. CuPc as a hole transport layer was sublimed to obtain thin films via vacuum process and the chemical structure of CuPc (formula: $C_{32}H_{16}CuN_8$, molecular weight: 576.078, melting point: >360 °C, T_g: 240 °C, Tokyo Kasei Kogyo Co. Ltd.) is shown in Fig. 1(a). Other materials used are F_4-TCNQ as a dopant (formula: $C_{44}H_{32}N_2$, molecular weight: 276.15, melting point: >285 °C, Acros Organics), C60 as a electron transport layer (formula: C_{60}, molecular weight: 720.64, melting point: >280 °C, T_g: 174 °C, Sigma–Aldrich, 99.5%), and Lithium fluoride (LiF) (molecular weight: 25.9374, melting point: 870 °C, Tokyo Kasei Kogyo Co. Ltd.) and the chemical structure of F_4-TCNQ is shown in Fig. 1(b). In case of electron blocking layer (EBL), we considered small organic molecule thin films such as bathocuproine (BCP, Acros Organics).

2.2. Film formation

Vacuum deposition technique by thermal evaporation was used to obtain a homogeneous layer with well-controlled thickness. Before deposition, the ITO-coated glass was treated by acid solution followed by rinsing with de-ionized water and acetone and dried under nitrogen gas for cleaning the ITO-coated glass. A 5% solution of PEDOT:PSS was spin-coated on to the pre-cleaned ITO glass substrate at a rotational speed of 2000 rpm for 15 s, then baked at 90 °C in a vacuum oven for 1 h for forming a thin film with a thickness of about 40 nm. Furthermore, the surface layer of PEDOT:PSS was treated with oxygen plasma for 15 s, with a power of 150 W at atmospheric pressure. CuPc was deposited onto the PEDOT:PSS layer and the deposition rate was controlled to 1.1 Å/s to obtain 70 nm thickness of the CuPc film. Also, 5 wt% F4-TCNQ-doped CuPc film was obtained by co-evaporation. Thickness of each layer was measured using well calibrated quartz crystal thickness monitor (CRTM-6000, ULVAC kiko. Ltd.). At this deposition rate, the surfaces of deposited films were found preferentially uniform throughout the deposition experiments in the present study. The deposition of all the organic materials was carried at a base pressure of 10^{-6} torr and the substrate was not intentionally heated during the device fabrication process. The cathode in all devices was composed of 100 nm of aluminum. The active area of all devices was subject to the pre-patterned ITO glass.

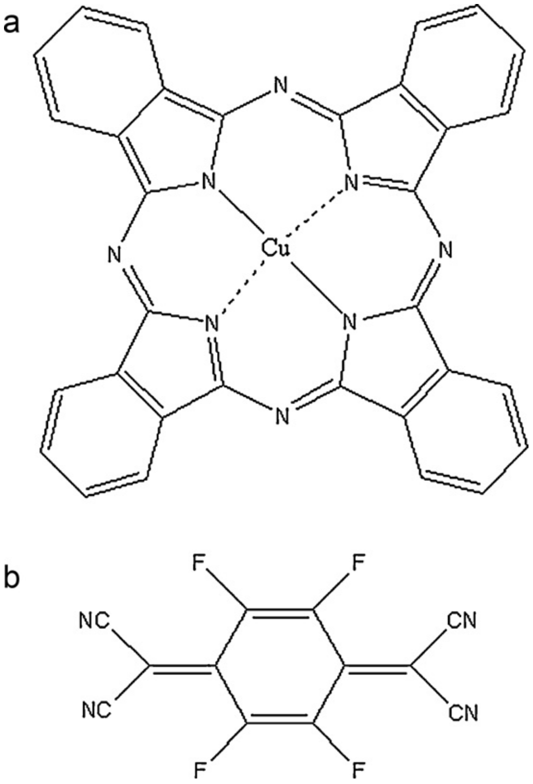

Fig. 1. Chemical structure of copper phthalocyanine (CuPc) (a), Tetrafluoro-tetracyanoquinodimethane (F_4-TCNQ) (b).

2.3. Film treatment and analysis

After vacuum deposition, thermal annealing of all the deposited CuPc and 5 wt% F_4-TCNQ-doped CuPc thin films were performed in a cylindrical furnace. During thermal annealing, the temperature was maintained at 150 °C, which is near the glass transition temperature of CuPc to form a denser film. Film thickness was monitored with a deposition monitoring system (CRTM-6000, ULVAC Kiko. Ltd.) and was measured using a SEM (HITACHI S-4200), as well. The current density–voltage (*J*–*V*) characteristics were measured using a multi-source meter (KEITHLEY 2400) and a solar simulator (XES 301S, SAN-EL Electronics). XRD (Rigaku Model D/Max 2400 and AFM (Nanoscope III-a, Digital Instruments Co. Ltd.) analysis were conducted to investigate the morphology of prepared films.

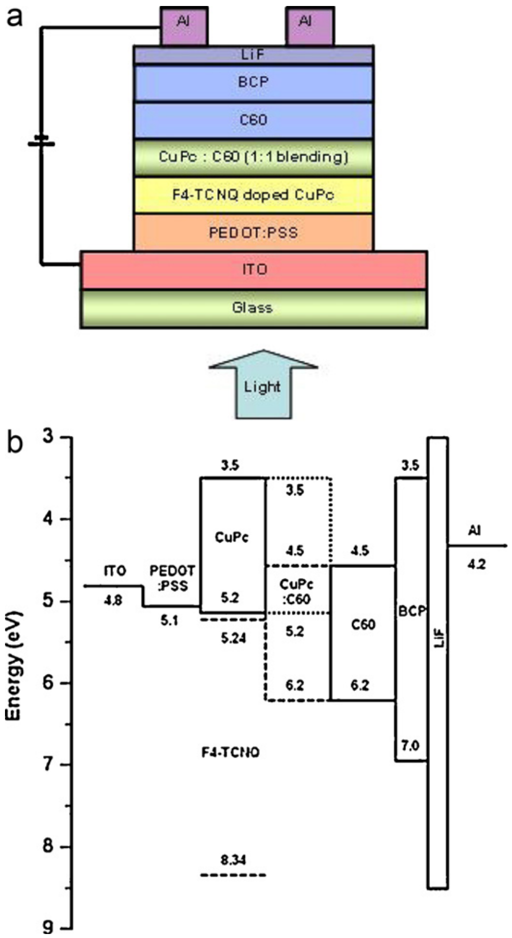

Fig. 2. Schematic structure and energy level diagram of multi-layered organic photovoltaic device.