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Solution processable PEDOT:PSS based hybrid electrodes for organic field effect transistors

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ABSTRACT

We report high performance solution processed conductive inks used as contact electrodes for printed organic field effect transistors (OFETs). Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) electrodes show highly improved very low sheet resistance of 65.8 ± 6.5 Ω/square (Ω/□) by addition of dimethyl sulfoxide (DMSO) and post treatment with methanol (MeOH) solvent. Sheet resistance was further improved to 33.8 ± 8.6 Ω/□ by blending silver nanowire (AgNW) with DMSO doped PEDOT:PSS. Printed OFETs with state of the art diketopyrrolopyrrole-thieno[3,2-*b*]thiophene (DPPT-TT) semiconducting polymer were demonstrated with various solution processable conductive inks, including bare, MeOH treated PEDOT:PSS, single wall carbon nanotubes, and hybrid PEDOT:PSS-AgNW, as the source and drain (S/D) electrode by spray printing using a metal shadow mask. The highest field effect mobility, 0.49 ± 0.03 $cm^2 V^{-1} s^{-1}$ for DPPT-TT OFETs, was obtained using blended AgNW with DMSO doped PEDOT:PSS S/D electrode.

1. Introduction

Transparent electrode materials for flexible optoelectric and electric devices are the subject of intensive research for use in organic light emitting diodes, organic and perovskite photovoltaics, organic field-effect transistors (OFETs), touch panels, and various sensors [1–5]. Conductive ink materials realize these devices by cost effective graphic art printing process [6–13]. Indium tin oxide (ITO) is widely used as the transparent electrode for conventional rigid and flexible substrates due to its excellent conductivity and low sheet resistance [100–1 Ω/square (Ω/□)], as well as high transparency to visible light (~90%). However, it is difficult to apply to highly flexible substrates with very small bending radii due to its intrinsic brittleness [14,15]. Single wall carbon nanotube (SWCNT), silver nanowire (AgNW), and poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) have been widely studied as potential candidates for highly flexible and printable transparent electrodes due to their various advantages, such as ease of manufacture; stable formulation using environmentally friendly solvents, such as water and various alcoholic solvents; low processing temperature; good mechanical stability; and high optical transmittance.

However, every material has advantages and disadvantages [16–20]. Despite SWCNT possessing good electrical conductivity, the electrical conductivity of printed SWCNT film requires improvement to extend its application range. The randomly networked morphology of SWCNT film, chemical functionalization, and various non-conductive additives for better solubility are considered the main reasons for its relatively low conductivity [21–23]. Much effort has been made to enhance the electrical conductivity of printed SWCNT networked film [24–27]. AgNW has better conductivity than ITO, but relatively high material cost, intrinsic weakness at grain boundaries, optically haziness, and less stable formulation are challenging [28–31]. PEDOT:PSS is the most widely used conducting polymer, and has advantages in material cost and stability in the ink state, but suffers from a low conductivity and ambient stability [32–34]. Therefore, a combination of those materials is highly desired to realize optimal materials for

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highly conductive and flexible transparent electrodes [35].

We investigate the effects of sheet resistance and the work function of charge injection electrodes on OFET performance based on state of the art diketopyrrolopyrrole-thieno[3,2-b]thiophene (DPPT-TT) semiconducting polymer. Several high performance conductive inks: SWCNT, PEDOT:PSS, and hybrid PEDOT:PSS-AgNW, were developed and spray printed with a metal shadow mask to define the bottom-gate bottom-contact (BG/BC) OFET channels. OFET carrier injection improvement along with high conductivity was obtained by doping DMSO into PEDOT:PSS, and further remarkable OFET performance improvement was achieved by blending with AgNW or phase separation of non-conducting PSS from PEDOT by MeOH treatment. Conductivity or carrier injection, which defined OFET performance was analyzed with ultraviolet photoemission spectroscopy.

2. Experimental

SWCNT was produced using high-pressure catalytic CO (Raw HiPco, RØ ~0.8–1.2 nm, length ~100–1000 nm) decomposition, purchased from Carbon Nanotechnologies Inc. and used without further purification. To obtain a stable dispersed SWCNT solution, 10 mg of SWCNT was dispersed in 50 ml of *N*-methylpyrrolidone (anhydrous, 99.5%, Sigma-Aldrich) with prolonged ultrasonication using a flat tip ultrasonic homogenizer (VCX130, Sonic & Materials Inc.) for 10 h at 11 W cm^{-2}. To avoid overheating during sonication, the SWCNT dispersion was immersed in a water bath with a continuous flow of cold water. Dispersed SWCNT solution was centrifuged at 10,000 rpm for 15 min (Vision, VS-15000CFN II) to remove residual catalytic metal particles, impurities, and SWCNT bundles.

Aqueous PEDOT:PSS solution was filtered through a 0.45 μm cellulose acetate filter, then mixed with 5 wt% DMSO (99%, Junsei) as doping solvent. AgNW (0.3 wt%) was dispersed into isopropyl alcohol (IPA) (Eiden Corp., RØ ~25 nm, length = ~20–30 μm), and used for blending without further purification. PEDOT:PSS was blended with AgNW with volume ratio of 1:1%v, and the mixture stirred overnight to obtain uniform solution.

BG/BC OFETs were fabricated on HMDS treated SiO_2 (300 nm)/N^{++} Si substrates. SiO_2 substrates were cleaned with RCA I (DI water: NH_4OH: H_2O_2 = 5:1:1 vol%) and RCA II (DI water: HCl: H_2O_2 = 5:1:1 vol%) solutions; followed by oven drying at 110 °C. To remove adsorbed moisture on SiO_2 surfaces, Si/SiO_2 substrates were immersed into a hexamethyldisilazane (HMDS) (Sigma-Aldrich) solution for 3 h and rinsed with chloroform to wash out unreacted HMDS. After successfully printed S/D electrodes onto the rigid substrates, flexible hybrid electrode was also fabricated on polyethylene naphthalate (PEN) (Fig. 4(a)). Furthermore, continues 10,000 times bending cycles with decreasing bending radius until 7.5 mm (Hansung System, Inc. Seoul, Korea) were used to investigate the durability of PEDOT:PSS film, each SWCNT and AgNW were blended with PEDOT:PSS dispersion (1:1%v for each ratio).

Different conductive inks: SWCNT, PEDOT:PSS-DMSO, PEDOT:PSS-MeOH, and PEDOT:PSS-AgNW were deposited by spray printing using a commercially available pneumatic spray nozzle (Iwata, HP-SB) onto HMDS treated Si/SiO_2 substrate under ambient conditions. Patterns were made using an S/D metallic shadow mask, adjusting process conditions, such as N_2 flow rate, distance between nozzle and substrate, and temperature, as required for the different inks. Spray printing flow rate was fixed at 2.3 ml min^{-1}, which was optimum to obtain the desired fine pattern [36]. The distance between nozzle to substrate was fixed at 15 cm, and substrate temperature was controlled by hotplate at ambient condition.

PEDOT:PSS was printed at a substrate temperature of 120 °C, with N_2 gas pressure maintained at ~0.1 MPa, and followed by annealing at 150 °C for 10 min. After completion of spray printing, the metallic shadow mask was manually removed to obtain high resolution printed S/D electrodes on the HMDS treated Si/SiO_2 substrate (Fig. 1(b)). The channel width of the patterned S/D electrodes was 1 mm, with varied channel lengths: 50, 100, 150, and 300 μm. DMSO doped PEDOT:PSS S/D electrodes were treated by immersing into methanol (MeOH) for 10 min and annealing for 5 min at 140 °C.

The p-type semiconductor DPPT-TT polymer was used as receiver and dissolved into 1-2-dichlorobenzene (DCB, anhydrous, 99%, Sigma-Aldrich) to obtain 10 mg ml^{-1} solution. The active layer was deposited by spin coating on top of the channel region and S/D electrodes, followed by annealing at 200 °C for 30 min in a nitrogen filled glove box.

OFET output and transfer characteristics were measured using a Keithley 4200 in a nitrogen filled glove box under dark conditions. Channel length and width of spray printed electrodes were calculated using optical microscope (OM, Olympus BX-51) and further surface morphology of the S/D electrodes was investigated using scanning electron (SEM) (JEOL JSM-7100F) and atomic force microscopy (AFM) images of the polymer films were obtained using an atomic force microscope (Digital Instrument Multimode AFM controlled by a Nanoscope IIIa scanning probe microscope controller) in taping mode. Sheet resistance of the S/D electrodes films were measured using the four point probe method (RCHECK 4 point meter, EDTM), and 6 different points were averaged for each sample. S/D electrode energy levels of atomic core and work function were investigated using X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), performed by a PHI 5000 VersaProbe II with He I (21.2 eV) source.

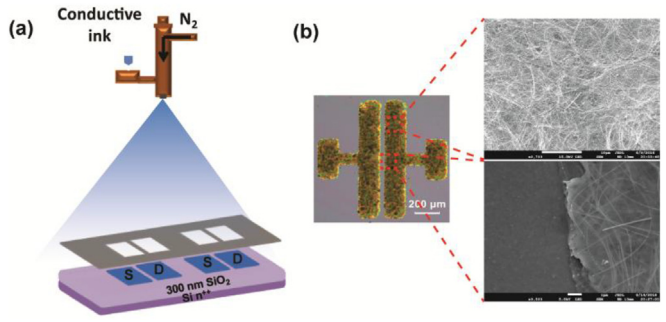

Fig. 1. (a) Spray printing conductive inks to construct organic field effect transistors; (b) optical image PEDOT:PSS-AgNW source and drain electrode (insert: SEM images).

3. Results and discussions

Fig. 1(a) shows the process to fabricate OFET S/D electrodes, as described in the experimental section. The very thin shadow mask was soft landed onto the substrate without any additional pressure for proximity contact using a strong magnetic plate on the opposite side. The smallest patterning size (~50 μm) used in this study limited hole sizes in the metal shadow mask, thickness of mask, and distance of metal mask to substrate. DPPT-TT was spin coated on top of the spray printed S/D electrodes as an active layer to complete the fabrication.

Table 1 summarizes the fundamental characteristics, such as field effect mobility (μ_{FET}), I_{ON}/I_{OFF} ratio, and threshold voltage (V_{Th}) of DPPT-TT OFETs, calculated from the transfer curves (Fig. 2). Field effect mobility in the saturated regime (μ_{FET}, at V_D = −80 V) was calculated from [37],