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Improved ambipolar charge injection in organic field-effect transistors with low cost metal electrode using polymer sorted semiconducting carbon nanotubes

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Solution-processed thin film transistors can be implemented using simple and low cost fabrication, and are the best candidates for commercialization due to their application to a range of wearable electronics. We report an ambipolar charge injection interlayer that can improve both hole and electron injection in organic field-effect transistors (OFETs) with inexpensive source-drain electrodes. The solution processed ambipolar injection layer is fabricated by selective dispersion of semiconducting single walled carbon nanotubes using poly(9,9-dioctylfluorene). OFETs with molybdenum (Mo) contacts and interlayer (Mo/interlayer OFETs) exhibit superior performance, including higher hole and electron mobilities, device yield, lower threshold voltages, and lower trap densities than those of bare transistors. While OFETs with Mo contacts show unipolar p-type behaviour, Mo/interlayer OFETs display ambipolar transport due to significant enhancement of electron injection. In the p-type region, transistor performance is comparable to devices with gold (Au). Hole mobility is increased approximately ten-fold over devices with only Mo contacts. The electron mobility of Mo/interlayer OFETs is 0.05 $cm^2V^{-1}s^{-1}$, which is higher than devices with Au electrodes. The p-type contact resistances of Mo/interlayer OFETs are half those of OFETs with Mo contacts. Trap density in Mo/interlayer OFETs is one order magnitude lower than that of pristine devices. We also demonstrate that this approach is extendible to other metals (nickel) and n-type semiconductors with different energy levels. Injection by tunnelling is suggested as the mechanism of ambipolar injection.

1. Introduction

Organic field-effect transistors (OFETs) have attracted interest for their potential application as inexpensive, flexible, and stretchable electronics [1–3]. The wide range of potential applications include flexible displays, memory, and chemical sensors [4–7]. Charge injection determines OFET performance, because organic semiconductors (OSCs) forms normally strong Schottky contact with metal electrode [8,9]. In contrast to silicon transistors, achieving the Ohmic contact in OFETs has been still difficult due to absence of the efficient doping technique, such as ion implantation. In particular, contact resistance (R_c) has a more dominant influence on transistor performances with short channel length (L) [1,2,9]. It is difficult to achieve downscaling of the transistor dimension for fast switching speed of circuits due to the contact limitation. Recently, Bittle et al. and Uemura et al. reported independently that large R_c also leads to overestimation of field-effect mobility in OFETs [10,11].

Au has been widely used for OFET source-drain (S-D) electrodes due to its excellent electrical conductivity, high work function (Φ), and environmental stability [1]. However, Au is approximately 51,000$/kg, which limits its use in commercial applications. For mass production of large area OFETs, a replacement of expensive Au with an inexpensive metal electrode is required. Copper (Cu), molybdenum (Mo), carbon nanotubes, and conducting polymers have been used for the charge injection electrode in p-type OFETs [12–14]. Mo has been widely used in the thin-film transistor (TFT) backplane for organic light emitting diodes with large area due to

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its high conductivity (~$5 \times 10^{-6}\Omega$ cm) and relatively low price (~26 \$/kg) [12,15]. However, its relatively low Φ (4.3–4.86 eV) [15] Mo can form a strong Schottky barrier with most p-type OSCs.

Several approaches have been reported to resolve the problem of charge injection induced by the Schottky barrier in OFETs [9,16,17]. Insertion charge injection layers between OSCs and the S-D electrode, such as self-assembled monolayers [18], conjugated polyelectrolytes [19], metal oxide [20], and local doping of OSCs [21], are common techniques to obtain better contact. These techniques can improve charge injection of one type of charge carrier, either hole or electron since the interlayer can shift Φ of the injection electrode in one direction. Less attention has been devoted to simultaneously improving hole and electron injection for ambipolar devices [9,22,23].

Here, we report a solution processable charge injection layer for improvement of both hole and electron injection in ambipolar OFETs with low cost Mo S-D electrodes using poly(9,9-dioctylfluorene) (PFO) wrapped semiconducting single walled carbon nanotubes (s-SWNT). Inserting a thin PFO wrapped s-SWNT interlayer (PFO:s-SWNT) between the OSC and Mo electrode, OFETs based on poly(thienylenevinylene-co-phthalimide)s (PTVPhI-Eh) as an ambipolar semiconductor showed significantly improved device performance, including higher hole (μ_h) and electron mobility (μ_e), lower threshold voltages, lower trap density, and better yield than the OFETs without the interlayer. Hole mobility of devices with Mo/PFO:s-SWNT was enhanced approximately 10-fold over bare devices and were comparable to devices with Au contacts. In particular, μ_e of the OFETs with interlayer (0.05 $cm^2V^{-1}s^{-1}$) was much improved than devices with Au contact (0.0039 $cm^2V^{-1}s^{-1}$). The hole trap density of the OFETs with Mo/PFO:s-SWNT decreased by approximately one order of magnitude over OFETs without the interlayer. The PFO:s-SWNT interlayer also improved both hole and electron injection in OFETs with nickel S-D metals or other OSCs, indicating generality of the interlayer.

2. Experimental

2.1. Preparation of conjugated polymer wrapping SWNT interlayer solution

The molecular weight (Mw) of PFO used in this study was ≤20,000 g/mol, Sigma Aldrich. SWNTs grown by the HiPco process (diameter 0.8–1.2 nm, purified <13 wt% iron) were purchased from Unidym Inc. All other chemicals were purchased from Sigma Aldrich. The PFO was dissolved in toluene (1 mg/ml) on a 60 °C hot plate over 2 h. After complete dissolution and cooling, the SWNT powder was added to the solution at 0.5 mg/ml, and dispersed in an ultrasonic bath (Branson 5510) for 1 h at approximately 18 °C. The homogenized solution was then centrifuged (VS-15000CFNII, Vision Scientific) at 10,000 g using a fixed rotor, and the supernatants were collected.

2.2. Fabrication of Mo electrode

The glass substrates (Corning Eagle 2000) was pre-patterned by negative photolithography (AZ 5214, MicroChemicals). Before the deposition of Mo, Ni as an adhesion layer was thermally evaporated. Mo thin electrode were deposited on the substrates by DC magnetron sputtering (DaON 1000S). The Mo target was had purity of 99.99%. The distance between the target and the substrate was fixed at 15 cm. The purity of used argon was 99.999%. Mo target in a high-vacuum system evacuated by rotary and turbo-molecular pumps. The DC power and the Ar gas pressure were 100 W and 1.12×10^{-3} Torr, respectively. To remove the contaminants on the surface, the Mo target was pre-sputtered for 30 min before the deposition. The Mo electrodes were deposited with rotation at a speed of 15 rpm in order to achieve homogeneous films. Finally, the photoresists was removed by the AZ 100 remover (Micro-Chemicals). The channel width W = 1 mm, channel length L were 10, 20, 30 and 50 μm.

2.3. Fabrication of OFETs

The substrates were cleaned in an ultrasonic bath with deionized water, acetone, and 2-propanol for 2 min each. The polymer/SWNT dispersion solution was spin coated onto the substrates at 2000 rpm for 60 s, and the resulting films were annealed in air at 200 °C for 20 min. The conjugated polymer PTVPhI-Eh (M_w = 35,800 g/mol) was synthesized for this work, following the method reported elsewhere [24]. P(NDI2OD-T2) were purchased from Polyera corporation. PTVPhI-Eh and P(NDI2OD-T2) were dissolved in anhydrous chlorobenzene (CB) to obtain 5 mg/ml concentrations, respectively, and were then spin coated at 2000 rpm in a dry nitrogen glovebox (O_2 < 10 ppm). The semiconducting films were baked at 110 °C for 20 min on a hotplate to remove residual solvent. Poly(methyl methacrylate) (PMMA) (M_w = 120kD, Sigma Aldrich) was used as the gate insulator for PTVPhI-Eh and P(NDI2OD-T2) OFETs without further purification and dissolved in n-butyl acetate (80 mg/ml). The dielectric solution was spin coated on top of the semiconducting film at 2000 rpm for 60s, and the final thickness was approximately 500 nm. After depositing the dielectric, the resulting film was baked at 80 °C for 30 min. Finally, aluminium gate electrodes (50 nm) were thermally evaporated using shadow masks in a high-vacuum chamber (~10^6 Torr).

2.4. Characterizations

UV–Vis-NIR spectra were measured using a Perkin-Elmer Lambda 750. UPS and XPS measurements were performed using AXIS-NOVA (Kratos, Inc.) at base pressure 4.2×10^{-9}torr using the He I photon line (hυ = 21.2 eV) from a He discharge lamp as the excitation source. The resolution was 25 meV. For FET electrical characterizations, a semiconductor parameter analyser (Keithley 4200-SCS) was used in a dry nitrogen glovebox (O_2 < 10 ppm). In the saturation regime, charge carrier mobilities were extracted from the transfer curves according to

$$I_d = \mu_{sat} \times C_i \times \frac{W}{2L} \times (V_g - V_{th})^2,$$

where I_d is the drain current, and μ_{sat} is the saturation mobility.

3. Result and discussion

Fig. 1(a) shows the top-gate bottom contact (TGBC) structure chosen for this study, because the semiconductor could be encapsulated by the overlying gate dielectric and gate layer to minimize degradation in air. The Mo S-D electrodes were fabricated by the photolithography lift-off technique. The PFO:s-SWNT solution was prepared following a previously detailed method that is easy and efficient due to use of low-speed centrifugal force (10,000 g) [9,25,26]. The thickness, surface morphology and work function of the PFO:s-SWNTs were measured in our previous paper [9]. The interlayer was deposited by simple spin coating onto the Mo S-D electrode without patterning. Fig. 1(b) shows the Φ of Au [27–29], Mo, and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of PTVPhI-Eh. Bottom contact Au electrodes typically show relatively lower Φ(4.4–4.7 eV) than clean Au etched by argon beam (~5.0 eV)