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Generalized enhancement of charge injection in bottom contact/top gate polymer field-effect transistors with single-walled carbon nanotubes

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ABSTRACT

We investigate the influence of small amounts of dispersed single-walled carbon nanotubes (SWNTs) on the contact resistance and device characteristics of bottom contact/top gate polymer field-effect transistors (FETs). Five conjugated polymers representing different classes of polymer semiconductors with different HOMO/LUMO levels are employed, namely, polythiophenes (P3HT), polyphenylenevinylenes (MDMO-PPV), polyfluorenes (F8T2), naphthalene-bis(dicarboximide) bithiophene copolymers (P(NDI2OD-T2)), and diketopyrrolo-pyrrole-bithiophene copolymers (DPPT-TT). In all cases the presence of dispersed SWNTs reduces non-ohmic contact resistance and lowers threshold and onset voltages for charge transport. In some cases inherent ambipolar charge transport in conjugated polymers (F8T2 and P(NDI2OD-T2)) is revealed. The concentration of the SWNTs within the semiconducting layer remains below the percolation limit and thus the apparent mobilities and on/off ratios are still determined by the polymer and independent of the specific type of the carbon nanotubes (metallic or semiconducting). The degree of enhancement depends both on the energy level offset between the injecting gold electrode and the HOMO/LUMO level (i.e., Schottky barrier) and the charge carrier mobility of the respective polymer. The simplicity of this injection enhancement method and its broad applicability make it a step toward high performance polymer transistors without injection limitations.

1. Introduction

Efficient charge injection into the semiconducting layer is crucial for the overall performance of organic field-effect transistors (FETs) [1,2]. The charge injection efficiency is often limited by Schottky barriers that originate from an offset between the work function of the injecting electrode and the highest occupied molecular orbital (HOMO) for hole injection or the lowest unoccupied molecule orbital (LUMO) for electron injection of the organic semiconductor [3]. A large injection barrier manifests itself directly in the current-voltage characteristics. Typically a suppression of current at low source–drain voltages is found in the output characteristics. In bottom contact/top gate FETs a large contact resistance also leads to higher apparent onset voltages. This staggered configuration using solution processable polymer gate dielectrics (e.g., poly(methyl methacrylate) (PMMA) or Cytop®) has become one of the most popular FET geometries for high mobility polymer transistors [4]. This popularity is partially due to processing concerns for flexible substrates and the advantageous encapsulation of the semiconductor by the top dielectric, but also due to the reduction of contact resistance compared to the also frequently used bottom contact/bottom gate (coplanar) FETs [5,6]. The lower contact resistance is a result of the larger injection area and the additional gate field that supports charge injection.

Various methods are feasible to improve the injection of one charge carrier type for FETs that suffer from large

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Schottky barriers due to an energy level mismatch between the electrode workfunction and the organic semiconductor. For example, self-assembled monolayers [7–9], metal oxide buffer layers [10–14] or polymer layers [15,16] can be applied to the electrodes, which modify the effective workfunction of the metal and thus can either improve hole injection (higher workfunction) or electron injection (lower workfunction). However, strategies for improving both hole and electron injection at the same time are far less advanced. Single-walled carbon nanotubes (SWNTs) have been suggested as a potential electrode material for organic electronic devices due to their high conductivity, flexibility and potential for solution processing and printing. Further, their near one-dimensional geometry and high aspect ratio can facilitate tunneling across the Schottky barrier and thus improve carrier injection [17,18]. Several groups have reported examples of organic FETs with arrays of SWNTs extending from metal electrodes into the channel [17,19–22]. Others successfully used patterned or aligned SWNTs directly as the injecting electrodes [21,23–26].

In a previous report, we demonstrated a very simple method for improving the injection of both holes and electrons into large band gap polyfluorenes such as poly(9,9-di-n-octylfluorene-alt-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene) (F8) in a bottom contact/top gate FET structure (schematic geometry in Fig. 1a) by adding small amounts of SWNTs to the semiconducting polymers [27]. Importantly the density of the nanotubes within the polymer remained below the percolation limit and thus charge transport was still determined by the charge carrier mobility of the polymer and off-currents remained low. Nevertheless, the threshold and onset voltages for both hole and electron transport were substantially lowered and higher ambipolar currents were obtained. The injection barriers were notably lowered as indicated by more linear output curves in the low source–drain voltage regime. Two possible mechanisms were proposed. First the reduction of the bulk resistance of the polymer layer over the bottom contacts, which is known to contribute to the overall contact resistance [6]. And second, the strong electric field-enhancement at the tips of the one-dimensional carbon nanotubes. In both cases the enhancement should be independent of the type of nanotube, whether metallic or semiconducting, and the semiconducting polymer. Thus we proposed that this method should be applicable to a broad range of polymer FETs that suffer from injection barriers. Here we show that this is indeed the case by applying the concept to many different semiconducting polymers, improving both hole and electron injection.

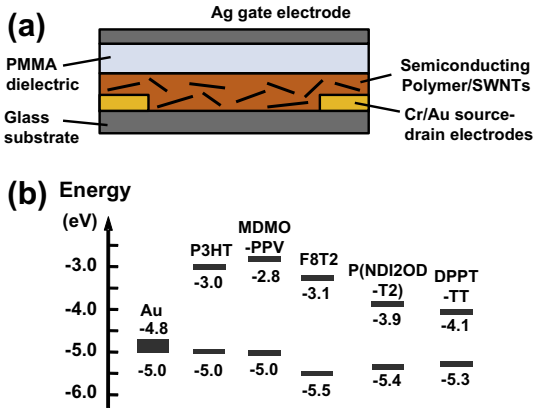

Fig. 1. (a) Schematic illustration of bottom contact/top gate polymer field-effect transistor with carbon nanotubes dispersed in the semiconducting layer. (b) Workfunction of gold and HOMO and LUMO energy levels of P3HT, MDMO-PPV, F8T2, P(NDI2OD-T2) and DPPT-TT.

In this study we use five very different polymers with very different conjugated backbones as well as HOMO and LUMO levels as shown in (Fig. 1b): regio-regular poly(3-hexylthiophene) (P3HT), poly[2-methoxy,5-(3′,7′-dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV), poly(9,9-dioctylfluorene-alt-bithiophene) (F8T2), poly([N,N-9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-bithiophene)) (P(NDI2OD-T2)), poly[3,6-dithiene-2-yl-2,5-di(2-octyl-1-dodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5′,5″-diyl-alt-thieno-[3,2-b]thiophene] (DPPT-TT). Their molecular structures are shown in (Fig. 2a). P3HT is a semicrystalline model polymer semiconductor and has been extensively researched. Although the HOMO level of P3HT is close to the workfunction of gold, non-ohmic contacts are found in P3HT FETs depending on the device geometry. Previous work by Sarker et al. showed that aligned arrays of SWNTs as injecting electrodes in a bottom gate geometry enabled improved charge injection in P3HT nanowires especially for short channels [24]. MDMO-PPV as a typical representative of the amorphous poly(phenylene vinylene)s also has a HOMO level at about −5.0 eV, which matches the workfunction of gold electrodes. Bottom gate/bottom contact MDMO-PPV field-effect transistors show clearly non-ohmic injection behaviour for ITO/gold electrodes [28]. F8T2, as another polyfluorene copolymer, has been extensively studied with respect to contact resistance [5,6,29]. Its ionization potential is large (−5.5 eV), leading to higher injection barriers for holes, while the lower LUMO level may allow weak electron injection and transport. Naphthalene bis(dicarboximide)-based polymers have gained attention as outstanding candidates for high-mobility n-type polymers such as the P(NDI2OD-T2) [30,31]. Caironi et al. found that solution-processed P(NDI2OD-T2) FETs, with a bottom contact/top gate configuration and Au electrodes, show a low contact resistance for electron injection despite the existing Schottky barrier [32]. The offset between the HOMO level of P(NDI2OD-T2) and work function of gold is not insurmountable (∼0.5 eV) and Baeg et al. achieved enhancement of hole transport in top-gated P(NDI2OD-T2) FETs by using a high-k dielectric [33]. Another promising class of polymer semiconductors are the diketopyrrolopyrrole (DPP) copolymers, which have recently shown extremely high charge carrier mobilities [34,35]. DPPT-TT, with thieno[3,2-b] thiophene (TT) and two thiophene moieties in the repeat unit has a narrow bandgap of 1.2 eV and has been shown to exhibit high and balanced ambipolar mobilities although still contact limited [36]. Here we will show that the injection of either holes or electrons and thus the contact properties of all