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Annealing and doping-dependent magnetoresistance in single layer poly(3-hexyl-thiophene) organic semiconductor device

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ABSTRACT

We compare the current density–voltage (J–V) and magnetoconductance (MC) response of a poly(3-hexyl-thiophene) (P3HT) device (Au/P3HT(350 nm)/Al) before and after annealing above the glass transition temperature of 150 °C under vacuum. There is a decrease of more than 3 orders of magnitude in current density due to an increase of the charge injection barriers after de-doping through annealing. An increase, approaching 1 order of magnitude, in the negative MC response after annealing can be explained by a shift in the Fermi level due to de-doping, according to the bipolaron mechanism. We successfully tune the charge injection barrier through re-doping by photo-oxidation. This leads to the charge injection and transport transitioning from unipolar to ambipolar, as the bias increases, and we model the MC response using a combination of bipolaron and triplet-polaron interaction mechanisms.

1. Introduction

Poly(3-hexyl-thiophene) (P3HT) is a widely employed material in organic photovoltaics (OPV) [1] and organic field effect transistors (OFET)[2]. Photo-oxidization doping in P3HT includes two reaction routes. One is fully reversible, forming charge transfer complexes (CTC) [3] and the other is related to the formation of singlet oxygen under participation of triplet excitons on the chains of P3HT [4]. Photo-oxidation doping in P3HT has been found to provide a supply of charge carriers (holes) which can freely move within the organic [4]. Annealing above the glass transition temperature can lead to de-doping and will also result in a reversible shift of the Fermi level (a rise of ~0.3 eV after de-doping) [5,6]. The photo-oxidization doping effect can give rise to "flat-band" conditions which will improve the charge injection at both electrodes [7,8]. Doping and de-doping by annealing also affect the density of states (DOS) within the P3HT with a reported increase of the standard deviation σ of the deep trap DOS after de-doping [9]. The annealing effect in P3HT also results in an enhancement of the π–π stacking in the crystal domains [10] and improves the degree of crystallinity [11]. This can result in an improvement in charge carrier mobility in different kinds of devices [12–15].

Organic magnetoresistance (OMR) is the magnetic field effect on electrical transport, luminescence, photocurrent and efficiency in organic semiconductors (for recent reviews, please see [16–18]). The OMR response due to both bipolaron and triplet-polaron interaction mechanisms, has been observed in P3HT based devices [19–22]. Our previous work [19] proves a transition from negative MC to positive MC due to a change in the dominant mechanism as the bias increases in an Au/P3HT/Al device. Doping effect results in band bending at both metal–organic

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interfaces which enables charges to overcome the Schottky injection barriers, even at zero bias. Thus, the device would be expected to be in a "flat-band" state making it difficult to produce a truly unipolar system in forward bias. If one de-dopes by annealing one can re-introduce significant injection barriers at both anode and cathode. As reported in the literature, the charge injection barrier can be subsequently tuned by reversible doping [7,8]. This makes it possible to investigate the transition of the MC response from unipolar (hole only) to ambipolar injection and transport in forward bias. This work is thus motivated by both technological and fundamental scientific interest.

2. Experimental details

The poly(3-hexyl-thiophene) P3HT was dissolved in 1,2-dicholobenzene at a concentration of 30 mg/ml before repeatedly spin coating the solution at 1000 rpm for 1 min each time, resulting in smooth 350 nm films on an Au coated substrate. All P3HT films were annealed at 100 °C for 20 min in nitrogen to remove any remaining solvent before cathode deposition. The vacuum deposition of aluminium was carried out at a pressure of $\sim 10^{-6}$ mbar, with deposition rates ranging from 0.5 Å s^{-1} to 5 Å s^{-1}. Magnetoconductance (MC) measurements were taken with the device operating in constant voltage mode. The magnetic field measurements were made from 0 to ~260 mT. A Keithley 236 source-measure unit, in constant voltage mode was used to average the current measurements over 16 readings. The drive voltage was only applied to the device when the magnetic field was stable. Dark injection measurements were carried out using a TTi (TG5011) pulse generator to provide the bias and the current was monitored as a voltage drop across a 50 Ω load resistor at the input of an Agilent infiniium digitising oscilloscope. Signal averaging over 64 measurements increased the signal to noise ratio. In order to de-dope the organic layer, annealing at a temperature of 150 °C was carried out under vacuum ($\sim 10^{-6}$ mbar) for 1 h. The re-doping procedure was carried out by exposing the device under incandescent light (3.75 mW cm^{-2}) in ambient atmospheric conditions (46% relative humidity and temperature of 25 °C).

3. Results and discussion

Fig. 1 shows a double logarithmic plot of current density versus voltage (*J–V*) for the pristine (pre-doped), annealed and re-doped Au/P3HT(350 nm)/Al device. Before annealing, as shown in Fig. 1, the *J–V* appears as an almost featureless straight line, with no sharp "turn on" transitions, confirming that the oxygen doping effect results in efficient hole injection and extraction. For both annealed and re-doped samples, a "turn on" appears at ~1 V suggesting an injection barrier has been overcome above that bias. Above ~2 V bias all samples display approximately quadratic *J–V* characteristics as expected for space charge limited transport (SCLC). In this region ($V > 2$ *V*) there is a decrease of more than 3 orders of magnitude in current density under the same bias after annealing, compared to the pristine (pre-doped) results, which partially recovers

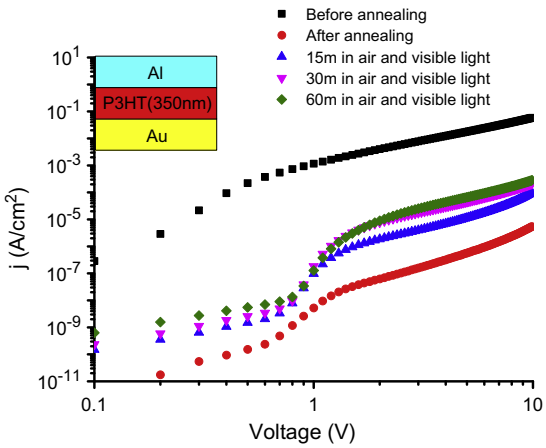

Fig. 1. Current density versus voltage characteristics in the pristine (black squares), annealed (red circles) and re-doped samples. The re-doping exposure was varied: 15 min (blue up-triangles), 30 min (magenta down-triangles) and 60 min (olive diamonds). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

after re-doping. These changes can be attributed to the disappearance of band bending through de-doping and the consequent charge injection barrier enhancement as reported in the literature [7,8]. We note that there is significant current density recovery through re-doping.

Fig. 2 shows schematic diagrams of pristine (pre-doped), annealed and re-doped Au/P3HTAl devices under short circuit conditions. Due to the oxygen doping effect on both interfaces, even at zero bias (Fig. 2a), we would expect the device to be in a "flat-band" state. After annealing (Fig. 2b), the removal of the dopants results in the return of significant Schottky barriers at both metal–organic interfaces, in agreement with the appearance of the "turn on" at ~1 V in Fig. 1. This is consistent with the "flat band" conditions requiring a bias defined by the difference in the effective work functions, 5.1 eV for Au [23] and 4.2 V for Al [24] in the undoped case. After re-doping (Fig. 2c) band bending can occur, at least partly, at both interfaces in agreement with the current density recovery in Fig. 1.

Dark injection (DI) measurements of the mobility were carried out under different bias as shown in Fig. 3. Before annealing the DI curves display clear transient peaks (Fig. 3a) which yield a field independent hole mobility of $\sim 10^{-4}$ cm^2/V s as shown in Fig. 3b. This is in agreement with mobilities reported in the literature [12,13]. After annealing, however, the DI transient peak disappears, as shown in Fig. 3a. This is entirely consistent with the re-appearance of a significant injection barrier at the anode, due to removal of the doping effect, since DI measurements require highly efficient injection conditions in order to provide sufficient charge for space charge limited transport. The steady state (long time) currents in Fig. 3a display a corresponding current density drop as in Fig. 1.

We plot the magnetoconductance (MC) response versus magnetic field (*B*) in Fig. 4 under different bias and sample conditioning. The MC can be detected under a bias as low