Solution Processed High Performance Thin-film Transistors Using Polymer/SWCNT Composite Ink

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ABSTRACT

Semiconducting single-walled carbon nanotubes (s-SWCNTs) are considered to be the most promising candidates for high-performance field-effect transistors (FETs). In the present study, a new type of conjugated copolymer containing peri-Xanthenoxanthene and carbazole units, named PCzPXX, has been synthesized and used for selectively sorting SWCNTs. The solution form of sorted SWCNTs has been used to fabricate TFTs by dip-coating method. These TFTs exhibited p-type behaviors with charge carrier mobility as high as 5.5 cm^2/Vs and on/off current ratio of 10^7 without any 'burn-off' or post-treatment.

Keywords: polymer, SWCNT, TFTs

INTRODUCTION

Semiconducting single-walled carbon nanotubes (s-SWCNTs) are considered to be the most promising candidates for high-performance field-effect transistors (FETs) in printed and flexible electronics [1-4]. However, the inherent insolubility of carbon nanotubes in most organic and aqueous solvents and mixing of metallic and semiconducting nanotubes have hindered their widespread applications.

Over the past years, various conjugated polymers have been used to separate semiconducting SWCNTs from metallic SWCNTs [2, 10], such as homopolymers (ie. P3AT, poly(phenylene vinylene) and polyfluorene) and a series of fluorine- and thiophene-containing copolymers, based on the mechanism that polymer molecules preferentially wrap over semiconducting tubes. While they all can form strong supramolecular complexes with SWNTs which facilitates the separation and dispersion of SWCNTs in solvents, the TFTs made from the SWCNT inks were not as good as expected [3].

Herein a new type of conjugated copolymer containing peri-Xanthenoxanthene and carbazole units, named Poly[N-9′-heptadecanyl-2,7-carbazole-alt-1,7-Dioctyl-3,9-Peri-Xanthenoxanthene] (PCzPXX), has been synthesized using Suzuki polycondensation. The polymer has been used to selectively disperse s-SWCNTs with high efficiency. The solution form of sorted SWCNTs have been used to fabricate TFTs by dip-coating method on a highly doped Si substrate which acted as the gate electrode and SiO_2 (300 nm) on top of the silicon substrate as the dielectric layer. They exhibited p-type behavior with charge-carrier mobility as high as 5.5 cm^2/Vs and on/off current ratio of 10^7 without any 'burn-off' or post-treatment.

EXPERIMENTAL RESULTS

To make polymer/SWCNT composite ink, PCzPXX (Fig 1a) was first dissolved in toluene, (concentration of 0.5 mg/mL). High-Pressure CO (HiPCO) SWNTs were added into the solution, followed by the ultrasonic processing for two hours until polymer coated to SWCNT surface. Finally, the polymer/SWCNT composite ink was obtained after centrifugal processing. All the following work was based on this ink.

UV/Vis/NIR spectroscopy was taken on the supernatants to measure the relative amount of dispersed SWCNTs (Figure 1b). We observed that the PCzPXX solution (without SWCNTs) showed only a single absorption peak at ~450 nm. The additional vibronic peaks observed suggest that the polymer is now strongly bound to the SWCNTs (in the case of the polymer/SWCNT solution) or the substrate.

In order to validate the performance of the ink, we fabricated bottom gate TFTs using drop-coating method [2, 10, 12]. Figure 2a is the schematic of a SWCNTs thin-film transistor. Au/Ti electrodes for source and drain were patterned with 20 μm of channel length (Figure 2b, L=20 μm, W=200×3 μm) on a heavily n-doped Si substrate as the gate and a 300 nm SiO_2 as the dielectric layer. The solution was made by diluting the polymer/SWCNT composite in toluene and dilution ratio was 20. The SWCNTs film was deposited by soaking the substrates in the polymer/SWCNT dispersion, Then the device were blown dry with dry nitrogen gas and baked in an oven at 150℃ for 2 h.

After fabrication, the state of SWCNT film was observed by atomic force microscopy (AFM) as shown in Figure 2b. SWCNTs were fully percolated within the channel [1] and no polymer residue is seen on surface of

SWCNT film. The tube density of SWCNT is about 180~200 SWCNTs/μm^2.

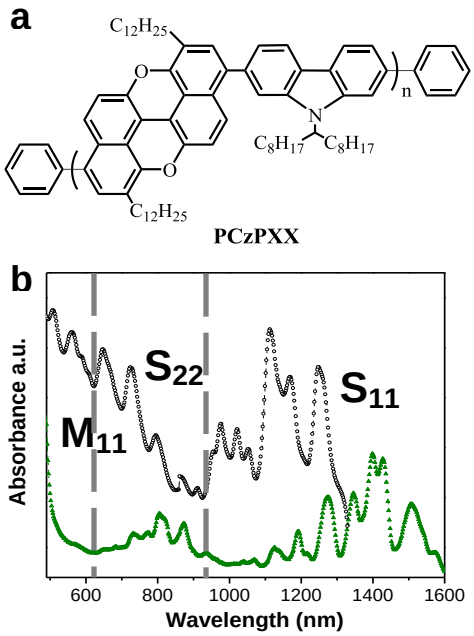

Fig. 1 (a) The structure of PCzPXX; (b) UV-Vis-NIR Absorption spectra of polymer-wrapped SWCNT solution (Green line), compare to those of SDS-dispersed SWCNT solution (Black line).

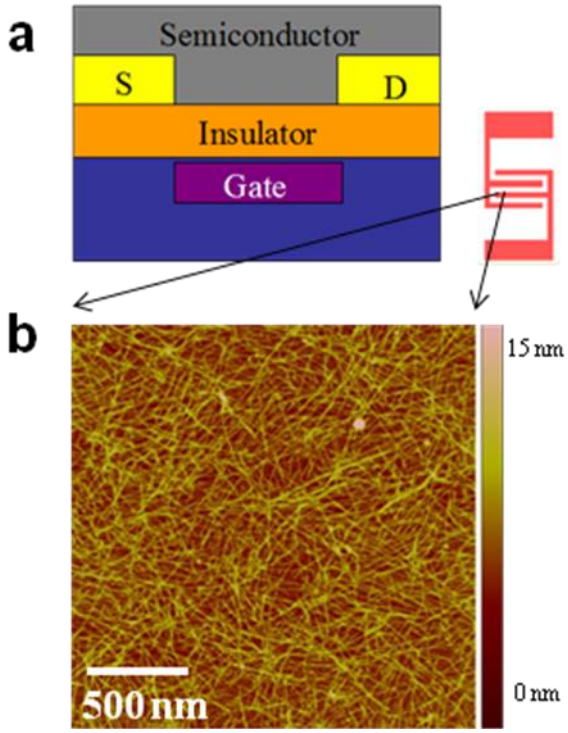

Fig. 2 (a) Schematic of a SWCNTs thin-film transistor, Au/Ti electrodes for source and drain were patterned with 20 μm of channel length on a heavily n-doped Si substrate as the gate and a 300 nm SiO_2 as the dielectric layer. The SWCNTs film was deposited by soaking the substrates in the polymer/SWCNT dispersion; b) AFM image of the SWCNT network deposited in a thin-film transistor measured in the channel region.(scan area: 2×2 μm)

Among all devices, no short-circuiting was observed and the averages on/off ratio of ~5×10^6 were obtained without any 'burn-off' or post treatment. In addition, hole mobility as high as 5.5 cm^2/Vs with an on/off ratio was 1.5×10^7 and the average mobility was 3.5 cm^2/Vs. The on/off ratio can be further increased by adjusting the soaking time. The highest on/off ratio was 5×10^7. However, the charge-carrier mobility was not obvious decrease at this on/off ratio. Figure 3a is transfer curves of fabricated TFTs, the drain-source voltage is -1V. High positive threshold voltage was encountered, which was probably attributed to the influence of oxygen and water. Polymer or atomic layer deposition passivation can be used to reduce this effect.

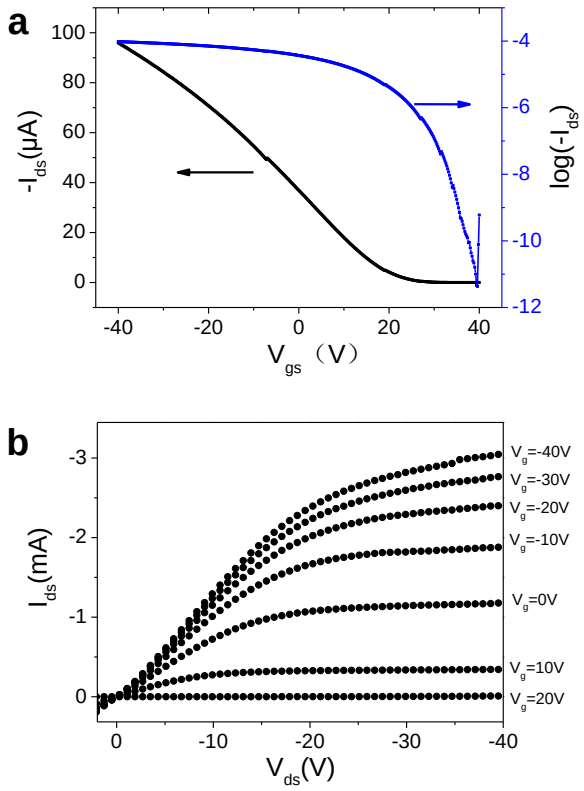

Fig. 3 Characteristics of fabricated TFTs (a) transfer curves (V_{ds}=-1) and Output curves

DISCUSSION

It is found that toluene is the best solvent for the dispersion because PCzPXX has good solubility in toluene, which ensures good solubility of PCzPXX coated SWCNT composite after ultrasonic processing. The centrifugal processing can therefore selectively separate and disperse s-SWCNTs with high efficiency.

The AFM image of SWCNT film shows that the density of SWCNT is far higher than other reported results [1, 2, 5], while the on/off ratio is still high. Normally, high density SWCNTs results in low on/off ratio because the existence of metallic SWCNTs tend to short the channel above a percolation threshold. The experimental result confirms that the present sorting method can achieve very high purity of semiconducting SWCNTs in the solution. The uniformity of device property is also improved, as shown by the mobility distribution shown in Figure 4, which is the measurement result for 20 TFTs. Most of the TFTs have mobility around 3-4 cm^2/Vs.

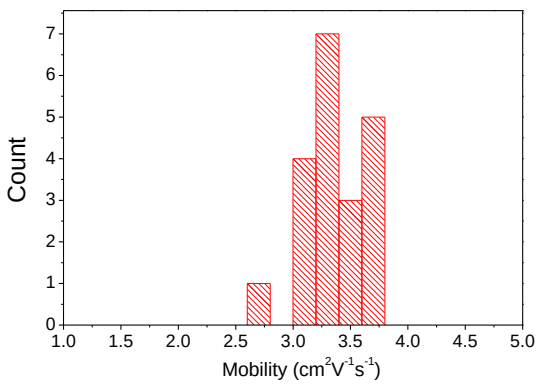

Fig. 4 Twenty devices mobility statistical histogram

The mobility was calculated by (1.1) using the linear gate voltage and drain-source current.

$$\mu = 10^4 \times (\frac{dI_{ds}}{dV_g}) \times \frac{L}{W} \times \frac{1}{C_{ox} V_{ds}} \qquad (1.1)$$

I_{ds} and V_g means drain-source current and gate voltage respectively. L and W stand for the channel length and width; $d\ I_{ds}/d\ V_g$ obtained by I_{ds}-V_g cure linear fitting. C_{ox} means capacitance of insulation layer per unit area, achieved by 1.2:

$$C_{ox} = \frac{\varepsilon_0 \varepsilon_r A}{d} \qquad (1.2)$$

Insulation layer (SiO_2) dielectric constant of ε_r=3.9; vacuum dielectric constant of ε_0=8.85×10^{-12} $F\ m^{-1}$; A means unit area, SiO_2 layer thickness of $d = 300$ nm. We can easy to get C_{ox}=1.15×10^{-4} $F\ m^{-2}$.

CONCLUSION

In summary, we reported a new type of conjugated copolymer PCzPXX that can selectively disperse HiPCO s-SWCNTs using a simple sonication and centrifugation process. The polymer/SWCNT composite ink was subsequently used to fabricate thin-film transistors, which demonstrated high mobility, high on/off ratio and high uniformity without the need for additional processes such as polymer removal or burn-off. The new solution process paves the way for low cost fabrication TFTs and other potential applications.

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