Printed High-performance Carbon Nanotube Thin Film Transistors Based on PFO-BT Sorted Large-diameter Semiconducting Carbon Nanotubes

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ABSTRACT

A simple and valid method has been developed for printing thin-film transistors (TFTs) with inks made from poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-2,1-3-thiadiazole)] (PFO-BT) sorted semiconducting carbon nanotubes (SWCNTs). Sorted sc-SWCNT inks were directly printed on SiO_2/Si substrates with pre-patterned gold electrode arrays by an aerosol jet printer. Printed bottom-gate TFTs with mobility up to 55.5 $cm^2V^{-1}s^{-1}$ and on/off ratio up to 10^6 have been achieved with short printing cycles. Interestingly, printed top-gate TFTs also showed excellent electrical properties with high on/off ratio and high mobility using atomic layer deposition of Al_2O_3 as the dielectric layer and printed silver electrodes as top-gate electrodes. As a demonstrator, printed inverters based on the top-gate TFTs have been constructed and a maximum voltage gain of 11 at V_{dd} of 2 V have been obtained.

Keywords: SWCNTs, thin-film transistors, PFO-BT, aerosol jet printing

1 INTRODUCTION

Recently, printable electronics have become a hot topic because large-area and flexible electronic systems can be produced at low-cost. [1-7] Printed thin film transistors (TFTs) are the key components in applications such as backplane for displays, logic circuits and artificial electronic skin. [8-19] With the advances in new materials and new process techniques, the electrical properties of printed TFTs, in particular, mobility and on/off ratio, have been rapidly improving in the last few years; however, poor uniformity is still a critical issue in large array of printed TFTs.

Commercial single-walled carbon nanotube (SWCNTs) are the mixture of metallic and semiconducting species, and it is difficult to achieve TFTs with high mobility, high on/off ratio and high yield if metallic species are not selectively removed or eliminated from the SWCNTs prior to use. Various approaches, such as density gradient ultracentrifugation (DGU), polymer wrapping and gel chromatography, have been developed to selectively remove or eliminate metallic species in commercial SWCNTs. [20-35] Among them, polymer wrapping has become one of the most used methods to sort sc-SWCNTs from commercial SWCNTs since Bao's work was published in 2011. [23] A number of researches have been reported using various polymers to selectively sort the sc-SWCNTs,[15, 20-25, 32] including the authors' work which demonstrated that cheap and commercially available poly(9,9-dialkyl-fluorene) derivatives such as poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-2,1-3-thiadiazole)] (PFO-BT) has the ability to sort sc-SWCNTs from commercial arc discharge SWCNTs. [15] However, transistors based on PFO-BT sorted sc-SWCNTs have not showed high mobility (usually less than 5 $cm^2V^{-1}s^{-1}$) even after printing or drop-casting many times. [15]

In the present work, sorted SWCNT solutions by PFO-BT have been characterized by UV-Vis-NIR spectrometer. TFTs have been fabricated by aerosol jet printing of PFO-BT sorted sc-SWCNT ink and their electrical properties have been measured by Keithyle 4200. Printed TFTs with low operation voltage, small hysteresis, high mobility (4.8 to 55.5 $cm^2V^{-1}s^{-1}$) and high on/off ratio (10^6 to 10^8) have been achieved after only printing the ink 2 times. Inverters based on the printed top-gate SWCNT TFTs showed voltage gain up to 11 at V_{dd}= 2 V. It opens a way to fabricate high-performance top-gate TFTs and simple logic circuits on the flexible substrates

2 EXPERIMENT

2.1 Materials and Instrument

Arc discharge SWCNTs (P2, diameter 1.2-1.6 nm) were purchased from Carbon Solution. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-2,1-3-thiadiazole)] (PFO-BT) (M_w=16 000 $gmol^{-1}$) was purchased from Shenzhen (China) Derthon Optoelectronic Materials Science & Technology. Nanosilver inks were purchased from Beijing Institute of Graphic Communication. All products were directly used without further purifications.

Optical absorption measurements were performed in a Perkin Elmer Lambda 750 UV-Vis-NIR spectrometer. All electrical measurements were carried out in ambient using a Keithley semiconductor parameter analyzer (model 4200-SCS). A NSCRIPTOR DPN system (NanoInk inc., IL, USA) and Dimension 3100 AFM (Veeco, Santa Clara, CA) were used in AFM imaging. Sorted sc-SWCNT solutions and nanosilver inks were printed by an aerosol Jet 300P system(Optomec Inc., USA). Contact angle is measured by using a contact angle setup (OCA20, Data physics Germany).

2.2 Preparation of printable SWCNT inks

To prepare sc-SWCNT inks, 2mg of arc discharge SWCNTs were dispersed in 15mL xylene with 9mg PFO-BT via probe-ultrasonication for 30 min (Sonics & Materials Inc., Model: VCX 130, 60W). Then, the resulting SWCNT solutions were centrifuged at 21000 g for 30min to remove metallic species and big bundles. The supernant was carefully collected and used to fabricate TFT devices without any other purification. Figure 1 showed the optical images of the resulting SWCNT inks before and after centrifugation.

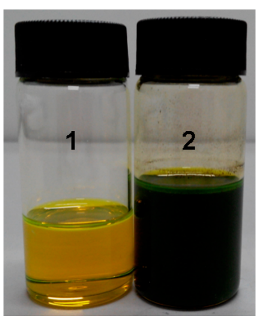

Figure 1. The optical image of sorted sc-SWCNTs by PFO-BT in xylene before (2) and after (1) centrifugation.

2.3 Fabrication and electrical properties of TFT Devices

To assess the quality of sorted sc-SWCNT inks, sorted sc-SWCNT inks were deposited on prepatterned interdigitated gold electrodes (with different fingers by photolithography, finger dimensions: width 1000μm or 200μm, length 20μm and interfinger spacing 20μm, respectively.) on oxygen-plasma-treatment SiO_2(the thickness is 300nm)/Si substrates by both aerosol jet-printing and drop-casting. For the printing process, sorted SWCNT solutions were printed onto the channels of pretreated devices, followed by washing with xylene for 3 times. The printing procedure was only repeated 2 times, and the density of sorted sc-SWCNTs was high enough to form a percolation path and to reach the desired current level. The details of printing conditions are listed as follows: SWCNT inks were atomized to form aerosols by sonication at a power of 25 W. Sheath gas flow and atomizer flow are 50 and 20ccm, respectively. Printing speed is 0.5mm sec^{-1}. The nozzle size of printed head is 150μm. All operations are at room temperature. For the drop-casting procedure, 15 μL sorted sc-SWCNT solutions were dropped onto prepatterned interdigitated gold electrodes, followed by drying at room temperature and rinsing with xylene for 3 times. The procedure was repeated 4 times. After that, the devices were dipped into hot xylene for 30 min to further remove the residual polymers.

To obtain top-gate TFTs with independently controlled gates, sorted sc-SWCNT inks were firstly printed on prepatterned interdigitated gold electrodes on SiO_2/Si substrates. After that, 70 nm thick Al_2O_3 thin films were deposited on top of pre-deposited SWCNT thin films at 200 °C by atomic layer deposition (ALD) (Cambridge NanoTech Inc.). Then, silver top-gate electrodes were printed on the top of gold electrodes by aerosol jet printing. Finally, two top-gate TFTs were connected with printed silver lines, and an inverter was ready to use.

The electrical properties of SWCNT TFTs were measured at room temperature. The mobilities of SWCNT TFTs are estimated by $\mu = \left(\frac{dI_d}{dV_g}\right) \times \frac{L}{W} \times \frac{1}{C_i V_{ds}}$.[13, 14] Here, C_i is the oxide capacitance per unit area. L and W represent the channel length and width, respectively.

3 RESULTS AND DISCUSSION

In order to demonstrate that sc-SWCNT were selectively sorted from P2 by PFO-BT in xylene with the aid of sonication, the resulting solutions were characterized by UV-Vis-NIR spectroscopy. Figure 2 represents the adsorption spectra of P2 SWCNTs before and after sorting by PFO-BT. As shown in Figure 2, the metallic peaks in the range of 650-850 nm disappeared, and the sc-SWCNT peaks in the range of 900-1300 nm became very sharp, which indicates that sc-SWCNTs disperse well in xylene after reaction with PFO-BT.

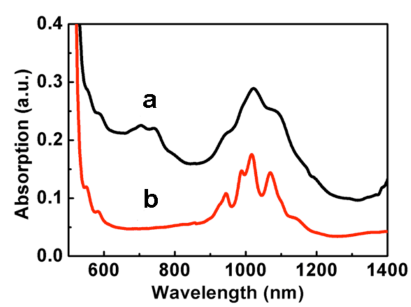

Figure 2. Adsorption spectra of sorted SWCNTs from arc discharge SWCNTs by PFO-BT in xylene before (a) and after (b) centrifugation at 21000g for 1 h.

In order to ensure that sc-SWCNTs have been selectively sorted, the sorted SWCNT solutions were deposited on SiO_2/Si substrates with pre-patterned gold electrodes by areosol jet printing method and the electrical properties of printed TFTs were then measured using Keithley 4200-SCS semiconductor parameter analyzer. Figure 3 shows the typical transfer and output characteristics of printed TFTs based on sc-SWCNTs. As shown in Figure 3, the device fabricated via aerosol jet printing exhibited high on/off ratio up to 10^5 and high charge mobility up to 55.5 $cm^2V^{-1}s^{-1}$. Figure 3c and 3d showed the histogram of the mobility and on/off ratios of TFT devices made with sc-SWCNTs sorted with PFO-BT. As shown in Figure 3c and 3d, mobilities and on/off ratios are in the range of 4.8-55.5 $cm^2V^{-1}s^{-1}$ and 10^5-10^8, respectively.

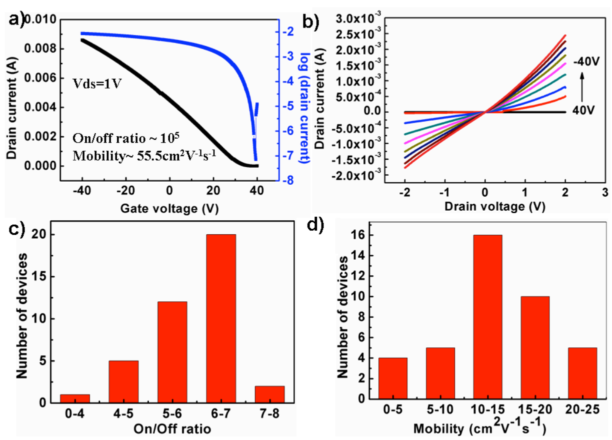

Figure 3. (a) Typical transefer and (b) output characteristics of printed TFTs based on sorted sc-SWCNTs, and the histogram of (c) on/off ratios and (d) the mobility of printed TFT devices based on sorted sc-SWCNTs

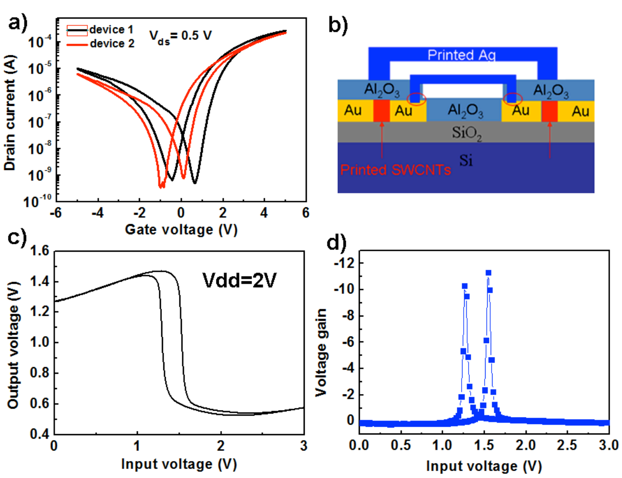

Figure 4. (a) Typical transefer characteristics of printed top-gate TFTs and (b) Schematic of printed inverter on SiO_2/Si substrate, and (c) input-output and (d) gain characteristics of the printed inverter at V_{dd}= 2 V.

Inverters composed of two top-gate TFTs were fabricated on a SiO_2/Si substrate using Al_2O_3 as the dielectric layer and printed silver electrodes as top-gate electrodes. Figure 4a shows the typical electrical properties of printed top-gate TFTs. Interestingly, the channel conduction of printed top-gate transistors showed slightly ambipolar characteristics with the strong n-type conduction after printing silver electrodes on top of bottom devices channels. As shown in Figure 4a, when the gate voltages were larger than 1 V, printed top-gate TFTs displayed n-type. Mobilities and on/off ratio of printed top-gate TFTs can be up to 4.6 $cm^2V^{-1}s^{-1}$ and 4×10^5, respectively. Figure 4b shows the schematic of an inverter with two top-gate printed TFTs. Figure 4c and 4d were the voltage input-output characteristics of the inverter, which exhibited low hysteresis and a maximum voltage gain up to 11 at V_{dd} of 2 V.

4 SUMMARY

In summary, Printed TFTs based on PFO-BT sorted sc-SWCNTs exhibited good uniformity and excellent electrical properties with high mobility, on/off ratio and low operation voltage. Printed top-gate TFTs with slightly ambipolar with strong n-type conduction were obtained using ALD of Al_2O_3 thin films as dielectric layer and printed silver electrodes as top-gate electrodes by aerosol jet printing. Futhermore, printed inverters based on the printed top-gate TFTs showed low hysteresis and the voltage gains up to 11 at V_{dd} of 2 V.

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