Fabrication and Characterization of Thin-film Transistors Based on Printable Functionalized Single-walled Carbon Nanotubes

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ABSTRACT

In this study, we successfully fabricated single-walled carbon nanotube (SCNT) thin-film transistors (TFTs) by ink-jet printing technology using the prepared high-quality SCNT ink. The SCNT inks were obtained by chemically functionalized CoMoCat 76 with 2, 2-azobisisobutyronitrile (AIBN). The absorption spectra, Raman spectra and photoluminescence excitation (PLE) spectra demonstrated that metallic species and small diameter semiconducting species in CoMoCat 76 were effectively eliminated after reaction with AIBN. As-prepared SCNTs inks were directly used to print TFTs using Aerosol Jet printing system without any purification. The printed top-gated and bottom-gated TFTs exhibited the effective mobility of ~0.5 cm^2/Vs and on/off ratio of over 10^3. Especially, hysteresis was eliminated using commercial polydimethoxysilane (PDMS) elastomer containing ion liquid as the top gate dielectric. The process opens the route to fabricate all printed high performance SCNT TFTs on flexible substrate.

Keywords: carbon nanotube thin-film transistors (TFTs), aerosol jet printing, free hysteresis, top-gated,

1 INTRODUCTION

Printed thin-film transistor (TFTs) enables large area electronic circuits without complicated lithography process and has become a hot topic [1,2]. High quality printable ink is the key to make high performance printed TFTs. Single-walled carbon nanotubes (SCNTs) have attracted great interests due to their special structures, excellent physical, chemical and mechanical properties, and potential applications in fields such as nanotechnology, electronics, optics, materials science, and architecture. SCNT networks are highly promising for high-performance TFTs [3-5]. However, it is difficult to obtain high mobility and high yield of semiconducting device because of the undesired presence of metallic nanotubes along with semiconducting nanotubes in coated SCNT networks or thin films [6]. Various approaches have been attempted to prepare semiconducting SCNT inks to enhance the semiconducting characteristics of devices. These methods, however, are not able to produce high quality SCNT-nets with high yield or involve complicated and costly procedures, or cannot obtain high performance TFT devices. Although SCNT have been employed in ink form for printed TFTs, the quality of SCNT ink is still far from perfect due to the presennce of metallic nanotubes in inks. Because of this drawback, all reported TFTs based on printed SCNT ink showed low on/off ratio (about 100).

Generally, it is necessary to fabricate the top-gated SCNT TFTs to realize their functions in radio frequency identification cards (RFID), logic circuits and so on, so there has been significant interest in developing new kinds of solution processible dielectric materials that can serve as gate insulators in SCNT TFTs. SCNT thin films are ultra-thin, about 2-3 nm, and it is very sensitive to the environmental changes. Solvents and other impurities can cause a serious decrease in the device mobility due to increase in scattering sites and electronic doping during coating or printing top dielectric layers. Fortunately, we found that commerical PDMS elastomer was able to efficiently screen off the impurity charges from surfactants, resulting in enhancing the effective mobility [7]. It's possible that the PDMS elastomer can be employed as a new gate dielectric materials for printing high-performance SCNT TFTs.

In this paper, the TFTs based on AIBN-functionalized CoMoCat 76 were fabricated by areosol jet printing method. The electrical properties of bottom-gated and top-gated TFTs having PDMS containing ion liquid as the dielectric layer on the same SCNT thin films were investigated. The results demonstrated that PDMS containing ion liquid has potential for acting as the printable dielectric material for SCNT TFTs. Therefore it promises low-cost and scalable production of printable high-performance SCNT TFT devices.

2 EXPERIMENTAL

2.1 Materials and Instruments

Benzoyl peroxide (BPO), 2,2-azobisisobutyronitrile (AIBN), dimethyformamide (DMF), sodium dodecyl sulfate (SDS) and sodium cholate hydrate (SC), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIM-TFSI) were obtained from Aldrich and were used as purchased. Commercial polydimethoxysilane (PDMS) elastomer containing silica was purchased from Dow Corning. The purified SWeNT@SG 76 nanotubes were purchased from SouthWest Nanotechnologies (USA). Other materials were directly used without further purifications. A confocal Raman microscope (WITec CRM200) equipped with 488 nm laser was used for Raman spectrum measurements. Optical absorption measurements were performed in a Perkin Elmer Lambda 9 UV-Vis-Nir spectrometer. Fluorescene characterization was performed on Jobin-Yvon Nanolog-3 spectrofluorometer with InGaAs detector. 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, CA, USA) were used in AFM imaging. SCNT inks and top electrodes (silver paste) were printed by using an Optomec's M3D aerosol Jet printing system (USA).

2.2 Preparation of SCNT Printing Inks and the Dielectric Inks

To obtain printable SCNT inks, 0.3 mg of CoMoCat 76 was dispersed in 30 mL of DMF solution via probe-ultrasonication for 30 min (Sonics & Materials Inc., Model: VCX 130). Then, organic radical initiator was added to 10 mL SCNT suspension, followed by 30 min ultrasonication. After reaction with organic radical initiators, the suspension was filtered through a 0.25 μm PTFE membrane, followed by repeated washing with DMF and acetone to remove the residuals. The powders collected from PTFE membrane were re-dispersed in different concentration of surfactant solutions. The resulting solutions were then used for fabrication of TFTs by areosol jet printing method. For drop-casting method, centrifugation was performed at 10000 rpm for 90 min to remove big bundles in the SCNT inks after re-dispersing in 2 wt % of co-surfactants (weight ratio, SDS: SC=1: 4). The supernatant was then drawn out from the centrifuge tube, and directly used for FET device fabrication.

In order to obtain the dielectric inks, PDMS elastomer and EMIM-TFSI (3:1 by weight) were dissolved in toluene, and then the solution was mixed for 4 h with continuous stirring in order to obtain a homogeneous solution, and the dielectric inks are then ready for use.

2.3 Fabrication of TFT Devices

The SCNT TFTs were fabricated by areosol jet printing or drop casting the solution of SCNTs across two Au electrodes (100 nm thick) pre-patterned on top of a SiO_2/Si substrate to form conducting channel of ~100 μm long and ~200 μm wide. The thicknesses of SiO_2 gate dielectrics are 300 nm.

For the drop-casting procedure, 25 μL of functionalized SCNT suspension was dropped onto the pre-treated devices, followed by drying at room temperature and rinsing of de-ionized water. The procedure was repeated until the density of the functionalized SCNTs is high enough to form a percolation path and to reach the desired current level.

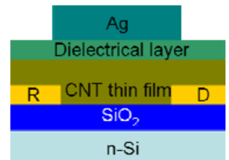

Figure 1. Schematic of the SCNT TFTs with PDMS containing ion liquid as the top gate dielectric.

The ink-jet printing procedure is similar to the drop-casting procedure except to print SCNT inks using aerosol Jet printing system. In order to fabricate the top-gate devices, the commercial PDMS elastomer containing ion liquid as the gate dielectric was spin-coated on SCNT thin film, and then silver paste as the top gate electrodes were printed on the gate dielectric (as shown in Figure 1).

3 RESULTS AND DISCUSSION

3.1 Spectra of CoMoCat 76 before and after Modification with Radicals

It has been reported that radicals can effectively eliminate the electrical properties of metalic species in SCNTs [8, 9]. In our experiments, AIBN was decomposed by the heat generated during probe-sonication. At the same time, sonication ensured that the SCNTs were homogenously dispersed and sufficiently reacted with the free radicals. Figure 2a represents the adsorption spectra of CoMoCat 76 SCNT ensemble before and after reaction with BPO and AIBN.

It was observed that the metallic peaks at 456 nm disappeared after reaction with AIBN and BPO in the weight ratio 1:164 and 1: 75, respectively. To further confirm the effective and preferential suppression of metallic tubes in the SCNT ensemble, Raman spectra of the pristine CoMoCat 76, BPO-modified CoMoCat 76 and AIBN-modified CoMoCat 76 were compared.

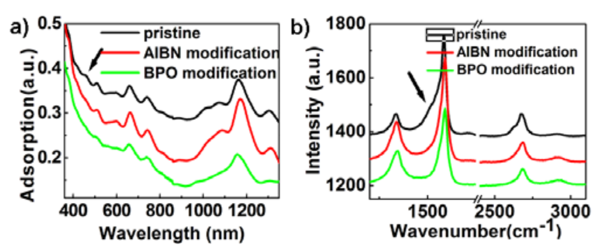

Figure 2. (a) Absorption spectra and (b) Raman spectra of CoMoCat 76 before and after reaction with AIBN and BPO in the weight ratio 1:164 and 1: 75, respectively.

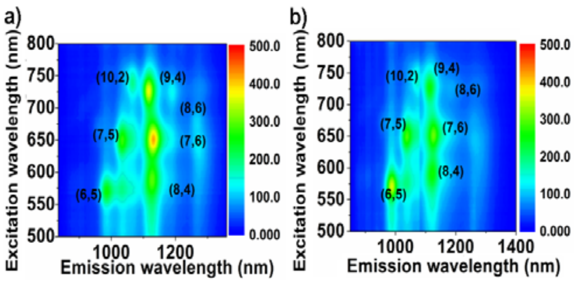

Figure 3. Photoluminescence excitation (PLE) spectra and absorption spectra of CoMoCat 76 (a) before and (b) after reaction with AIBN in the weight ratio 1:164.

As shown in Figure 2b, the intensity of longitudinal G band peak from metallic-species in CoMoCat 76 SCNTs at ~1550 cm^{-1} was reduced after modification with radicals, indicating the preferential suppression of metallic-species. At the same time, the D band peaks of CoMoCat 76 SCNTs were increased after reaction with radicals because of the destruction of graphitic lattice structure. Figure 3 represented photoluminescence excitation (PLE) spectra of pristine CoMoCat 76 and AIBN-modified CoMoCat 76. As are shown in Figure 3, the intensity of the (7,6) tubes increases while that of the small diameter tubes (6,5) decreases after reaction with AIBN. In summary, the adsorption spectra, Raman spectra and PLE spectra indicated the preferential suppression of metallic and small diameter tubes after modification with organic radicals, and the results are consistent with the previous reports [8].

3.2 Effects of Surfactant and SCNT Concentrations for Electrical Properties of Printed SCNT TFTs

In order to evalute the quality of as-prepared SCNT inks, TFTs based on functionalized SCNTs were firstly fabricated by simple drop-casting method and their electrical properties were measured using Keithley 4200-SCS semiconductor parameter analyzer. The on-off ratios of devices from pristine SCNT solutions are generally very low (ratio ranging from 5 to 100) due to coexistence of metallic and semiconducting SCNTs. Amazingly, all the as-prepared devices made from the functionalized CoMoCat 76 SCNT solutions exhibit on-off ratios ranging from 10^4 to 10^7 and the typical effective mobility ranges from 1~9 $cm^2/V{\cdot}s$. As shown in Figure 4, all devices based on functionalized CoMoCat 76 exhibited large hysteresis and high on/off ratio (over 10^5), but the effective mobility of devices based on AIBN-modified CoMoCat 76 SCNTs (about 6~9 cm^2/Vs) were higher than those of BPO-modified CoMoCat 76 SCNTs (about 1~3 cm^2/Vs), which is probably due to the introduction of the electron-withdrawing groups on carbon nanotube surfaces after modification with AIBN [8-10]. So AIBN-modified CoMoCat 76 SCNT solutions were used as the printing inks to fabricate TFTs by the areosol jet method.

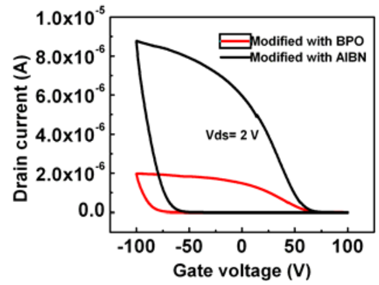

Figure 4. Typical transfer curves for the TFTs based on AIBN-modified and BPO-modified CoMoCat 76 by drop-casting method.

It's well-known that the concentrations of surfactants and SCNTs in the printable ink play a key role in the performance of TFTs. In order to obtain printable high-performance TFTs, effects of surfactant and SCNT concentrations were investigated. The results are shown in Table 1. The surfactant concentration in the SCNT ink is too low (less than 0.5%) to form areosol in the tube, at the same time, it is difficult for SCNT to disperse well in the low concentration surfactant slution. When the surfactant concentration increased to 0.75%, all printing devices showed metallic properties (on/off ratios are only 3-6) after printing 3 cycles using different SCNT concentration inks. It may be due to metallic SCNT or other conductive impurities preferentially coming out from inks, resulting in poor electrical properties.

Table 1 Effects of Surfactant and SCNT concentrations for electrical properties of SCNT TFTs

Serials of ink	SCNT concentration	Surfactant concentration	On/off ratio	Print cycles	Evaluation
a	0.015	0.75% SDS	<6	3	bad
b	0.0075	0.75% SDS	<6	3	bad
c	0.00375	0.75% SDS	<6	3	bad
d	0.015	1% SDS	10-100	5	not good
e	0.0075	1% SDS	500-10000	10	good
f	0.00375	1% SDS	X	12	X
g	0.015	2% SDS	X	12	X
h	0.015	2% SDS: SC=1:4	X	12	X

X reprersents the printed TFTs can't work, and the unit of SCNT concentration is mg/mL in Table 1.

If the surfactant concentration was changed to 1%, the high performance printable TFTs were obtained (mobility up to 0.5 cm^2/Vs, and on/off ratio up to 10^4) when adjusting the SCNT concentration to 0.0075 mg/mL after printing 10

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cycles. However, the surfactant concentration increased to 2%, the printed TFTs did not work, even after printing more than 20 cycles, which is probably attributed to that the concentration of SCNT in areosol is too low to form SCNT thin film on the substrate after repeatly rinsing with de-ionized water. So 0.0075 mg/mL SCNT ink containing 1% SDS was selected for the following experiments.

3.3 Electrical Properties of Printing Bottom-gated and Top-gated SCNT TFTs

Bottom-gated and top-gated SCNT TFTs were fabricated as described in section 3.2. The morphlogy and electrical properties of SCNT thin films were characterized by AFM and Keithley 4200-SCS. AFM image indicated that the lengths of SCNTs were in the range of 0.5 µm to 2 µm (Figure 5a). Figure 5b shows the transfer curves for printing SCNT TFTs. Compared to the electrical properties of devices fabricated using drop-casting method, both on/off ratio (over 10^3) and effective mobility (about 0.5 $cm^2/V \cdot s$) of the printing devices were less than those of the drop-casting devices. So it has opportunity to achieve higher-performance devices by adjusting the printing conditions.

As shown in Figure 5b, both bottom-gated and top-gated TFTs worked well. Electrical properties of bottom-gated and top-gated devices has no obvious differences, except the top-gate devices exhibited free hysteresis. ON currents and threshold voltages are dependent on the capacitances occuring between the gate electrode and the carbon nanotube channel. Higher capacitance translates into higher induced charge densities and therefore both higher ON currents and lower threshold voltages.

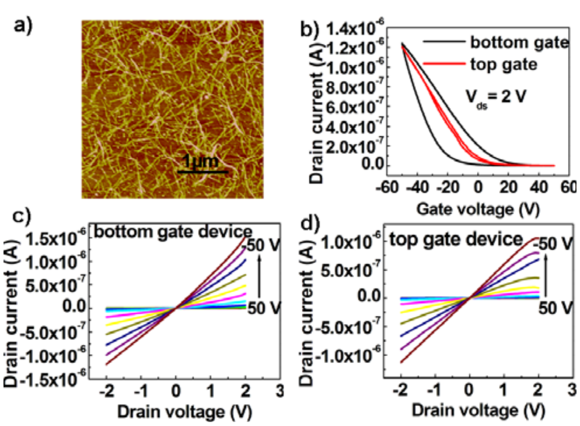

Figure 5. AFM image of AIBN-modified CoMoCat 76 thin film and electrical properties of the printing bottom-gated and top-gated TFTs based on AIBN-modified CoMoCat 76 SCNTs (b,c and d). The channel length and width are 100 µm and 200 µm, respectively.

The capacitances of bottom-gated device and top-gated devices are about 13 and 16 nF/cm^2, respectively, so ON currents and threshold voltages of the top-gated devices are similar to those of the bottom-gated devices. Figure 5c and 5d represented the output characteristics (I_d vs. drain voltage V_d) of the bottom-gated and top-gated SCNT TFTs. I-V curves of bottom-gated and top-gated devices are linear, suggesting these devices exhibit ohmic contact likely at metal-SCNT interfaces [7]. Further work is underway to increase the ratio of ion liquid to PDMS in an attempt to obtain the printable high-performance top-gated dielectric, and hence higher-performance SCNT TFTs.

4 CONCLUSIONS

In summary, SCNT TFTs based on functionalized CoMoCat 76 were successfully fabricated using the aerosol jet printing system. Furthermore, it is demonstrated that PDMS coating containing ion liquid can act as the top-gated dielectric, and the mixture of PDMS and ion liquid are used as a new printable dielectric ink. Further development is underway to fabricate all printed high performance SCNT TFTs and to build simple logic circuits on flexible substrate.

5 ACKNOWLEDGEMENT

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