Development of materials and printing methods for fabrication of thin-film transistors on flexible substrates

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ABSTRACT

In this study, we developed a valid method to fabricate all-printed functionalized CoMoCat 76 SCNT thin film transistors (TFTs) on PET substrates via a suite of printing technologies. The printing methods we investigated include inkjet printing, aerosol jet printing and a hybrid with nanoimprinting. Source and drain electrodes were first fabricated on flexible substrates by a hybrid printing of nanosilver ink, and then SCNT thin films were deposited on the channel of TFT devices by ink-jet printing. Subsequently, the side-gate electrode and ion gel dielectric layer were deposited by aerosol jet printing of nanosilver ink. The all-printed flexible TFTs exhibited the effective mobility up to 1.3 $cm^2 V^{-1} s^{-1}$ and on/off ratio up to 2×10^3. This work opens a way to fabricate scalable all-printed flexible electronics

Keywords: all-printed, semiconductor carbon nanotube inks, nanoprinting, flexible electronics,

1 INTRODUCTION

The development of printable electronic circuits on flexible substrates as a pathway to large-area and low-cost electronics has attracted significant interest. Printed thin-film transistor (TFTs) which enable such electronic circuits without complicated lithography process has become a hot topic [1-9]. However, the realization of printing TFTs on flixible substrates encounter a series of challenges. First, there have to be high quality printable inks for printing conductors, semiconducotrs and dielectrics. Second, there have to be suitable printing methods which are compitable to these inks as well as the substrates. Third, both the printable inks and printing methods have to be scalable for volume manufacturing in order to have any practical applications. Instead of printing organic TFTs which are of low charge mobility and prone to degradation in ambient environment, inorganic nanomaterials are becoming favourated materials in recent years for making the inks for printed TFTs. Inorganic nanomaterials, most noticeably the single-walled carbon nanotubes (SCNTs), have excellent physical, chemical, mechanical properties, chemical stability and high mobility. Some reports including the authors previous work have demonstrated that TFTs based on printed SCNT inks showed good electrical properties with high on/off ratio and high effective mobility[10-26]. As for the printing technology, different printing techniques have different merits and shortcomings. It is rarely the case that all the inks, conductor, semiconductor and dielectrics, can be tailored to fit to one single printing tool [26].

In the present work, we attempted to put together a suite of technologies for printing TFTs on flexible substates. The ink materials we investigated include optimized SCNT inks as printable semiconductors, development of composite ion-gel as dielectrics and nanosilver ink as conductors. The printing methods we investigated include inkjet printing, aerosol jet printing and a hybrid with nanoimprinting[27]. Large area source and drain electrode patterns were first fabricated on flexibe substrates by a hybrid printing method, and then SCNT thin films were deposited on the channel of TFT devices by ink-jet printing. Subsequently, the silver side-gate electrode and ion gel dielectric layer were deposited by aerosol jet printing. The all-printed TFT has the effective mobility up to 1.3 cm^2/Vs and on/off ratio up to 10^3.

2 EXPERIMENT

2.1 Materials and Instruments

The materials used in the experiments were 2,2-azobisisobutyronitrile (AIBN), dimethyformamide (DMF), sodium dodecyl sulfate (SDS) and sodium cholate hydrate (SC), copolymers of polystyrene (PS) and polymethylmethacrylate (PMMA) (PS-PMMA), and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIM-TFSI). They were obtained from Sigma-Aldrich and used as purchased. The single-wall carbon nanotubes SWeNT@SG 76 were purchased from SouthWest Nanotechnologies (USA). Other materials were directly used without further purifications. All electrical

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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, side electrodes (silver paste) and ion gel dielectric were printed by using an Optomec's M3D aerosol Jet printing system (USA).

2.2 Preparation of Printable SCNT Inks and Dielectric Inks

1 mg of CoMoCat 76 was dispersed in 100 mL of DMF solution via probe-ultrasonication for 30 min. Then, organic radical initiator was added to SCNT suspension, followed by 30 min ultrasonication (Sonics & Materials Inc., Model: VCX 130). 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.

To prepare printable water-based SCNT inks, 0.1 mg of chemically modified CoMoCat 76 SCNT was re-dispersed in 20 mL of 0.4% SDS/SC (5:3) and 0.1 mg/mL PVP ($M_w=10^4$) of surfactant aqueous solutions via probe-ultrasonication for 30 min. The resulting SCNT solutions were centrifuged at 10000 rpm for 30 min to remove big bundles, and the supernatant was drawn out from the centrifuge tube. After that, the SCNT solutions could be directly used for printing TFT devices.

In order to obtain the dielectric inks, PS-PMMA 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

Large array of source and drain electrodes were first fabricated on polyethylene terephthalate (PET) substrates by a hybrid printing method which involved nanoimprinting and nanosilver ink filling. Then copper was deposited by electroless plating on silver electrode surfaces to increase the conductivity and decrease the surface roughness [28]. The substrates were then immersed into 1% APTES aqueous solution for 30 min, and then baked at 100 °C for 5 min to form the amine-functionalized layer. The SCNT ink were deposited in the channel using an ink jet printer (Dimatrix 2831). Subsequently, the side-gate electrodes were deposited by aerosol jet printing of nanosilver ink. The devices were then annealed at 150 °C for 30 min to improve the electrical properties of SCNT thin films and to increase the conductivity of silver electrodes. Finally, ion gel dielectric layers were deposited in the channels of the devices by aerosol jet printing (Optomec). The structure of the printed side-gate device is shown in Figure 1.

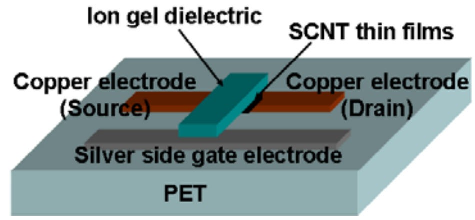

Figure 1. Schematic of all-printed SCNT TFTs on flexible substrates.

3 RESULTS AND DISCUSSION

Both printing methods and inks play key roles in the fabrication of high performance TFTs. In the past, drop casting was widely used to integrate water-based semiconductor SCNT inks into a TFT device [21, 22]. It is fine to fabricate a few testing device by drop casting, but not a viable method to fabricate large array of devices or a complex system. Besides, drop casting has difficulty to position inks accurately in the channels of TFTs. In the present work, inkjet printing has been used to deposit semiconductor SCNT thin films, which is similar to the drop-cast method but with high accuracy and precise control of ink volume. However, if the SCNT solution is directly used as the inks, the solutions can not drop out of printer nozzles. So it is necessary to tune the ingridents of SCNT inks for inkjet printing.

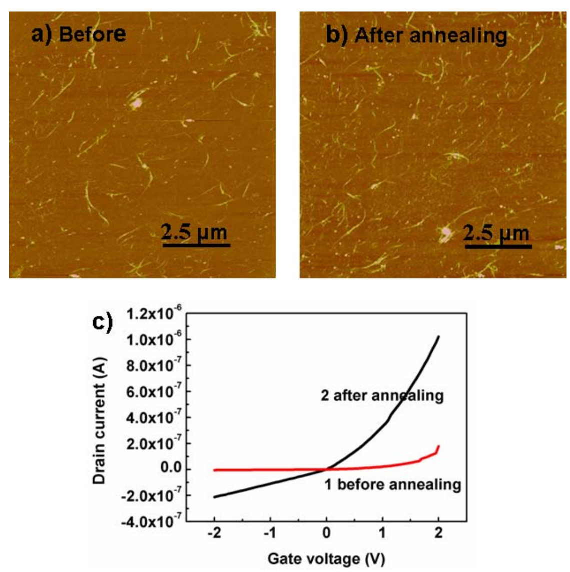

Figure 2. The typical AFM images of the printed SCNT thin films and Id-Vg curves before and after annealing at 150 °C for 30 min.

It is found that water-based SCNT ink can easily drop out of printer nozzles if the SCNT inks contain small amount of water soluble polyvinylpyrrolidone (PVP), which can change the fluidic characteristics of the SCNT solutions and facilitates the printing. However, PVP can severely degrade the electrical properties of the printed TFTs because it is an insulting material. In order to obtain the printable inks without degrading the printed TFTs, the surfactant concentration of 0.4% SDS/SC (5:3) and PVP ($M_w=10^4$) concentration of 0.1 mg/mL were selected in the following experiments. Figure 2 shows the typical AFM images and Id-Vg curves of the printed SCNT thin films before and after annealing at 150 °C for 30 min. Although the morphologies of SCNT thin films have no obvious change, the electrical properties of printed SCNT thin film are improved, which suggests that the contacts of SCNT-SCNT or SCNT-metal were improved after annealing at 150 °C for 30 min.

However, inkjet printing method has very strict requirement on ink viscosity, normally below 20 cp, which poses problems when printing high viscosity dielectrics ink such as ion gel solution. For high viscosity ink, aerosol jet printing method was used. With an aerosol jet printer, inks with viscosity up to 2000 cp can be printed. Because of its aerodynamic focusing function, fine features less than 10 μm in width can be printed. However, there is a problem to print water-based SCNT inks using aerosol jet printer. It is found in the experiments that the ingredients concentration in the ink is changing when prolonged printing is required, which results in poor uniformity of electrical properties in printed devices [25]. Furthermore, compared with ink jet printing method, it needs much more printing inks to fabricate the same number of devices. Therefore, the aerosol jet printing method was only used for printing dielectric layer and conducting electrodes.

It is known that high performance TFTs require short channel length. Both aerosol jet printing and ink jet printing are facing the challenge of fabricating source and drain electrodes with small gaps. In addition, the two methods cannot deposit layers with good adhesion to substrates, especially flexible substrates. To overcome the problem, a new hybrid printing method has been developed, which is based on a combination of nanoimprinting and ink filling. First, the substrate surface is textured into mesh-like patterns with nanoimprinting method. Then, nanosilver ink is filled into the engraved patterns, making it conductive. To further improve the conductivity and surface roughness, electroless plating of copper was carried out using the printed silver as the seed layer. Figure 3 shows source and drain electrodes made by the hybrid printing method before (gay-white color) and after electroless deposition of copper (red color). Because the nanosilver ink is confined within the textured area which was patterned by nanoimprinting, the gap distance between the electrodes can be precisely controlled. An additional advantage is that the electrodes strongly adhere to the substrate because the nanosilver is actually embedded into the substrate. The electrodes showed no noticeable change after sonication for 30 min. With nanoimprinting, large array devices over large area on flexible substrate can be easily fabricated.

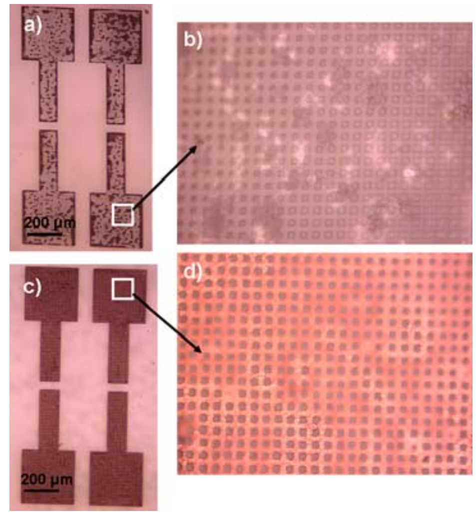

Figure 3. Source and drain electrodes made by the hybrid printing method before (a, b) and after (c, d) electroless deposition of copper.

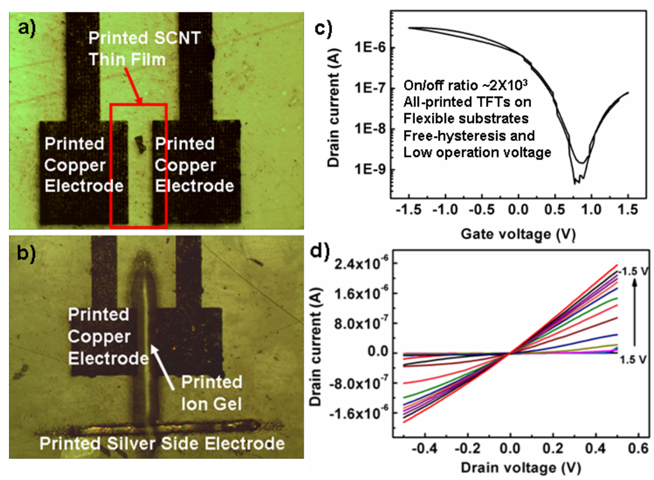

Figure 4. Optical images of printed TFT (a, b) using SCNTs ink as semiconductor on flexible substrates and the measured electrical properties (c, d).

Figure 4b shows a fabricated TFT device with printed source and drain electrodes, SCNT ink, ion gel dielectrics and a side gate electrode. Figure 3c and 3d showed the electrical properties of a typical all-printed SCNT TFT. The on/off ratio and effective mobility of the printed TFTs are 2×10^3 and 1.3 $cm^2\ V^{-1}s^{-1}$, respectively. It is free of hysteresis and has low operating voltage (about 0.8 V) which is the result of using ion gel as dielectric material [7, 25]. Furthermore, the on/off ratios and effective mobilities of all-printed flexible SCNT TFTs showed no obvious changes after exposed in air for 4 months, proving they are highly stable and paving the way for their practical applications in flexible electronics.

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4 SUMMARY

A simple and scalable method was developed to fabricate all-printed flexible TFT devices with a combination of nanoimprinting, ink jet printing and aerosol jet printing methods. The all-printed TFTs exhibited the effective mobility of ~1.3 $cm^2\ V^{-1}s^{-1}$ and on/off ratio over 2×10^3. Work is underway to further optimize the ingredients of printable inks with bigger diameter SCNTs, to deposit nickel and gold for work function matching and to fabricate devices with shorter gate length, in an attempt to further improve the performance of SCNT TFTs and to construct simple logic circuits on flexible substrates.

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