Transparent Conductive Film Fabrication by Carbon Nanotube Ink Spray Coating and Ink-Jet Printing

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***Abstract* — The present work reports on the development of a class of thin-film transparent electrodes for the PV devices based on spray coating of carboxyl functional multi-walled carbon nanotubes (MWCNT-COOH) aqueous dispersion and thin-film transparent transistors based on ink-jet printing MWCNT-COOH inks with proper fluidic characteristics. The MWCNT-COOH inks were formulated by addition of PEDOT-PSS to MWCNT-COOH aqueous dispersion. SEM shows the spray coating MWCNT-COOH films and the ink-jet printing MWCNT-COOH films are uniform. UV-vis transmission spectra indicate high transparency. Four probe measurements show excellent sheet resistance. The present work demonstrates that spray coating MWCNT-COOH films are promising for transparent electrodes in flexible and large area PV electronics and that ink-jet printed MWCNT-COOH films in patterns are promising for transparent transistors.**

***Index Terms* — Carbon nanotubes, Ink, Flexible printed, Thin film circuits**

I. INTRODUCTION

carbon nanotubes (CNTs) have excellent conductivity and large aspect ratio over 100, which is beneficial to form effective conductive networks with high flexibility. Their nanometer size, their unique quasi one dimensional structure and their electrical, mechanical, and thermal properties show lots of potential applications. Indeed, the intrinsic electrical resistivity of CNTs was found to be approximately as low as 10^{-6} Ω m. Random networks of CNTs provide an unusual type of electronic material that can be integrated into electronic devices by several methods (printing processes, airbrushing, solvent evaporation, spin coating, bar coating). The electrical properties of such materials make them attractive for numerous applications in electronics.However, the stability of CNT suspensions is difficult to achieve because the nanoparticles tend to aggregate easily due to their high van der Waals attraction. Working with covalent functionalized carbon nanotubes is now considered as a good compromise. Indeed, the functionalization strongly facilitates the separation of nanotube bundles into individual tubes, which allows obtaining a stable dispersion of CNTs in aqueous solvent [1, 2].

The recent developments in plastic electronics are expected to revolutionize the electronics industry. This will allow for a variety of applications to be envisaged, not attainable using conventional silicon chips because of their rigidity and limited size. Ink-jet printing and spray coating are of the most promising techniques for inexpensive large area fabrication of plastic electronics. In fact, a range of electronic and optoelectronic components can be printed and spray coated on plastic substrates, i.e., transistor circuits, photovoltaic (PV) films, organic lightemitting diodes (OLEDs), and displays.

Ink-jet printing is a popular method in the conventional printing industry due to fine pattern generation, non-contact injection, solution saving effects, high repeatability and scalability. In addition, ink-jet printing of CNTs can readily control pattern thickness, line width and uniformity. It has been recently reported that CNTs Strips were successfully printed using an ink-jet printing method [3-6]. Strips with a large length to width ratio are superior structures for thin-film transistors based on pristine MWCNT-COOH. However, strips tens of micrometers in width are inferior, with respect to electrical performance, to narrower ones with widths comparable to the MWCNT-COOH length. To date, no studies have reported narrow width (≤100 μm) CNT-based ink-jet patterning and its characterization as being suitable for conductive patterns.

Spray coating is another widely used technique for large area fabrication due to low expense, solution process and high repeatability. It can also control the film thickness, spray speed, and spray angle, which is important for large area and three dimensional fabrications. Spray coating CNT film shows promising alliance in transparent conductive films for PV electronics [7].

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Here, we present a method for large area conductive MWCNT coating deposition by spray coating and a method for conductive MWCNT patterns by direct ink-jet printing, which would modulate the line features and electrical characteristics of the patterns.

II. EXPERIMENT

A stable 0.1 mg/mL MWCNT-COOH aqueous dispersion was obtained by adding 1 mg of Commercial MWCNT-COOH (300-2000 nm) to 10 mL of deionized water (DI water) followed by sonication for 24 h. The dispersion was filtered by 0.45 µm porous PVDF filter. In order to achieve a highly uniform deposition, we employed a motor controlled two dimension airbrush spray coating to deposit the filtered and unfiltered MWCNT-COOH dispersion onto a preheated glass substrate. The MWCNT-COOH coatings in different thickness were achieved by spray coating MWCNT-COOH /H2O dispersion for 1 and 2 run with a certain N_2 presure.

Commercial MWCNT-COOH was mixed with DI water (0.2 mg/mL), and sonicated for 24 h. The dispersion was filtered with 0.45 µm porous PVDF filter, and a black homogenize dispersion was obtained. PEDOT-PSS was added to the dispersion as an additive for the ink. The MWCNT-COOH ink was printed in patterns on preheated glass substrate by Dimatix Materials Printer (FUJIFILM DMP-2800) to achieve transparent nanotube films.

III. RESULTS AND DISCUSSION

Optical properties of as sprayed MWCNT-COOH coatings were studied. The MWCNT-COOH coatings showed very high light transmittance in Fig. 1. The MWCNT-COOH coating sprayed with MWCNT-COOH/H2O ink filtered by 0.22 µm PVDF filter showed higher transmittance since long nanotubes were removed. Transmittance decreased as the spray coating run increased. As shown in Fig. 1, transmittance values are almost the same for MWCNT-COOH coatings with the same spray runs, suggesting the spray coating process is stable and repeatable. The unfiltered and filtered MWCNT-COOH coating samples with 2 runs spray still gave a transmittance around 75% and 85% (Fig.1), respectively, at 550 nm which is related with PV materials absorption band. It suggests the spray coating MWCNT-COOH films are highly transparent, which is promising for optical applications.

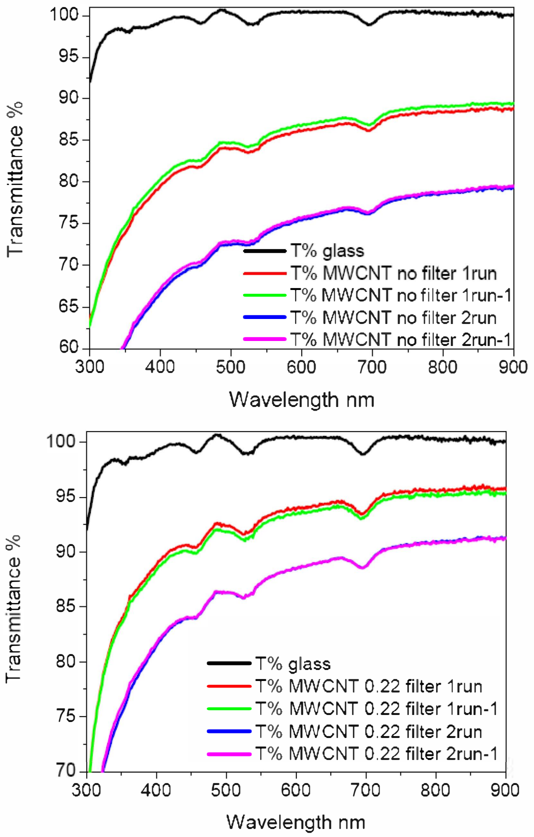

Fig. 1 Transmittance spectra of MWCNT-COOH spray coatings with MWCNT-COOH/H2O dispersion inks not filtered and filtered.

Fig.2 shows the scanning electron microscopy (SEM) images of unfiltered and filtered MWCNT-COOH spray coating samples. The SEM images indicate a homogeneous morphology of MWCNT-COOH coatings. No obvious aggregation of MWCNT-COOH has been observed. MWCNT-COOH exhibits uniform network structure which enables high conductivity with a smaller quantity of SWCNTs. If high transparency of the printed patterns is required, this network formation of MWCNTs was essential to produce high quality CNT thin conductive films.

In Fig. 2, it was observed that the networks of unfiltered MWCNT-COOH were more densified, and the space area unoccupied by MWCNT-COOH was much lesser. It reduces the surface resistance as well as the transparency. It explains how the transparency and the resistance of the MWCNT-COOH film are changed due to the network formation of MWCNT-COOH.

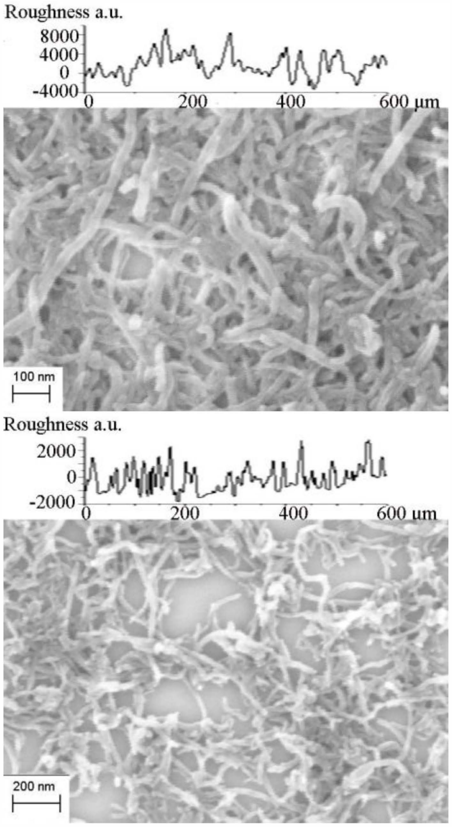

Fig. 2 SEM images of MWCNT-COOH spray coatings with nanotube inks not filtered and filtered.

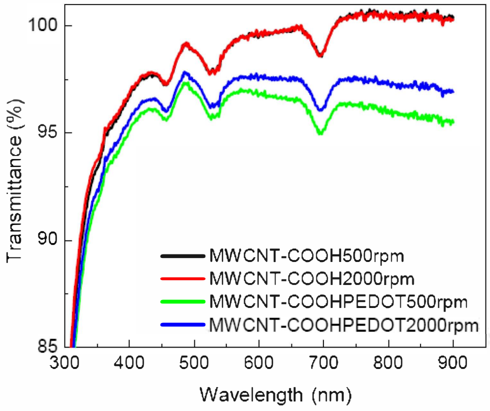

Fig. 3 Transmittance spectra of MWCNT-COOH coatings deposited by filtered MWCNT-COOH/H2O dispersions and MWCNT-COOH/PEDOT-PSS ink.

Fig. 3 shows the UV-vis of MWCNT-COOH/H2O dispersion and MWCNT-COOH/PEDOT-PSS ink spin coatings. It seems the MWCNT-COOH/PEDOT-PSS film is still highly transparent though PEDOT-PSS decreased a small percentage (<5%) of the transparency.

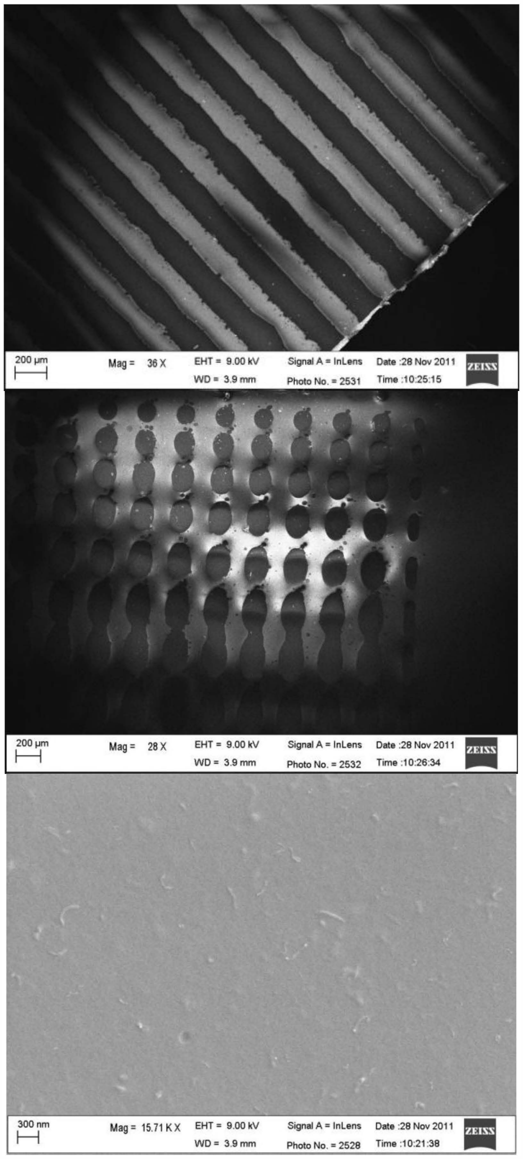

Fig. 4 SEM images of MWCNT-COOH ink-jet printing coatings

We also deposited the MWCNT-COOH coatings in line and dot patterns by ink-jet printing. Since the nozzles of the ink-jet printer are very small (d is around 450 nm), small size pattern is able to be printed (Fig. 4). However, the MWCNT-COOH ink has to be modified to achieve smooth printing. The MWCNT-COOH/H2O ink was mixed with PEDOT-PSS, followed by filtered with 0.22 μm PVDF filter. As shown in Fig. 4, the width of CNT strip is about 100 μm. In fact, the width can even be controlled to 50 μm .All the results obtained demonstrate the better jettability of the MWCNT-COOH/PEDOT-PSS ink [6]. The CNT network within this conductive ink is less impacted by the coffee-ring effect and therefore is homogeneous and continuous whatever the location within the printed pattern. It confirms that the positive impact on conductivity caused by the addition of doped PEDOT-PSS suspension is linked to the addition of conductive polymers but also to the induced distribution and orientation of CNTs.

The sheet resistance of thin film deposition from MWCNT-COOH/H2O ink and MWCNT-COOH /PEDOT-PSS ink was characterized by four probe measurements. The sheet resistance of 300 nm MWCNT-COOH film and MWCNT-COOH/PEDOT-PSS film was measured as $1.1*10^{6}\ \Omega/\square$ and $3.5*10^{3}\Omega/\square$ respectively. It suggests PEDOT-PSS is compatible with MWCNT-COOH and MWCNT-COOH network in MWCNT-COOH/PEDOT-PSS coatings might be more uniform. Also, the PEDOT-PSS have a little bit contribution to the film conductivity.

IV. CONCLUSION

In summary, MWCNT-COOH inks for spray coating and ink-jet printing are capable for transparent conductive film deposition. Compatible and stable MWCNT-COOH inks for ink-jet printing processes were formulated and used to print thin film electrodes or transistors. The present ink-jet printed transistors are of high yield, high reproducibility, and high scalability, although the device performance awaits further improvements, especially in comparison to reported devices with narrower MWCNT-COOH strips fabricated by means of lithography. These results demonstrate that thin-film transistors based on long MWCNT-COOH strips are compatible with presentday ink-jet printing technology and thus are promising building blocks for printing PV macroelectronics and flexible PV electronics.

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