Scalable Carbon Nanotube Thin Films: Fabrication, Properties and Device Applications

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ABSTRACT

Carbon nanotubes (CNT) have been under investigation for many years as a material suitable for applications in electronic devices. This paper will focus on the development and production of high quality, high performance, and scalable transparent and conductive CNT thin films using solution based roll to roll coating methods. We demonstrate both additive and subtractive methods for patterning conductive nanotube films. Various types of devices incorporating CNT thin films are demonstrated, including EPD e-paper, touch screen, OLED, flexible OPV, and TFT-LCD. Issues involving the integration of CNT electrodes into various devices are discussed, in particular conformal step coverage. Optical and mechanical properties, environmental stability and large scale uniformity together make Unidym's CNT thin films a viable alternative to transparent conductive oxides in applications requiring transparent, conductive electrodes.

INTRODUCTION

Thin films of carbon nanotubes (CNT) are a promising candidate in the development of alternatives to indium-tin-oxide thin films in applications requiring transparent, conductive films, and have been investigated by a number of groups. Films with high conductivities up to 6000 S/cm have been reported, and CNT integration into various devices such as organic solar cells, OLEDs, and LCD prototypes have been demonstrated.[1-6] However, most of these systems have suffered from one or more limitations. These limitations have included the high cost of CNT materials, film fabrication processes that are not scalable to large volumes, inferior conductivity, and poor lifetimes. Here we report the fabrication of high performance, scalable CNT films useful in applications for transparent conductors, and describe some applications of these materials demonstrating their usefulness in devices.

RESULTS

CNT material is synthesized by Unidym by thermal CVD using a proprietary catalyst and reactor system, and formulated into an aqueous ink with the proper rheology for slot-die roll-to-roll coating. The concentration of the CNT inks range from 0.2 mg/ml to 1.5 mg/ml, depending on the formulation (Figure 1(a)). CNT thin films were coated by using a conventional roll-to-roll slot-die coater with a custom die head. As show in Figure 1(b), the speed of coating can go up to 150 feet per minute. The ink formulation, ink-substrate interaction, drying and encapsulation are critical to obtain uniform and stable CNT thin films. Unidym has demonstrated 2000 ft long CNT coating which meets the specifications of most resistive and capacitive touch panel applications. Figure 1 (c) shows a 30 inch wide and 2000 ft long roll of CNT coating on PET substrate.

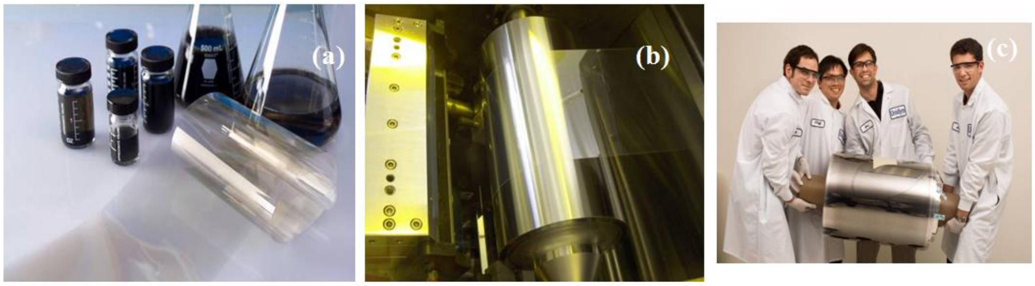

Figure 1. (a) CNT ink; (b) slot die coating set up; (c) a picture of 2000 ft long CNT film on PET substrate;

Figure 2 (a) shows the performance of CNT film coating on PET substrates as a transparent electrode. The sheet resistance and transmittance is controlled by the CNT dry thickness, which in turn is controlled by the CNT concentration and the wet laydown in the coating. For comparison, performance of ITO on PET is also shown in the Figure 2.[7] All transmittance data shown in Figure 2 depict the total film transmittance, which includes both the CNT film and the PET substrate (which is ~ 91% transmissive at 550 nm). Both the production film and the lab scale film are shown in the figure. The calculation of the DC conductivity for CNT thin films is based on R_s and CNT transmittance, with the exclusion of PET substrate transmittance.[4] The calculated DC conductivity is 2200 S/cm for production scale films and 3200 S/cm for lab scale films. Closing the gap between the production and lab scale films will depend on the scale-up process and roll-to-roll coating details. As shown in Figure 2 (a), the sheet resistance of CNT film on PET substrate is close to that of ITO on PET at a given sheet resistance. It is important to note that the loss of transmission in ITO is primarily due to reflection, while for Unidym’s CNT films transmission loss is due primarily to absorbance. This low reflectivity is advantageous in a number of display applications where first-surface reflectivity degrades optical performance.

Figure 2(b) shows an SEM image of a CNT film surface for roll-to-roll coated and encapsulated film on PET substrate. The dense network of overlapping individual CNTs and CNT bundles insures a robust network that is highly resistant to flexure of the underlying substrate, and other mechanical damage.

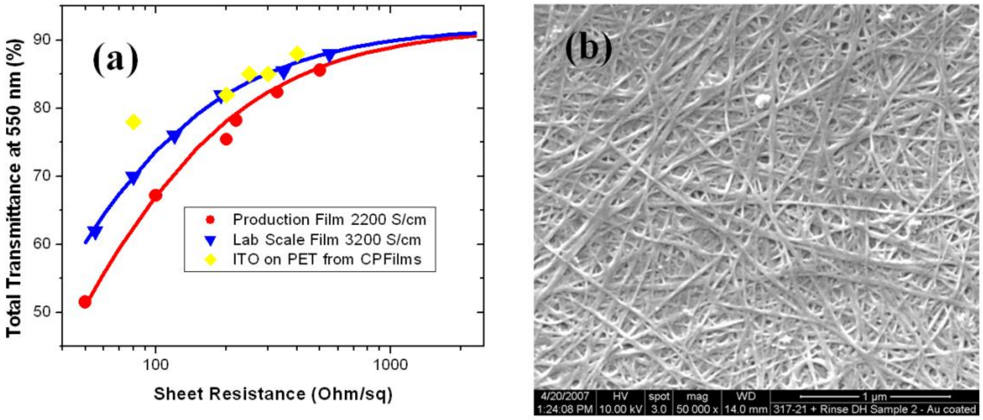

Figure 2. (a) Performance of CNT thin film as a transparent and conductive electrode; (b) SEM image of production CNT thin film coating.

For device integration of transparent CNT thin films, patterning is required. Subtractive methods for patterning CNT thin films includes lithography followed by O_2 plasma etching through a mask, and direct laser etching with or without the use of mask. Figure 3 (a) shows a patterned film in a TFT-LCD device. The detailed parameters are documented in our previous publication.[6] We also demonstrated that other types of plasmas such as Ar and CF_6 plasmas have high etching rate for CNTs. Lithography and plasma etching lead to well-defined patterned films with resolution down to 2 µm. Figure 3(b) shows a patterned film using direct laser patterning without the use of a mask. Direct laser patterning can be applied in a roll-to-roll fashion at high speeds, a method that is currently commercially used for ITO patterning. As opposed to subtractive patterning, CNT films can be patterned additively, using methods such as direct ink jet printing of CNT solution. The additive method is material saving and can be applied at high speeds. Figure 3(c) shows an ink-jet RFID circuit on photography paper printed with the use of an ink jet printer. The formulation concentration is 0.8 mg/mL and filtered through a 5 µm syringe filter. The volume of the jetted droplet is 10 picoliter, which spread on paper to a dimension of 30 µm. During the printing process, the substrate is heated to 40 C to facilitate the drying of the liquid. The patterning resolution achieved in Figure 3 (c) is 20µm. Electrical measurement of the films shows comparable electrical performance with slot die coated CNT films.

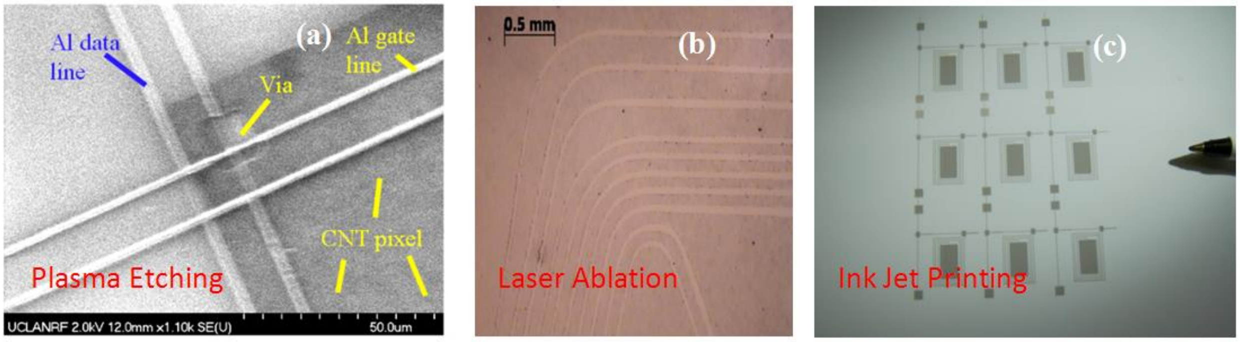

Figure 3. Patterning methods for transparent and conductive CNT thin films. Subtractive methods include (a) Lithography with a mask and plasma etching (b) Direct laser ablation without mask. Additive method includes (c) Ink jet printing.

Compared with traditional ITO electrodes, CNT thin films bring new optical properties and additional mechanical advantages which are beneficial for optoelectronics and flexible electronics. Figure 4 lists the optical properties, mechanical properties and uniformity of Unidym production CNT thin films. In Figure 4(a), the wavelength-dependent optics of a CNT film and ITO film are compared. The spectra for CNT film are flatter than ITO in the visible range, and the color of the CNT film is neutral while ITO is yellowish. Figure 4(b) shows the reflection of PET, CNT on PET and ITO on PET in the visible and infrared range. After CNT coating on PET, the reflection has little decrease compared to that of PET substrate itself. In the visible range, ITO on PET has much higher reflection than CNT on PET. The analysis is based on the optics for multilayer structures.[8] As such, the transmittance of an ITO electrode is determined by its reflection, while the transmittance of a CNT electrode is determined by its absorption.

Figure 4 (c) shows the reflection, absorption and transmittance of CNT thin films at 550 nm on PET substrates. The thickness of CNT thin films was measured by AFM and optical profiling the edge of patterned films. The thickness was confirmed by comparing the data from the two methods. The absorption of CNT film increases linearly with film thickness while the reflection remains the same. CNT material has a high absorption coefficient of 0.24 at 550 nm.[9] The difference between transmittance of CNT itself and CNT on PET is mainly due to the absorption of the CNT thin films.

Figure 4 (d) illustrates some of the superior mechanical properties of CNT thin films, compared to ITO. CNT films can be bent down to 2 mm without any electrical failure, while ITO on PET begins to fail at a bending radius of 4 mm. The mechanical flexibility and robustness makes CNT electrodes ideal for flexible electronics applications.

Film optical and electrical uniformity is critical for commercial use of the product. Figure 4(e) shows the uniformity of the Unidym production film coated with high speeds up to 300 feet per minute. In this particular sample, the average sheet resistance is 210 Ohm/sq and standard deviation is less than 4% for a 20 inch by 20 inch film. We also found that the standard deviation for optical transmittance is less than 4% for the same CNT film.

Environmental stability is also evaluated by soaking CNT films at 85C and 85 RH for long periods of time and measuring the sheet resistance before and after the soaking. For transparent electrode applications, the requirement for environmental stability varies but generally the resistance change needs to be less than 30% after a 1000 hour soak. Figure 4 (f) shows the stability of two films after 150 hours soaking in 85C and 85 RH environment. The two films included a Unidym proprietary binder at two different thicknesses.

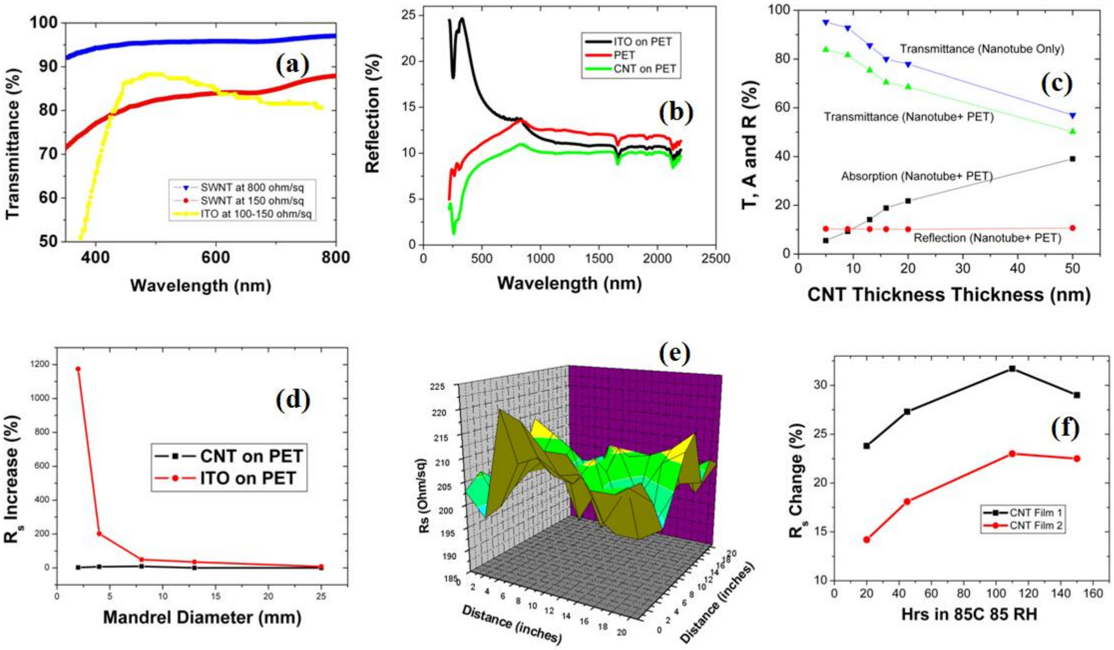

Figure 4. Performance of transparent CNT films: (a) Visible spectra of CNT and ITO films; (b) Reflection in visible and infrared range; (c) Reflection, absorption and transmittance of CNT

films with increasing film thickness; (d) Bending test of CNT and ITO; (e) Uniformity of (f) 85C/85 RH stability of production CNT films on PET substrate.

Transparent and conductive CNT films have immediate applications in optoelectronics. The first wave of device application for Unidym transparent electrode is touch panels and liquid crystal displays (LCDs), followed by organic light emitting diode (OLED) displays and solar cells. Functional prototypes including resistive and capacitive touch screens, 14.4” EPD e-paper, 5.5” VGA full color TFT-LCD, OLED and OPV devices have been demonstrated.[6] The devices have similar performance with ITO based device but have better mechanical properties. Figure 5 shows a functional resistive touch screen devices. The current performance of CNT electrodes is 600 Ohm/sq sheet resistance and 85% total transmittance. The finished panel has shown much better single point actuation durability, which is due to the CNT mechanical flexibility and robustness.

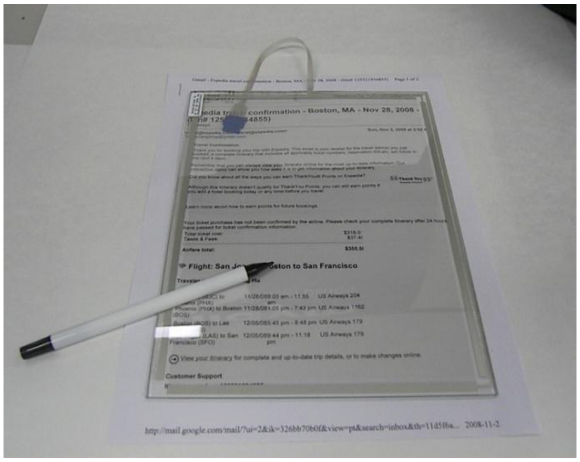

Figure 5. Demonstrated 4 wire resistive touch panel.

For device integration of CNT films in electronic or optoelectronic devices, various challenges exist. Step coverage across different layer heights in a device is a particularly important requirement, one that is not well met in several competitive nanoscale conductive materials. Figure 6 shows an example of CNT coating on a color filter plate of an LCD, with discontinuous edge structure due to different subpixel filter heights. Due to their large aspect ratio, strong nanotube-substrate interaction and their mechanical flexibility, CNTs shows outstanding conformal coating on step structure. Such types of coating ensure good electrical connection for different regions of devices.

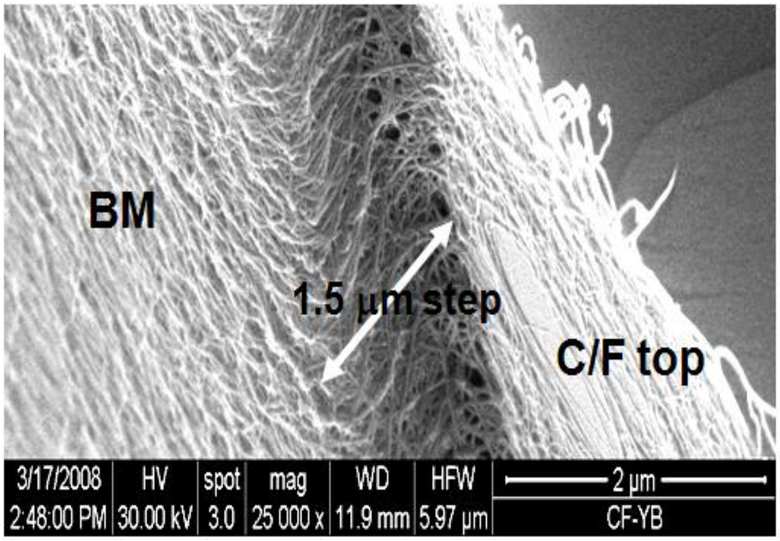

Figure 6 Conformable coating of CNT on color filter edge.

CONCLUSIONS

In conclusion, we demonstrate the achievement of scalable conductive and transparent CNT thin films. These films have shown equivalent or better optical and mechanical properties than ITO-based electrodes, and show dramatic superiority in flexibility. Integration into a number of different device structures has been achieved, demonstrating the potential for practical application of these materials and processes.

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