Front. Optoelectron. China 2009, 2(4): 425–428
DOI 10.1007/s12200-009-0076-y

RESEARCH ARTICLE

Electrical properties of transparent conducting carbon nanotube films

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Abstract Single walled-carbon nanotube (SWCNT) thin film is one of the candidates for the next-generation flexible and transparent conductive thin film, which is a crucial component in various applications such as electrodes of flat-panel displays, solar cells, light emitting diodes, and touch panels. An intensive research work is underway to develop thin and flexible SWCNT films. The most important requirement of an SWCNT thin film is that it should show a low sheet resistance coupled with a high transparency. In this work, thin films of SWCNTs are prepared by vacuum filtration. The electrical properties of the as-prepared, annealed and HNO_3-treated SWCNT films have been investigated. It is found that the square resistance can be significantly changed upon anneal and HNO_3-treatment. A room-temperature ethanol alcohol sensor based on the SWCNT film has also been demonstrated.

Keywords transparent electrode, single walled-carbon nanotube (SWCNT) film, vacuum filtration

1 Introduction

Even though single-tube devices based on single walled-carbon nanotubes (SWCNTs) have excellent properties [1–3], the devices are usually fabricated randomly since it is very difficult to find two completely identical SWCNTs through current available technologies. From the application aspect, the SWCNT film, which contains SWCNTs with all kinds of chiralities, is very attractive because it can suppress the difference from individual nanotubes. Up to now, the available technologies for SWCNT synthesis usually produce a mixture of nanotubes with different diameters. An as-prepared SWCNT can be either a metal or a semiconductor depending on its chirality. Fortunately, the separation of metallic SWCNTs from a mixture of the nanotube raw material becomes possible [4]. However, a highly conductive SWCNT film coupled with high transparence is strongly desired.

In this work, thin films of SWCNTs are prepared by vacuum filtration. The electrical properties of the as-prepared, annealed and HNO_3-treated SWCNT films have also been studied. It is found that the square resistance can be significantly changed upon anneal and HNO_3-treatment. A room-temperature ethanol alcohol sensor based on the SWCNT film before and after annealing and HNO_3-treatments has also been demonstrated for the first time.

2 Experiment

In the experiment, we used commercially available HiPco purified nanotubes as starting material. 1 mg SWCNTs was dispersed in 200 mL aqueous solutions of 1% v/v surfactant (Triton-100) via 1 h ultrasonication and 0.5–1 h centrifugation. To form a nanotube film, vacuum filtration method was adopted and the process was similar to that reported by Wu et al. [5]. The dispersed SWCNT suspension was vacuum filtered onto 0.1 μm pore size mixed cellulose ester membrane (Millipore) and followed by washing with copious quantities of deionized water to remove the surfactant. The thickness of nanotube films formed on the membrane can be well controlled by the amount of SWCNT suspension. In this experiment, 5 mL, 10 mL, 20 mL, 35 mL, 50 mL, and 200 mL SWCNT suspensions were used for thin film deposition (hereafter, we call the samples 5 mL, 10 mL, 20 mL, 35 mL, 50 mL, and 200 mL SWCNT thin film, respectively). To transfer the nanotube film onto a glass substrate, the still wet membrane was placed onto the substrate with the film side down, which makes the nanotube film intimately contact with the glass substrate. The assembly was subsequently

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Received June 30, 2009; accepted August 28, 2009

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covered with a piece of clean filter paper to absorb the moisture and compressed with a 2 kg mass to keep the thin film flat overnight. Then, the dried membrane was simply peeled off from the membrane/nanotube/glass assembly.

The as-prepared nanotube films were thoroughly cleaned in acetone and then in ethanol for future electrical property measurements. Post-treated samples were prepared by annealing the as-prepared nanotube films at 300°C in an Ar gas environment for 24 h with or without following HNO_3-treatments. The HNO_3-treatments were carried out by submerging the annealed nanotube/glass assembly in 12 M HNO_3 for 2 h. Atomic force microscopy (AFM) topography images of the SWCNT thin films were acquired in the tapping mode using a multimode AFM (Veeco Instruments). The strip electrodes on the SWCNT thin film were painted using commercially available Ag paste (Ted Pella Inc.), then silver wires were used to contact the Ag strip electrodes and the sample stage of a cryostat (VPF-500, Janis Research) for electrical property tests. All electrical property tests were conducted using a Keithley 4200 SC semiconductor analyzer. The chemical sensing properties of the SWCNT films were characterized by comparing the electrical resistances measured between the two Ag strips of each sensor under vacuum and ethanol alcohol vapor. The transmittance data of the SWCNT films were measured by Lambda 35 spectrometer.

3 Results and discussion

Figure 1 shows photographs taken by an ordinary camera, and Figs. 1(a)–1(f) correspond to 5, 10, 20, 35, 50, and 200 mL SWCNT films, respectively. It is easily seen that with the increase of the amount of SWCNT solution for vacuum filtration, the film transparence decreases obviously. For the 5, 10, and 20 mL SWCNT film, the transparency is 95%, 89%, and 83%, respectively, which is unaltered after any treatments mentioned in the context. The transparence for the other SWCNT films is lower than 75%, which is too low from the application aspect. In this work, we focused our experiments on 5, 10, and 20 mL SWCNT films.

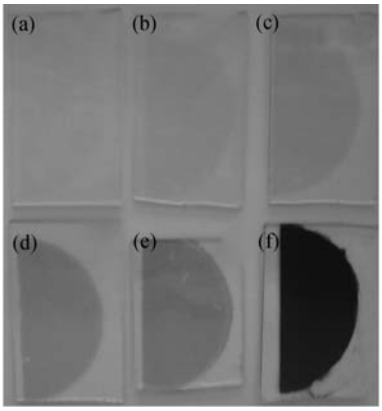

Fig. 1 Photographs taken by an ordinary camera. (a) 5 mL SWCNT film; (b) 10 mL SWCNT film; (c) 20 mL SWCNT film; (d) 35 mL SWCNT film; (e) 50 mL SWCNT film; (f) 200 mL SWCNT film

Figure 2 displays the AFM images of several SWCNT transparent conducting films. Because of the tubular structure of the carbon nanotubes, they form a network in the thin films, which always have nanoscale porosity. Figure 2(a) shows the as-prepared 5 mL SWCNT film, from which large voids can be easily observed. Figure 2(b) shows the annealed 5 mL SWCNT film, and Fig. 2(c) shows the HNO_3-treated 5 mL SWCNT film. Comparison of Fig. 2(a) with Figs. 2(b) and 2(c) reveals the effect of post-anneal and HNO_3-treatments on the as-prepared 5 mL SWCNT film. The morphology is obviously different for SWCNT films after post-treatment. It is found that the post-treatment results in a denser SWCNT film, improves the film quality, and eliminates the large voids. Figure 2(d) is an AFM image of the annealed 10 mL SWCNT film, which is thicker than the 5 mL SWCNT film (Fig. 2(b)); however, it shows no distinctive difference in morphology. From Fig. 2, it is also found that there are few straight and long SWCNTs through the network, which may form unobstructed electrical paths through the network.

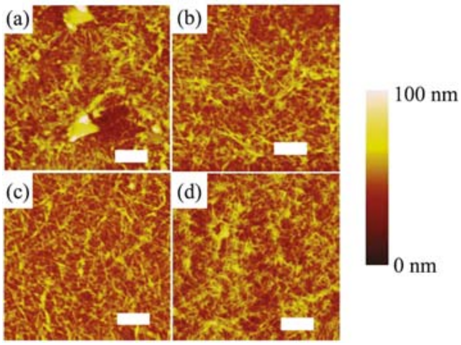

Fig. 2 AFM images of SWCNT transparent conducting films (scar bar is 1 μm). (a) As-prepared 5 mL SWCNT film; (b) annealed 5 mL SWCNT film; (c) HNO_3-treated 5 mL SWCNT film; (d) annealed 10 mL SWCNT film

Several strips of SWCNT film with a width of 5 mm were tailored from a big SWCNT film. Both ends of each strip were painted with Ag paste, which formed Ag film electrodes. Two-point resistance measurements were made on the strips of SWCNT film as a function of length (the distance between two electrodes on SWCNT film). This method was used as opposed to four-probe measurements to ensure uniform current flow through the entire cross-section of these SWCNT films. The net resistance of the SWCNT film and the contact resistance between the SWCNT film and the Ag paste can be easily determined [6]. Under optimal conditions, the contact resistance was less than 10 Ω at room temperature. As shown in Fig. 3, the square resistance (R_{sq}) of the as-prepared SWCNT films is 848, 1810, and 17098 Ω/sq for 20, 10, and 5 mL SWCNT films, respectively. Post-annealing of the as-prepared films increases the resistance from 848 to 2728 Ω/sq for 20 mL SWCNT film, 1810 to 4525 Ω/sq for 10 mL SWCNT film, and 17098 to 33600 Ω/sq for 5 mL film. However, the resistances of the acid-treated samples decrease from 848 to 588 Ω/sq for 20 mL SWCNT film, 1810 to 801 Ω/sq for 10 mL SWCNT film, and 17098 to 6590 Ω/sq for 5 mL SWCNT film. For all the films shown in Fig. 3, it is observed that the anneal increases the resistance, while the HNO_3-treatment makes more conductive SWCNT films, which may be understood by the doping effect of SWCNT films. The as-prepared SWCNT film is naturally doped by oxygen in air environment, which makes the SWCNT film a naturally p-type semiconductor. However, annealing can remove the dopant and make the film more resistive. It is not difficult to understand that HNO_3-treatment makes the annealed SWCNT film more conductive since the SWCNT film is doped again.

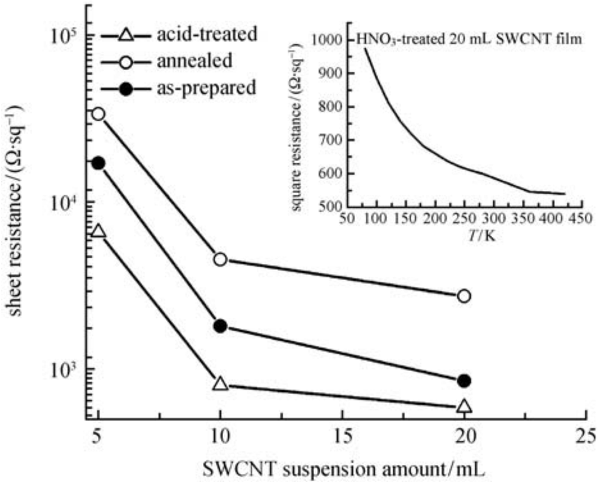

Fig. 3 Change of square resistance (R_{sq}) for SWCNT films under different post-treatments. The inset shows the low temperature measurement for the HNO_3-treated 20 mL SWCNT film

Figure 3 also reveals that as the amount of SWCNT solution increases, the decreasing rate of the resistance slows down, as predicated by the well-known percolation theory [1].

The two-point low temperature test was also performed on HNO_3-treated 20 mL SWCNT film, as shown in the inset of Fig. 3. Although the SWCNT material contains a small fraction of metallic nanotubes, HNO_3-treated SWCNT film shows a semiconducting-like behavior, suggesting the possible presence of tunneling barriers at the intertube junctions, which may suppress the electron tunneling.

SWCNT is expected to be a promising material for gas sensors because of its large surface-to-volume ratio [7]. To investigate the possible application of the SWCNT thin film as a gas sensor, the electrical responses of a 5 mL SWCNT film to ethanol alcohol vapor before and after post-treatments were measured, as shown in Fig. 4. In our experiments, the percentage relative resistance change has been calculated for determination of the sensor sensitivity, as shown in the following:

$$\frac{\Delta R}{R_i}(\%) = \frac{R_i - R_f}{R_i}(\%), \tag{1}$$

where R_i and R_f are the electrical resistance of the SWCNT films before and after exposure to ethanol alcohol vapor, respectively. The sensors were placed in a cryostat chamber and a rotary pump was connected to the outlet of the chamber. We measured the resistances both in a 10^{-3} Torr vacuum and a 2-minute streaming ethanol alcohol vapor, which was formed by closing the valve for the pump and opening the valve for the ethanol alcohol reservoir. The pressure of the ethanol alcohol vapor increases from 1×10^{-3} Torr to 2.5 Torr during the measurement.

Figure 4 shows 5 mL HNO_3-treated film exposed to 3-pulse ethanol alcohol vapor. The pulse width is 120 s, and the interval between two pulses is 150 s. In Fig. 4, the sensitivity of the SWCNT thin film at room temperature shows obvious change before and after the exposure to ethanol alcohol vapor, and it also reveals that the sensitivity changes because of the anneal as well as HNO_3-treatment of the SWCNT films. For high resistive (annealed) film, the sensitivity is 1.8%; for medium resistive (as-prepared) SWCNT film, the sensitivity increases to 2.7%; and for the acid-treated SWCNT film with the smallest resistance, the sensitivity is 4.2%. These results can be explained by the electrical charge transfer between ethanol alcohol vapor and p-type semiconducting

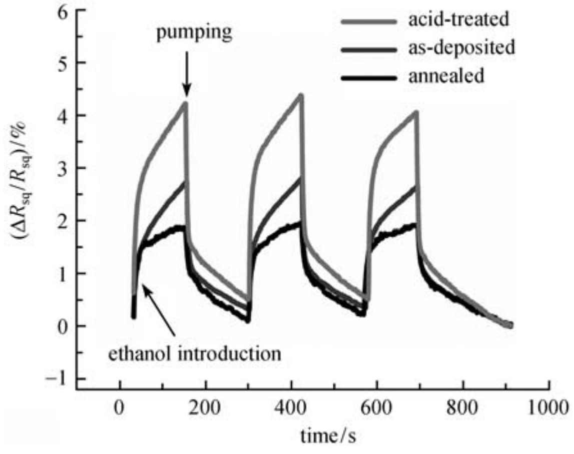

Fig. 4 Sensitivity of SWCNT thin films to ethanol alcohol vapor at room temperature

SWCNT thin film [8]. After exposure of SWCNT thin film to ethanol alcohol vapor, the ethanol alcohol vapor intercalated SWCNT film was formed. The resistance of SWCNT thin film increases because electrons are transferred from the ethanol alcohol vapor molecule to the valence band of SWCNT thin film and the density of holes decreases. For different resistive SWCNT films, the density of holes decreases with the increase of film resistance. When the different SWCNT films were exposed to ethanol alcohol vapor, the density of holes changes more profoundly for the low resistive SWCNT film than that of the SWCNT film with high resistance, which may account for the fact that the low resistive SWCNT film sensor shows a higher sensitivity. Because all these samples were measured under a constant current (10 μA), the dissipative power of the SWCNT film sensor is proportional to their respective resistances, which suggests that there is hope for the HNO_3-treated SWCNT film to be used to make a cost-effective sensor.

4 Conclusion

SWCNT films were prepared by vacuum filtrating the Triton-100-dispersed HiPco nanotubes. The surfactant (Triton-100) can be sufficiently removed from the SWCNT thin film via water flush and annealing. The resistance changes of the as-prepared, annealed, and HNO_3-treated SWCNT films have been studied. The results indicate that the post-treatments alter the electrical properties of the SWCNT thin film significantly, which may give us a hint for fabrication of a highly transparent conducting SWCNT film. A cost-effective room-temperature ethanol alcohol sensor based on the SWCNT film has been demonstrated for the first time.

Acknowledgements This work was supported by the National Hi-Tech Research and Development Porgram of China (No. 2008AA01Z207) and Scientific Research Foundation for the Returned Overseas Chinese Scholars.

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