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Fluctuation-induced tunneling dominated electrical transport in multi-layered single-walled carbon nanotube films

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ABSTRACT

Low temperature measurements may give some insight into the transport mechanism of single-walled carbon nanotube (SWCNT) films, which could lead to an optimal SWCNT film with designed photoelectric properties. Despite intense research efforts on the low temperature transport in SWCNT films, it is still an open question for the low temperature transport in multi-layered SWCNT films. In this work, the multi-layered SWCNT films were prepared with a layer by layer vacuum filtration. It suggests that the space between different layers of the multi-layered SWCNT can be ignored. For deposition of different-layered SWCNT films using the same total amount of SWCNT suspension, the increase of the layer numbers can reduce the density of the resulting films, which may account for the low temperature transport. The effect of thermal annealing and subsequent nitric acid treatment on the electrical properties of the SWCNT films has also been investigated. At the temperature range of 80–300 K, the transport of the multi-layered SWCNT films can be explained by a fluctuation-induced tunneling model. Our results could build a bridge connecting measured temperature coefficient of resistance and the microscopic tunneling barrier.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are attractive materials from both fundamental and technological points of view. For fundamental research, individual SWCNTs have been attracted a lot of attention especially in the nanoelectronics domain, such as a field effect transistor, which outperforms the state of art silicon technologies in various figures of merit [1]. However, an as-prepared SWCNT can be either metallic or semiconducting depending on its chirality. In general, one third of the synthesized SWCNTs are metallic, while the other two thirds are semiconducting [2,3]. Even though the separation of metallic SWCNTs from a mixture of both metallic and semiconducting SWCNTs has recently become possible [4], the repeatable fabrication of two identical SWCNT devices is further than a near future work. SWCNT films draw a lot of attention in recent years, since the ensemble averaging over tubes makes that SWCNT films can be mass produced in a cost effectively manner with a series of repeatable properties. Moreover, from the point of technological application, SWCNT film can be used in SWCNT thin film transistors [5], a potential replacement of indium tin oxide (ITO) electrode, especially on flexible substrates [6,7], infrared bolometers [8], gas sensors [9], and optical modulators [10]. Q. Cao et al. presented a comprehensive review which covers relevant work in this field over the last 10 years or so [11].

Vacuum filtration has been found an effective approach for repeatable fabrication of SWCNT films with a designed thickness and film density [6]. In this work, an improved vacuum filtration method (hereafter, it was called a layer-by-layer vacuum filtration) was adopted for the fabrication of multi-layered SWCNT films. A layer-by-layer vacuum filtration for fabrication of SWCNT films has been proposed previously, aiming at a high quality of transparent and conductive electrode which can be used as an ITO replacement, especially on flexible substrates [12]. Low temperature measurements may give some insight into the transport mechanism of SWCNT films, which could lead to an optimal SWCNT film with designed electrical properties [13]. Despite intense research efforts on the low temperature transport in SWCNT films [14–16], the study on the low temperature transport in the multi-layered SWCNT films has not been found.

Moreover, in addition to being a potential replacement for ITO as a conductive and transparent electrode material, SWCNT thin films have also attracted a lot of attention recently due to their large bolometric photoresponse and high temperature coefficient of resistance (TCR) [17]. High TCR SWCNT films are highly desired for its potential application in infrared (IR) sensor. The TCR for a multi-layered SWCNT film has not been reported. In this work, a layer-by-layer vacuum filtration was adopted for the fabrication of multi-layered SWCNT films. The low temperature transport in the single and multi-layered SWCNT films has been investigated comparatively. The effect of thermal annealing and nitric acid (HNO_3)-treatment on the electrical properties of the multi-layered SWCNT films has also been discussed. Aiming to ultimately produce an SWCNT film with optimal electrical

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and optical properties, our experiment provides insight into the design and selection of SWCNT films.

2. Experiments

In this research, we used home-made purified SWCNTs for fabrication of SWCNT films. The SWCNT raw material was prepared by an ethanol chemical vapor deposition (CVD) using Co catalyst, as we reported before [3]. The as-synthesized SWCNT raw material (soot) was scratched from the Si substrate and purified by HNO_3. To form a nanotube film, an improved layer-by-layer vacuum filtration method was adopted and the process for each layer of the SWCNT films was similar to that reported by Wu et al. [18]. The SWCNT soot was dispersed in aqueous solutions of 1% v/v surfactant (Triton-100) via 1 h ultrasonication and 0.5 h centrifugation. The concentration of the obtained SWCNT suspension is about 5×10^{-3} mg/ml. The obtained SWCNT suspensions were 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 so-called layer-by-layer method is described as follows: after the first layer of SWCNTs was transferred to the glass substrate, a second vacuum filtrated layer of SWCNTs will be transferred on the first layer, and the third vacuum filtrated layer will be transferred on the second layer.

All samples in this work can be written as sample(s) n–m, where n denotes the amount (ml) of SWCNT suspension used for the film preparation, while m denotes the layer number. The film thickness and the standard error associated with the thickness measurements are tabulated in Table 1. It is not difficult to know that the film density can be calculated with an equation $\rho = M/S\cdot d$, where ρ denotes volume density, M denotes the mass, d is film thickness, and S denotes the film area, which keeps a same value for all SWCNT films prepared with the same apparatus for vacuum filtration. For simplicity, in this work, the so-called “relative density” is also defined as the ratio of a film density to the density of sample 1–1, as presented in Table 1. Table 2 tabulates the low temperature properties of some typical SWCNT thin films. According to above definition, sample 1–2 is a two-layered SWCNT film, and thereinto each layer was prepared using 1 ml SWCNT suspension. Sample 2–1 has only one layer prepared by vacuum filtration with 2 ml SWCNT suspension. Sample 2–3 is a three-layered SWCNT film, the suspension amount for each layer of this film is exactly the same as that of the sample 2–1. The as-prepared SWCNT films were thoroughly cleaned in acetone and then in ethanol for future electrical property measurements. Post-treated samples (samples 2–3a and 2–3aN) were prepared by annealing the as-prepared SWCNT film named sample 2–3 at 300 °C in an Ar gas environment for 12 h with and without subsequent HNO_3-treatments, respectively. The HNO_3-treatments were carried out by submerging the annealed SWCNT film in 12-M HNO_3 for 0.5 h.

Table 1
The thickness and relative density of the SWCNT thin films.

Sample name	Sample description	Thickness (nm)	Standard error	Relative density (ρ_{n-m}/ρ_{1-1})
1–1	1 ml SWCNT suspension, 1 layer	22.0	1.7	1.0
6–1	6 ml SWCNT suspension, 1 layer	83.0	3.8	1.59
2–1	2 ml SWCNT suspension, 1 layer	35.0	2.5	1.26
2–2	2 ml SWCNT suspension, 2 layer	70.0	3.7	1.26
2–3	2 ml SWCNT suspension, 3 layers	105.0	5.3	1.26
1–2	1 ml SWCNT suspension, 2 layers	45.0	3.5	0.98

Table 2
The low temperature properties of the SWCNT thin films.

Sample name	Sample description	T_b (K)	T_s (K)	TCR (%/K) (at 280 K)
1–2	1 ml SWCNT suspension, 2 layers	55.0	21.1	−0.065
2–1	2 ml SWCNT suspension, 1 layer	34.5	17.5	−0.042
2–3	2 ml SWCNT suspension, 3 layers	23.7	19.8	−0.028
2–3a	Sample 2−3 after annealing at 300 °C, 12 h	30.9	16.6	−0.038
2–3aN	Sample 2–3a after HNO_3-treatment	7.7	12.1	−0.010

Atomic force microscopy (AFM) topography images of the SWCNT thin films were acquired in the tapping mode. AFM was also used to measure the thickness of the SWCNT films. The dependence of the resistivity on temperature has been measured using a dc standard four-probe method. Before measurement, Ag metal film was deposited on the SWCNT films to get a good ohmic contact. The resistance between the electrodes with different spacing was then measured and used to determine the contact resistance of the silver/nanotube contact and the intrinsic resistance of the SWCNT films, as reported in references [6] and [19]. Our results show that compared with the intrinsic resistance, the contact resistance is small. The dimension of the SWCNT films under test was 2 mm × 20 mm, and the area of the circular electrodes is less than 2 mm in diameter. The constant current was flowing along the longer edge (20 mm) and the voltage drop between the inner two electrodes was recorded automatically with a program-controlled Keithley voltmeter during low temperature measurement. For measurement of temperature-dependent resistivity, SWCNT film fixed in a cryogenic system was first cooled down from room temperature. The measurements were then taken while SWCNT films were heating in the temperature range of 80–280 K. Since the maximum temperature is well below the T^*_{dedop} (350 K) suggested by Teresa M. Barnes et al. [16], it is not difficult to understand that no obvious hysteresis was observed in the temperature-dependent resistivity obtained from different cycles of heating or cooling.

3. Results and discussion

Fig. 1a shows isolated SWCNTs grown on a 5-pulse Co catalytic substrate as we reported before [3], which allows us to derive the diameter of SWCNTs from AFM topography data, and the typical results are shown in Fig. 1b. For every nanotube, tens of positions were measured to calculate the value of the average heights. The diameter distribution was calculated with the value of average height from more than 50 CNTs. It is found that the nanotube diameters are in the range of 0.6 nm to 1.6 nm, with a mean diameter about 1.0 nm. Fig. 1c illustrates SWCNT bundles grown on 10-pulse Co catalytic substrate with a high ethanol pressure during CVD. The increase of pulse number and ethanol pressure increases the yield of SWCNTs. The as-synthesized SWCNT bundles shown in Fig. 1c was scratched from the Si substrate and purified by HNO_3. After purification, the obtained soot contains at least 90% SWCNTs by weight, and was used as the raw material for SWCNT film fabrication. Fig. 1d shows a typical AFM image of the SWCNT films fabricated by vacuum filtration. The root mean square (rms) roughness for the SWCNT film deduced from AFM data is about 8.0 nm, which is nearly same as the previous report [20].

The multi-layered SWCNT films were prepared with the “improved” vacuum filtration. Since each layer can be thoroughly washed from both sides of the layer with copious amounts of water [12], it is thought that the advantage of the layer-by-layer vacuum filtration over “normal” vacuum filtration reported by Wu et al. [18] might be that the improved vacuum filtration produces a “clean” multi-layered SWCNT film if we neglect (or remove) the residues of the (cellulose ester) membrane left after every deposition.

As suggested by Wu et al. [18], the density and thickness of SWCNT films can be controlled well with the “normal” vacuum filtration. With