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Growth-temperature induced metal–insulator transition in bamboo-shaped multiwalled carbon nanotubes

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Abstract

Temperature-dependent resistivity measurements were carried out on bamboo-shaped multiwalled carbon nanotubes (CNT) grown on cobalt-catalyst-deposited $A1_2O_3$/Ti substrates by a thermal chemical vapor deposition. The resistivity decreased with increasing growth temperature, and a reduced activation energy analysis showed that the CNT moved from the critical regime to the metallic regime with increasing growth temperature. The improved electrical conductivity with increasing growth temperature is attributed to the improved crystallinity and the increased diameters of the CNT. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the discovery in 1991 [1], the carbon nanotubes (CNTs) have generated much enthusiasm and scientific curiosity due to their unique properties [2] and potential applications [3–7]. In general, the electrical properties of defect-free nanotubes depend on the structure, i.e. the diameter, the number of concentric cells, and the chirality [8–10]. Single-walled carbon nanotubes (SWNTs) can be metallic or semicondutive depending on the carbon arrangements [8–10]. In semiconductive CNTs, the band-gap is inversely proportional to the diameter [8,9]. Therefore, structure control of the CNTs is very important in controlling the electrical properties of the CNTs and it is illuminating to study the electrical properties of CNTs with various structures such as SWNTs, multiwalled carbon nanotubes (MWNTs), nanotube ropes, and bamboo-shaped CNT.

In earlier electrical transport measurements on individual SWNTs by Tans et al., [11] Coulomb blockade properties were reported, indicating that the SWNTs indeed act as genuine quantum wires. Besides, Coulomb blockade and Luttinger-liquid behaviors were shown from measurements on rope ('bundle') SWNTs [12,13]. The first four-probe measurements of the individual MWNTs by Ebbesen et al. [14] showed a great diversity in the conduction properties. In electrical transport measurements on individual MWNTs, both ballastic conduction [15,16] and diffusive transport [17,18] were reported. Bachtold et al. [18] demonstrated that current flows only through the outermost shell by measurements of the Aharonove-Bohm oscillation in MWNTs. For rope and unoriented bulk SWNTs, [19,20] the resistivity was reported to increase with increasing temperature at high temperatures, and a low-temperature upturn was also seen. The low-temperature upturn is not fully understood but may be due to one-dimensional localization [19]. For bundles, [21,22] films, [23] and

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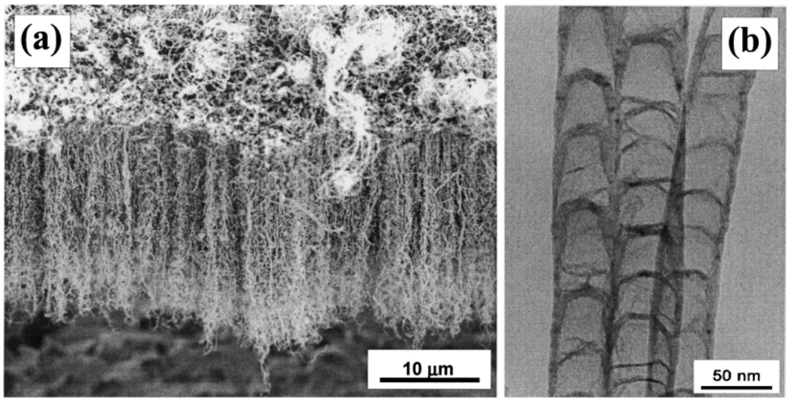

Fig. 1. (a) SEM micrographs of vertically well-aligned CNTs grown on Co catalyst deposited Al_2O_3/Ti substrates at 750 °C. (b) TEM image of the CNTs grown at 950 °C, showing the bamboo structure. Curvatures are directed to the root of CNT.

unoriented bulks [24] of MWNT, the resistivity increases gradually with decreasing temperature. In most cases of MWNT, despite the low resistivity sometimes found, positive $d\rho/dT$ characteristic of a metal is not shown. The bamboo-shaped MWNTs have been reported by several groups, [25–29] however, the electrical properties of individual and bundle bamboo shaped MWNTs have not yet been reported. In this work we report the first measurements of the resistivity along the tube axis in bamboo-shaped MWNTs.

It has been found that the structure of carbon materials is dependent on the growth conditions such as the reaction temperature, the catalysts, and the reaction gas, etc. Especially, the growth temperature is crucial for the crystallinity and structure of CNTs. Recently, we have reported structure control of nanotubes by varying the growth temperature [30]. By transmission electron microscopy (TEM), Raman spectroscopy, and scanning electron microscopy (SEM), it was found that the crystallinity of the graphene sheets and the average diameter of the CNTs increased as the growth temperature increased from 750 to 950 °C [30]. Since the conductivity of CNTs is important for both display and electrode applications, [31, 32] it is worthwhile to study their macroscopic electrical properties.

In this work, we report temperature-dependent resistivity

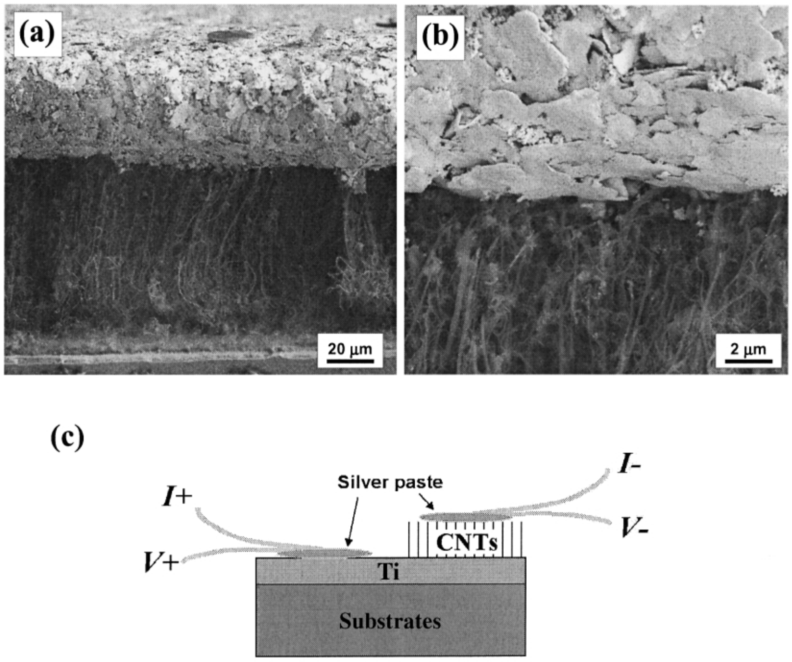

Fig. 2. (a) and (b) SEM micrographs showing the silver paste contact uniformly put on the bamboo-shaped MWNTs. (c) Schematic diagram of the four-probe electrical resistance measurement for the aligned MWNTs.

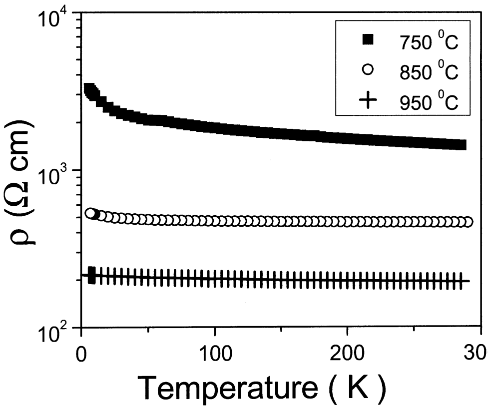

Fig. 3. The temperature dependent resisitivity of the bamboo-shaped MWNTs grown at 750, 850, and 950 °C. All the MWNTs show a negative temperature coefficient, $d\rho/dT < 0$.

measurements of the bamboo-shaped MWNTs, grown at 750–950 °C. The electrical properties of the nanotubes will be explained in terms of the crystallinity and the diameter of the CNTS.

2. Experiments

The bamboo-shaped MWNTs were grown on the Co deposited Al_2O_3/Ti substrates (Fig. 1). A 1 μm-thick Ti film, used as an electrode, was thermally deposited on the Al_2O_3 substrate, and the Co catalyst was subsequently deposited on the Ti film. The catalyst is responsible for diameter size and growth rate of CNTs [33].

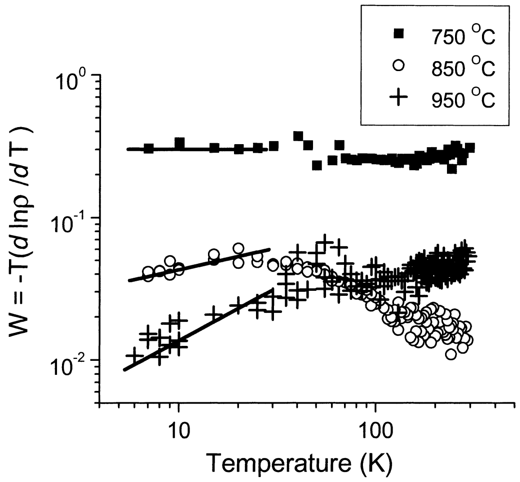

Fig. 4. The reduced activation energy vs temperature. In the low temperature regime below 30 K, metallic behaviors are shown ($dW/dT > 0$) for samples grown at 850 and 950 °C, whereas a critical (metal-insulator transition) behavior is shown ($dW/dT = 0$) for the sample grown at 750 °C. In the critical regime, the resistivity follows a power law as a function of temperature, $\rho(T) \propto T^{-\beta}$, where $\beta = W = 0.35 \pm 0.02$. Solid lines are guides to the eye.

The resistance was measured in the temperature range 6–295 K by a four-probe method, with contacts of gold wires by silver paste on the surface of the CNTs and on the Ti film (Fig. 2). While unoriented bulk SWNT resistance measurements by a four-probe method with silver paste contacts have been done by the Fisher group [19], our exceptionally well oriented samples and the electrical contacts, as are shown in Figs. 1 and 2, provided us with a unique opportunity to investigate the average axial conduction in bamboo-shaped MWNTs, which is expected to closely resemble that along a single rope. The average resisitivity was roughly calculated from the measured resistance, the active area of the electrodes, and the lengths of the CNTs. The active area of the electrodes was 0.5 ± 0.1 mm^2. The lengths and diameters of the CNTs were measured by a scanning electron microscope (Hitachi S-800, 30 kV).

3. Results and discussions

The temperature-dependent resistivity measurements for the CNTs are shown in Fig. 3. It is noticed that the resistivity of the CNTs grown at 750 °C is about two times higher than that of CNTs grown at 850 °C, and is about four times higher than that of the CNTs grown at 950 °C. All the CNTs show negative temperature coefficients ($d\rho/dT < 0$), which was also reported for the resistiviy measurements of the MWNT bundles [21,22] and films [23]. The resistivity of the MWNTs grown at 750 °C shows a rapid increase in the resisitivity with decreasing temperature, especially below 30 K, while little temperature dependence is noticed for the MWNTs grown at 850 and 950 °C. Following the previous studies of the electrical conduction in disordered systems, the reduced activation energy [34–36]

$$W = -T\frac{d \ln \rho(T)}{dT} \qquad (1)$$

was considered. dW/dT is supposed to be positive in the metallic regime, negative in the insulator regime, and zero in the critical (metal–insulator transition) regime. The reduced activation energy analysis applies well to the case of the Anderson localization [37] as in, for example, doped conducting polymers and strongly doped semiconductors [38,39]. The W vs. temperature plot is shown in Fig. 4 for samples grown at different growth temperatures. It is noted that at low-temperatures below 30 K the MWNTs grown at 850 and 950 °C show metallic behaviors and the MWNTs grown at 750 °C show a critical behavior. The successive decrease of dW/dT with increasing growth temperature is well consistent with that of the resistivity. In the critical regime, Larkin and Khmelnitskii found that the resistivity follows a power law as a function of temperature, $\rho(T) \propto T^{-\beta}$, where $\beta = W$ and $1/3 < \beta < 1$ [40]. As shown in Fig.

3, W is constant for the sample in the critical regime (CNTs grown at 750 °C), with $\beta = W = 0.35 \pm 0.02$.

In our previous work, the diameter of CNTs increased at higher growth temperatures due to the agglomeration effect of the catalyst, resulting in larger catalyst particles [30]. Besides, at a higher growth temperature diffusion of carbons is easier at the surface of catalyst particles, [33] and the supplement of carbons under the steady-state conditions is enhanced. Then, the enhanced growth rate of the CNTs and crystallinity of the graphene sheets forming the CNTs walls [33] result in the improved electrical conduction properties of the CNTs with increasing growth temperature. The average diameter of CNTs increased from 30 to 130 nm as the growth temperature increased from 750 to 950 °C [30]. The larger diameter corresponds to a greater localization length of the charge carriers, [41] giving rise to the improvement of the electrical conduction properties.

In summary, the resistivity from bamboo-shaped MWNTs, grown on cobalt-catalyst-deposited Al_2O_3/Ti substrates by a thermal chemical vapor deposition, successively decreased with increasing growth temperature. According to the reduced activation energy analysis, the MWNTs grown at 850 and 950 °C showed metallic behaviors, whereas the MWNTs grown at 750 °C showed a critical behavior. The improved electrical properties of the MWNTs grown at higher temperatures can be explained by the increase in the crystallinity of the graphene sheets and in the localization length.

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