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Metallic conductivity in bamboo-shaped multiwalled carbon nanotubes

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Abstract

Temperature-dependent resistivity measurements were carried out on bamboo-shaped multiwalled carbon nanotubes (MWNTs) grown by thermal chemical vapor deposition. They were deposited on Al_2O_3/Ti and SiO_2/Ti substrates using cobalt and iron catalysts, respectively. As a result, a metallic conductivity, i.e. resistivities with a positive temperature slope, was observed for the MWNTs grown on the SiO_2/Ti substrates. The different temperature behaviors of the resistivity for the MWNTs grown on different substrates are discussed in view of the substrate morphology and crystallinity. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbon nanotubes (CNTs) constitute a new class of materials with a broad range of potential applications such as gas reservoirs, battery electrodes, and field emission displays [1–4]. The growth of high quality and large amount of CNTs is essential for their practical applications. Various synthetic methods such as arc discharge [5], laser vaporization [6], pyrolysis [7], organometallic precursor pyrolysis [8], and plasma-enhanced [9] or thermal chemical vapor deposition (CVD) [10,11] have been developed for the production of CNTs. Because of many advantages such as high purity, high yield, simple process, selective growth, vertical alignment, and large-area uniformity, synthesis of CNTs using CVD method has attracted much attention. In order to find the best conditions of CVD synthesis of the CNTs, many trials have been made with various substrate morphologies [12,13] and catalysts [14,15].

In this work we have synthesized bamboo-shaped multiwalled carbon nanotubes (MWNTs) by thermal CVD using different substrates and catalysts, and their electrical properties were investigated by the measurements of the temperature-dependent resistivity. The resistivity has generally been reported to increase gradually with decreasing temperature for the cases of bundles [16,17], films [18] and unoriented bulks of the MWNTs [19]. Despite low resistivities sometimes observed for the MWNTs, positive $d\rho/dT$ characteristic of a metal has not yet been reported. In this work, improved electrical properties of MWNTs have been obtained by employing different substrates and growth temperatures. Besides, a metallic behavior of decreasing resistivity with decreasing temperature, i.e. positive $d\rho/dT$, has been observed for MWNTs grown on Fe catalyst deposited SiO_2/Ti substrates.

2. Experiments

The bamboo-shaped MWNTs were grown by thermal CVD on Co catalyst deposited Al_2O_3/Ti substrates at temperatures of 750–950 °C, and on Fe catalyst deposited SiO_2/Ti substrates at temperatures of 850–950 °C (Fig. 1). A 1-μm thick Ti film, used as an electrode, was thermally

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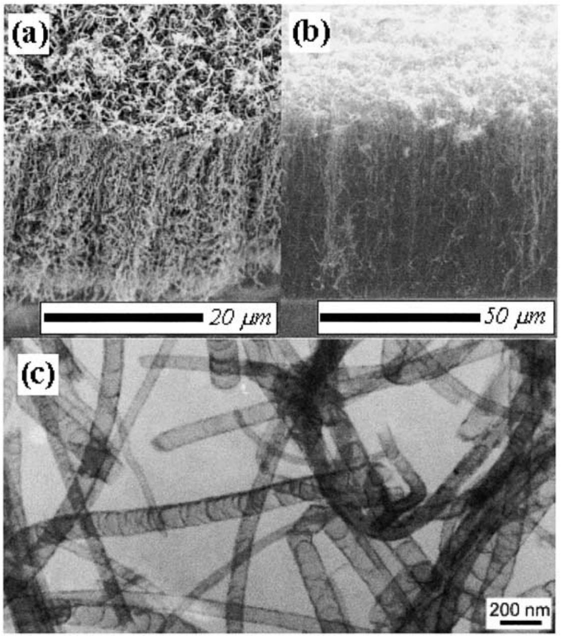

Fig. 1. SEM micrographs of vertically well-aligned MWNTs grown at 950 °C on (a) the Co catalyst deposited Al_2O_3/Ti substrate and on (b) the Fe catalyst deposited SiO_2/Ti substrate. (c) TEM image for the bamboo-like structured CNTs grown using the Fe catalyst, showing the closed tip without encapsulated catalytic particles and the curvature of compartment layers directed to the tip.

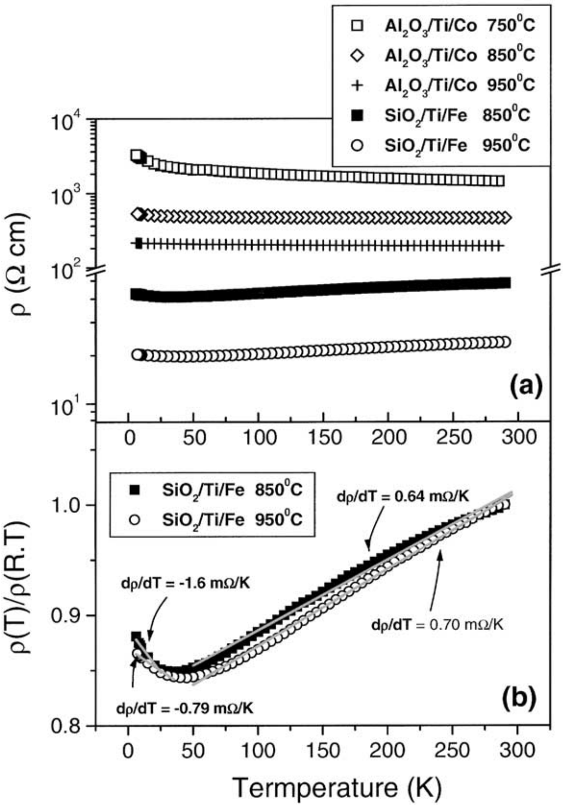

Fig. 2. (a) The temperature-dependent resistivity of bamboo-shaped MWNTs grown on the Co catalyst deposited Al_2O_3/Ti and Fe catalyst deposited SiO_2/Ti substrates, at the temperatures of 750, 850, and 950 °C. (b) Enlarged view of (a) for the MWNTs grown on the Fe catalyst deposited SiO_2/Ti substrates, showing positive dρ/dT, a metallic character, and a low-temperature upturn.

deposited on the Al_2O_3 and SiO_2 substrates, and the Co and Fe catalysts were subsequently deposited on top of Al_2O_3/Ti and the SiO_2/Ti, respectively. The catalysts are responsible for the diameter sizes and growth rates of the CNTs [20].

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 layer. The active area of the electrodes was 0.5 ± 0.1 mm^2, and the resistivity was calculated from the measured resistance, the active area of the electrodes, and the lengths of the CNTs. The scanning electron microscope (SEM) images were used to measure the lengths of CNTs and the substrate morphology. Atomic force microscope (AFM) was also used to investigate the substrate morphology.

3. Results and discussions

The temperature-dependent resistivities for the bamboo-shaped MWNTs are shown in Fig. 2. The resistivities of MWNTs grown on the Al_2O_3/Ti substrates are an order of magnitude higher than those of MWNTs grown on the SiO_2/Ti substrates. It is also noticed that higher growth temperatures give rise to smaller resistivities. For the MWNTs grown Al_2O_3/Ti substrates showing negative temperature slopes, the resistivity of the MWNTs grown at 750 °C is about two times higher than that of the MWNTs grown at 850 °C, and is about four times higher than that of the MWNTs grown at 950 °C. The situation is similar for the samples grown on the SiO_2/Ti substrates. In other words, the resistivity of the sample grown at 850 °C is about two times higher than that grown at 950 °C.

It is worthwhile to pay attention to the temperature slopes of the resistivities, dρ/dT, at high temperatures above about 50 K. The sample grown on the Al_2O_3/Ti substrate at the lowest temperature of 750 °C shows a noticeably positive slope in the temperature dependence of the resistivity that increases rapidly with decreasing temperature, whereas those grown at higher temperatures of 850 and 950 °C show only very weak temperature dependences, with almost zero slopes. In our work, it was found by a reduced activation energy analysis that the MWNTs grown on the Al_2O_3/Ti substrates at 850 and 950 °C show metallic behaviors and the MWNTs grown at 750 °C show a critical (metal–insulator transition) behavior [21]. In contrast to the case of the Al_2O_3/Ti substrates showing negative dρ/dT, the MWNTs grown on the SiO_2/Ti substrates show positive

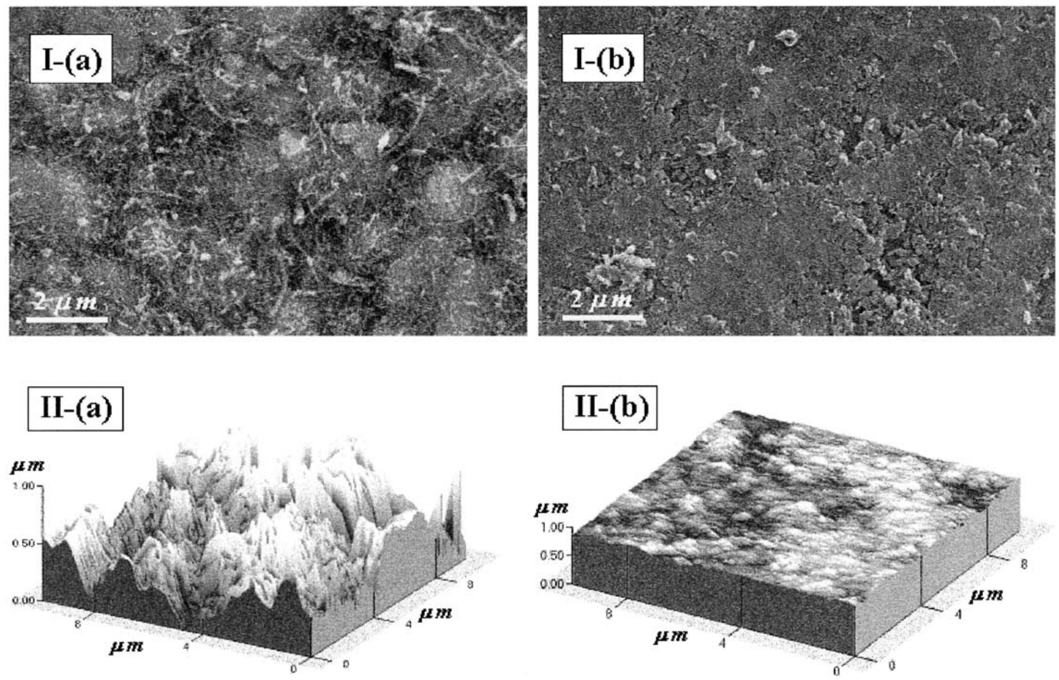

Fig. 3. (I) SEM images for (a) Co catalyst deposited Al_2O_3/Ti and (b) Fe catalyst deposited SiO_2/Ti substrates; (II) AFM images for (a) Co catalyst deposited Al_2O_3/Ti and (b) Fe catalyst deposited SiO_2/Ti substrates.

$d\rho/dT$ as indicated in Fig. 2(b), a metallic character, as well as a low-temperature upturn which has also been reported for ropes and unoriented bulks of single-walled carbon nanotubes (SWNTs) [22,23].

It is worthwhile to consider the origin of the different electrical properties for different growth conditions. The lower resistivity of the MWNTs grown at higher temperatures has been explained by the increase in the crystallinity of the graphene sheets and in the localization length [21,24]. In order to understand the different electrical properties of MWNTs grown on different substrates, the substrate morphologies were investigated. Fig. 3 shows the SEM micrographs of the substrates taken after carefully removing the MWNTs on the substrates with a razor. As a result, the roughness of the Al_2O_3/Ti substrates was found to be an order of magnitude greater than that of the SiO_2/Ti substrates (Table 1). The higher roughness of the Al_2O_3/Ti substrates can be attributed to the fact that Al_2O_3 substrate is in polycrystalline form whereas the substrate SiO_2 is in amorphous form, which was confirmed by X-ray diffraction. The substrate morphology is an important factor in the CVD growth of CNTs [12,13], and the lower roughness of the SiO_2/Ti substrates would give rise to improved crystallinity of the CNTs, and better electrical properties. The catalyst is another factor of determining the electrical properties of the CNTs. In our previous work, it was found that Fe catalyst gave rise to much better crystallinity of CNTs than the Co catalyst did [14].

In summary, temperature-dependent resistivity measurements were carried out on bamboo-shaped MWNTs grown on Al_2O_3/Ti substrates and SiO_2/Ti substrates. As a result, the resistivities were found to successively decrease with increasing growth temperature, and lower resistivities were measured for the samples grown on the Fe catalyst deposited SiO_2/Ti substrates than for those grown on the Co catalyst deposited Al_2O_3/Ti substrates, which were explained in terms of the crystallinity of the MWNTs. Besides, positive temperature slopes characteristic of metallic properties were observed from the samples grown on the Fe catalyst deposited SiO_2/Ti substrates.

Table 1
Roughness values for the Co catalyst deposited Al_2O_3/Ti and Fe catalyst deposited SiO_2/Ti substrates ($R_{pv} = Z_{max} - Z_{min}$, $R_{rms} = \sqrt{\sum_{n=1}^{N}(Z_n - \bar{Z})/(N-1)}$, $R_{ave} = \sum_{n=1}^{N}(|Z_n - \bar{Z}|)/N$. Z: height, N: number of samples)

	R_{pv} (nm)	R_{rms} (nm)	R_{ave} (nm)
Al_2O_3/Ti/Co	1530 ± 529	200 ± 22.4	156 ± 20.2
SiO_2/Ti/Fe	252 ± 132	24.0 ± 14.0	18.4 ± 11.9

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