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Conduction Mechanism of the Bamboo-Shaped Multiwalled Carbon Nanotubes

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Temperature-dependent resistivity measurements were carried out on bamboo-shaped multiwalled carbon nanotubes (BS-MWNTs) vertically grown on cobalt catalyst deposited Al_2O_3/Ti substrates and iron catalysts deposited SiO_2/Ti substrates at 750 - 950 °C by thermal chemical vapor deposition. The resistivity decreased with increasing growth temperature, and showed lower values in the case of SiO_2/Ti substrates than in the case of the Al_2O_3/Ti substrates. A heterogeneous model, compromising quasi 1-D metal terms and the fluctuation-induced tunneling through thin barriers between metallic regions was introduced to explain the conduction mechanism. As a result, it was proposed that the important factor for the conduction mechanism of BS-MWNTs is the inter-sheet conduction by discontinuous graphitic sheets at the compartments.

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I. INTRODUCTION

Since their discovery [1], carbon nanotubes (CNTs) have been attracting interest because of their attractive properties and potentials for practical use [2–5]. 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 [6–8]. Single-walled carbon nanotubes (SWNTs) can be metallic or semiconductive depending on the carbon arrangements [6–8]. In semiconductive CNTs, the bandgap is inversely proportional to the diameter [6, 7]. 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, multi-walled carbon nanotubes (MWNTs), nanotube ropes, and bamboo-shaped CNT.

In this work, we report temperature-dependent resistivity measurements of the bamboo-shaped MWNTs (BS-MWNTs) grown on cobalt catalyst deposited Al_2O_3/Ti substrates and iron catalysts deposited SiO_2/Ti substrates at 750 - 950 °C by thermal chemical vapor deposition. By introducing a heterogeneous model [9, 10] compromising quasi 1-D metal terms and the fluctuation-induced tunneling through thin barriers between metallic regions for the measured temperature-dependent resistivity, we attempted to determine important factors for the conduction mechanism of BS-MWNTs.

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II. EXPERIMENTS

The BS-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. A 1 μm-thick Ti film, used as an electrode, was thermally 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 [11].

The resistance was measured in the temperature range 6 to 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. 1). While unoriented bulk SWNT resistance measurements by a four-probe method with silver paste contacts have been done by the Fisher group [12],

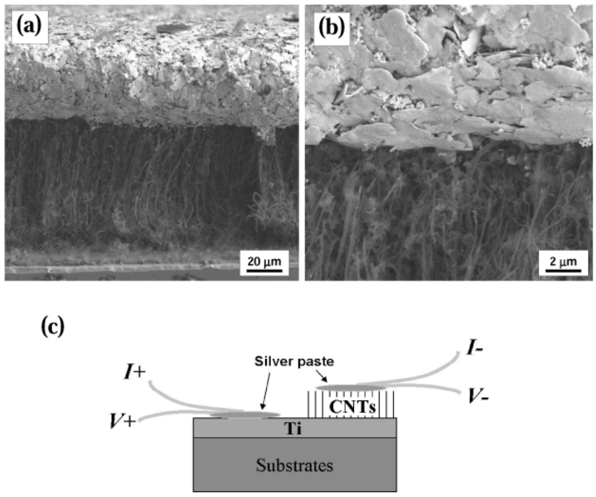

Fig. 1. (a) and (b) SEM micrographs showing the silver paste contact uniformly put on the bamboo-shaped MWNTs. (c) Schematic diagram of the four-probe electrical resistance measurement for the aligned MWNTs.

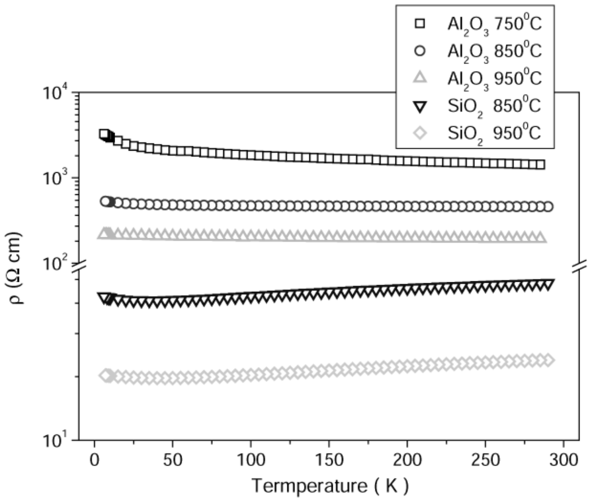

Fig. 2. The temperature dependent resisitivity of bamboo-shaped MWNTs grown on the Co catalyst deposited Al_2O_3/Ti and Fe catalyst deposited SiO_2/Ti substrates, at the temperatures of 750, 850, and 950^{o}C.

our exceptionally well oriented samples and the electrical contacts, as are manifest in Fig. 1, 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 resistivity 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 $\pm$ 0.1 mm^2. The scanning electron microscope (SEM) images were used to measure the lengths of the CNTs.

III. RESULT AND DISCUSSIONS

The temperature-dependent resistivities for the BS-MWNTs are shown in Fig. 2. The resistivities of BS-MWNTs grown on the Al_2O_3/Ti substrates are an order of magnitude higher than those of BS-MWNTs grown on the SiO_2/Ti substrates. It is also noticed that the higher growth temperatures give rise to smaller resistivities. For the BS-MWNTs grown Al_2O_3/Ti substrates showing negative temperature slopes, the resistivity of the BS-MWNTs grown at 750 °C is about two times higher than that of the BS-MWNTs grown at 850 °C, and is about four times higher than that of the BS-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. In our work, the lower resistivities of BS-MWNTs grown on the SiO_2/Ti substrates, which were explained in terms of the crystallinity of the BS-MWNTs resulting from the substrate morphologies [13].

In the BS-MWNTs discontinuous graphitic sheet regions exist near the compartments (Fig. 3) [11, 14]. Therefore, there may be two types of conduction: the intra-sheet conduction ('A') and the inter-sheet conduction ('B'). Accordingly, we can introduce a heterogeneous model [9,10],

$$\rho = \rho_m \exp(-T_m/T) + \rho_t \exp(T_C/(T+T_S)) \qquad (1)$$

where the first term represents a quasi 1-D metal term and the second term fluctuation-induced tunneling through thin barriers between the metallic region. T_m is the temperature corresponding to the $2k_F$ wavevector that spans the Fermi surface, T_C denotes the temperature below which the conduction is dominated by the charge carrier tunneling through the barrier, and T_S is the temperature above which the thermally activated conduction over the barrier begins to occur. In addition, ρ_m and ρ_t are parameters which include geometric factors. The intra-sheet conduction corresponds to

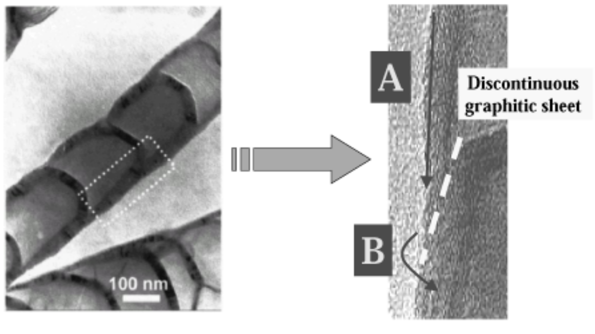

Fig. 3. The conduction mechanism of bamboo-shaped MWNTs; discontinuous graphitic sheets exist near the compartments of BS-MWNTs. 'A' is intra-sheet conduction and 'B' is inter-sheet conduction.

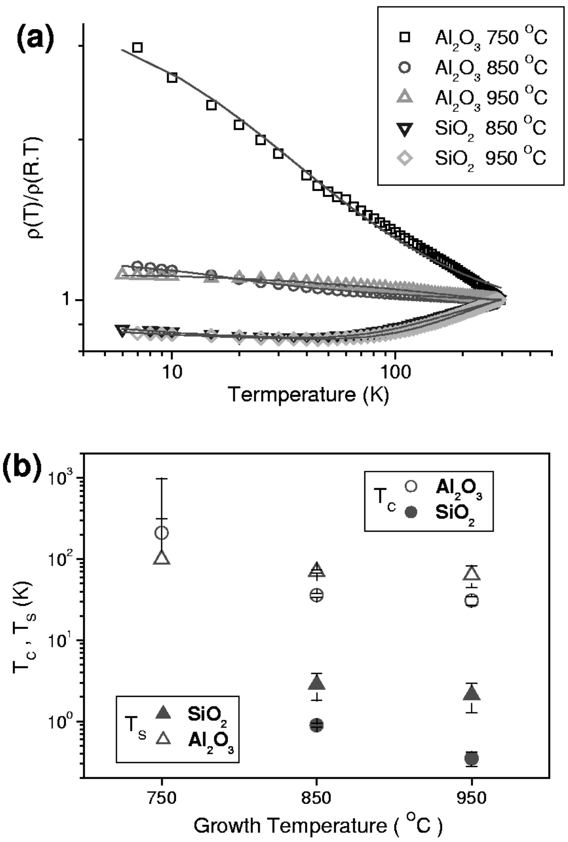

Fig. 4. (a) Normalized resistivity vs. temperature. The solid line is the heterogeneous model fit. (b) Temperature dependence of the fluctuation induced tunneling barrier related parameters T_C and T_S for various growth-temperatures.

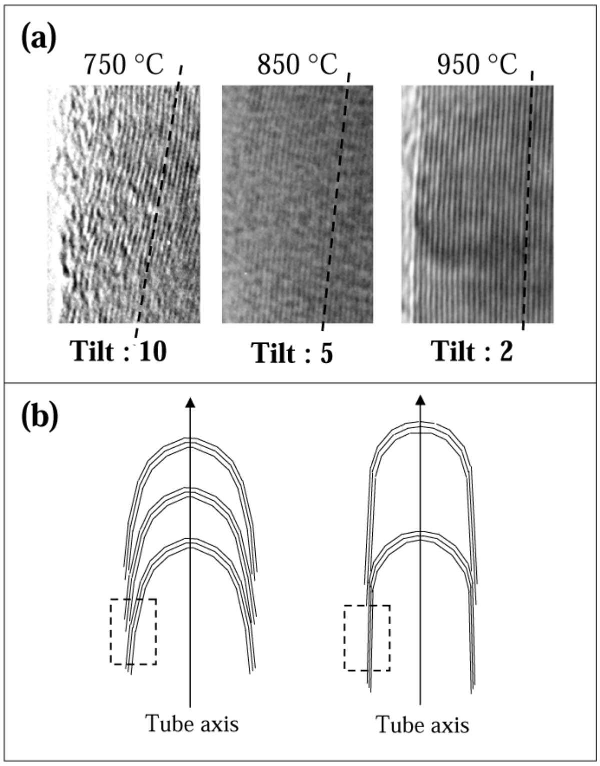

Fig. 5. (a) TEM wall images of BS-MWNTs grown on Fe catalyst deposited SiO_2/Ti substrates. (b) Schematic picture of the inter-sheet conduction dependent on the tilt angle of the graphitic sheets. For the larger tilt angle, more inter-sheet conduction takes place.

the quasi 1-D metal term because conduction only occurs in continuous graphitic sheets and the inter-sheet conduction corresponds to fluctuation-induced tunneling through thin barriers between the metallic regions.

The heterogeneous model fits are shown at Fig. 4(a). Mostly quite good fits are found except for the BS-MWNTs grown at 750 °C on Al_2O_3/Ti substrates. In our previous work, it was found by a reduced activation energy analysis that the BS-MWNTs grown on the Al_2O_3/Ti substrates at 850 and 950 °C show metallic behaviors, whereas the BS-MWNTs grown at 750 °C show a critical (metal-insulator transition) behavior [15]. This may explain the fact that a slight deviation is shown only for the BS-MWNTs grown on the Al_2O_3/Ti substrates at 750 °C. The parameters T_C and T_S obtained from the fitting are shown in Fig. 4(b). They show greater values for the BS-MWNTs grown on the Al_2O_3/Ti substrates than for the BS-MWNTs grown on the SiO_2/Ti substrates. Besides, they show smaller values for the higher growth temperatures. The lower values of T_C and T_S indicate that the fluctuation induced tunneling barrier is lower. The lower fluctuation induced tunneling barrier of the BS-MWNTs grown on the SiO_2/Ti substrates is affected by the improved crystallinity of the BS-MWNTs resulting from the more homogenous substrate morphology of the SiO_2/Ti substrates [13]. The lower fluctuation induced tunneling barrier of the BS-MWNTs grown at the higher temperature is explained by decrease of inter-sheet conduction. In our previous work, it was found that the increased growth rate for higher growth temperature lead to reduced tilt angle of the graphitic sheets toward the tube axis of the BS-MWNTs [16]. The decreased tilt angle toward the tube axis of BS-MWNTs lead to reduced inter-sheet conduction (Fig. 5). According to the base growth model [11], when the growth rate of the BS-MWNTs increases, the vertical graphitic sheet growth by surface diffusion of carbons becomes more active than the compartment graphitic sheet growth by bulk diffusion of carbons. So the higher growth rate of BS-MWNTs result in the fewer compartment graphitic sheet structures. In other words, BS-MWNTs grown at the higher temperature has the less inter-sheet conduction. Therefore, the improved electrical properties of the BS-MWNTs grown at the higher temperatures can be explained by the decreased inter-sheet conduction.

IV. SUMMARY

The temperature dependent resistivity measurements were carried out on BS-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 BS-MWNTs. Besides, the inter-sheet conduction near the compartments of BS-MWNTs proposed to be an important factor of the conduction mechanism of BS-MWNTs from the heterogeneous model fit.

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